

Shannonite, Pb_2OCO_3 , a new mineral from the Grand Reef mine, Graham County, Arizona, USA*

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Abstract

Shannonite, ideally Pb_2OCO_3 , is a new mineral species that occurs as mm-sized white porcellanous crusts, associated with fluorite, at the Grand Reef mine, Graham County, Arizona, USA. Other associated minerals are plumbojarosite, hematite, Mn-oxides, muscovite- $2M_1$, quartz, litharge, massicot, hydrocerussite, minium, and unnamed $\text{PbCO}_3 \cdot 2\text{PbO}$. Shannonite is orthorhombic, space group $P2_12_21$ or $P2_12_12_1$, with unit-cell parameters (refined from X-ray powder data): a 9.294(3), b 9.000(3), c 5.133(2) Å, V 429.3(3) Å³, $a:b:c$ 1.0327:1:0.5703, $Z = 4$. The strongest five lines in the X-ray powder pattern [d in Å (I)(hkl)] are: 4.02(40)(111); 3.215(100)(211); 3.181(90)(121); 2.858(40)(130); 2.564(35)(002). The average of eight electron microprobe analyses is PbO 89.9(5), CO₂ (by CHN elemental analyser) 9.70, total 99.60 wt.%. With O = 4, the empirical formula is $\text{Pb}_{1.91}\text{C}_{1.05}\text{O}_{4.00}$. The calculated density for the empirical formula is 7.31 and for the idealized formula is 7.59 g/cm³. In reflected light, shannonite is colourless-grey to white, with ubiquitous white internal reflections ($\times 16$ objectives), weak anisotropy, barely detectable birefractance, and no evidence of pleochroism. The calculated refractive index (at 590 nm) is 2.09. Measured reflectance values in air and in oil ($\times 4$ objectives) are tabulated. Transmission electron-microscopy studies reveal that individual crystallites range in size from 10–400 nm, are platy, and are anhedral. Physical properties for cryptocrystalline crusts include: white streak; waxy lustre; opaque; nonfluorescent under both long- and short-wave ultraviolet light; uneven fracture; brittle; VHN₁₀₀ 97 (range 93–100); calculated Mohs' hardness 3–3½. Shannonite is soluble in concentrated HCl and in dilute HNO₃ and H₂SO₄. The mineral name is for David M. Shannon, who helped collect the samples and who initiated this study.

* Geological Survey of Canada Contribution Number 20194

KEYWORDS: shannonite, new mineral, Grand Reef mine, Graham County, Arizona, lead oxycarbonate, reflectance data, X-ray data, electron-microprobe analyses, CHN elemental analysis, transmission electron-microscopy study.

Introduction

THE new mineral shannonite, ideally Pb_2OCO_3 , was first encountered on cerussite-bearing mineral specimens collected in 1989 from the base of the main 'glory hole' at the Grand Reef mine, Graham County, Arizona, USA. The inorganic equivalent of shannonite is well-known chemically; it is one of a series of intermediate products of the controlled thermal decomposition of lead carbonate to lead oxide at elevated temperatures. Unindexed X-ray powder data for all these intermediate decomposition products are tabulated in the Powder Diffraction File. Recently, Pring *et al.* (1990) reported on the occurrence of this phase, as an artificially formed, mine fire product pseudomorphous after cerussite, from the Kintore Opencut, Broken Hill, New South Wales, Australia. They also defined the symmetry and unit-cell parameters for this lead oxycarbonate.

The mineral is named for David M. Shannon (1942–), a well-known mineral dealer from Mesa, Arizona, USA, who helped collect the discovery samples from the Grand Reef mine and who provided the impetus for the senior author to undertake this study. The mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material, consisting of four specimens containing variable amounts of shannonite, is housed within the Systematic Reference Series of the National Mineral Collection of Canada, Geological Survey of Canada, Ottawa, Ontario, Canada, under catalogue number NMCC 67216. In addition, a polished section, containing two grains of shannonite which were used to provide the quantitative electron-microprobe and reflectance data, is preserved at the Natural History Museum, Great Britain as BM 1993, 487.

Occurrence and associated minerals

Shannonite is a rare constituent at the Grand Reef mine, Graham County, Arizona, USA. The mine is located in the Santa Teresa Mountains, about 60 miles NE of Tucson, Arizona. More specifically, the mine is located within the Aravaipa mining district, Laurel Canyon, and is about four miles NE of Klondyke, Arizona (Jones, 1980). Details regarding the history, geology and mineralogy of the Grand Reef mine can be found in the excellent review by Jones (1980).

Shannonite was initially identified on cerussite-bearing specimens collected in 1989 from the base of the main glory hole area of the mine. The specific site is about 10 feet E of a winze that drops from the SW corner of the hole (D. Shannon, pers. comm., 1992). This particular area has been worked for years by mineral collectors, and has yielded a number of large blocky cerussite crystals. However, only one small pocket of shannonite-bearing rock has been discovered to date. The Grand Reef mine is well-known for these 'one pocket' mineral occurrences, *cf.* Kampf *et al.* (1989) who describe the four new minerals grandreefite, pseudograndreefite, laurelite, and aravaipaite from a single vug. The shannonite-bearing specimens were collected from very hard silicified breccia, at least 2 feet below the lowest level of any original mining operations.

Shannonite is associated with grey crystalline fluorite, colourless to light yellow crystalline cerussite, yellow-brown microcrystalline crusts and yellow-green earthy crusts of plumbojarosite, brick red powdery crusts of hematite, black Mn-oxides, orange to brown porcellanous crusts of litharge, bright red-orange minium, yellow-green porcellanous crusts of massicot, light to dark yellow-brown porcellanous crusts of unnamed $\text{PbCO}_3 \cdot 2\text{PbO}$ (mixed with both shannonite and litharge), hydrocerussite (mixed with litharge and verified by X-ray powder diffraction), colourless crystalline quartz, and pale green-grey earthy crusts of muscovite $2M_1$. Whole-rock X-ray powder diffraction shows that the host rock is composed principally of quartz and fluorite.

Several of the specimens show a gradational trend from lead carbonate to lead oxide: cerussite to shannonite to unnamed $\text{PbCO}_3 \cdot 2\text{PbO}$ to litharge to massicot to minium. The shannonite was probably deposited by acid-rich groundwaters which have reacted with the pre-existing cerussite. Shannonite was formed not only from pre-existing cerussite, but also deposited from solution with other minerals to form crusts (the habit of the crusts is not compatible with their development as alterations after cerussite). The presence of shannonite in several closely spaced micro-environments suggests that it was formed over a substantial period of time. The lack of shannonite on specimens of cerussite from nearby portions of the mine suggests that unusual conditions of temperature and fluid composition were required for its deposition, and effectively eliminates any anthropogenic cause such as a mine fire. The development of small volumes of rock with unusual fluid

conditions at the Grand Reef mine has also been discussed by Kampf *et al.* (1989).

Physical properties

Shannonite at the Grand Reef mine occurs as mm-sized white opaque porcellanous crusts associated with fluorite. The white colour is diagnostic; if the colour inclines to a light yellow or a light yellow-brown, then the crust is most likely a mixture of shannonite and unnamed $\text{PbCO}_3 \cdot 2\text{PbO}$. These cryptocrystalline crusts of shannonite are brittle, have a waxy lustre, a white streak, an uneven fracture, and are nonfluorescent under both long- and short-wave ultraviolet light. Transmission electron-microscopy (TEM) studies indicate that individual crystals range in size from 10 to 400 nm with no obvious crystal forms. These individuals are platy, anhedral, and are probably colourless and vitreous with no apparent cleavage. The cryptocrystalline crusts have a VHN_{100} of 97, with a range of 93–100; the equivalent Mohs' hardness is 3–3½.

The measured density was unobtainable due to a dearth of pure unincluded (with either cerussite or unnamed $\text{PbCO}_3 \cdot 2\text{PbO}$) material suitable for a Berman balance determination. The calculated density for the empirical formula and $Z = 4$ is 7.31 g/cm^3 , and for the idealized formula is 7.59 g/cm^3 .

X-ray powder and TEM studies

Naturally occurring shannonite, at least that which has been examined to date, is unsuitable for X-ray single-crystal study. The X-ray powder-diffraction pattern is, however, virtually identical to that reported by Pring *et al.* (1990), who indexed their powder data on an orthorhombic unit cell. All d -values can be successfully indexed, including two weak ($I = 5$) reflections at 2.733 and 2.387 Å which are not reported in the powder data published by Pring *et al.* (1990).

The orthorhombic unit-cell parameters, proposed by Pring *et al.* (1990), were confirmed by TEM study utilizing a Philips EM400T electron microscope. A fine powder of shannonite was produced by grinding

TABLE 1. X-ray powder data for shannonite

$I_{\text{est.}}$	$d_{\text{meas.}} \text{ \AA}$	$d_{\text{calc.}} \text{ \AA}$	hkl	$I_{\text{est.}}$	$d_{\text{meas.}} \text{ \AA}$	$d_{\text{calc.}} \text{ \AA}$	hkl
30	6.49	6.47	110	10	2.152	2.155	330
5	4.65	4.65	200	20	2.059	2.061	041
		4.50	020			2.060	411
10	4.49	4.49	101			2.012	141
30	4.14	4.13	210	25	2.010	2.010	222
40	4.02	4.02	111	10	1.928	1.930	312
20	3.382	3.384	021	25	1.909	1.909	132
100	3.215	3.217	211	5	1.882	1.884	241
90	3.181	3.180	121			1.820	340
30	2.931	2.929	310	15	1.817	1.820	510
40	2.858	2.855	130	10	1.748	1.748	501
5	2.733	2.735	221	30	1.729	1.730	431
20	2.654	2.652	301			1.718	520
35	2.564	2.566	002	10	1.718	1.716	341
5	2.496	2.495	131			1.716	511
3	2.463	2.468	012			1.692	042
5	2.387	2.385	112	10	1.692	1.692	412
25	2.325	2.324	400	15	1.651	1.650	332
25	2.285	2.285	321	5	1.631	1.629	521
		2.250	040	30	1.595	1.595	251
30	2.251	2.250	410			1.581	213
		2.247	202	15	1.579	1.580	530
30	2.181	1.180	212			1.576	123

114.6 mm Debye-Scherrer powder camera
 Cu-radiation, Ni filter ($\lambda_{\text{Cu-K}\alpha}$ 1.54178 Å)
 intensities estimated visually
 not corrected for shrinkage and no internal standard
 indexed on a 9.294, b 9.000, c 5.133 Å

small hand-picked fragments between two clean glass microscope slides. A small quantity of the powder was then supported on a holey carbon film for TEM study. Energy-dispersive spectra confirm that the crystallites under investigation contained Pb and convergent beam electron-diffraction (CBED) patterns were obtained with the electron beam focused in microprobe mode. In all cases, the height of each crystallite under investigation was set so that it was in focus at a fixed objective lens current. This was done in order to optimize the reproducibility of the camera length in diffraction mode. Six CBED patterns were collected and analysed by a computer program. Two of these patterns contain systematic absences of the type $h00$ with $h \neq 2n$ and $00l$ with $l \neq 2n$. This dictates that the space group is at least $P2_122_1$. Unfortunately, we were unable to find a zonal pattern that contains the b -axis. If $0k0$ with $k \neq 2n$ exists as a systematic absence, then the space group would be $P2_12_12_1$.

Shannonite is thus orthorhombic with space group $P2_122_1$ or $P2_12_12_1$. A fully indexed powder pattern is presented in Table 1. The refined unit-cell parameters, a 9.294(3), b 9.000(3), c 5.133(2) Å, V 429.3(3) Å³, and $a:b:c = 1.0327:1:0.5703$, are based on 17 reflections, between 3.382 and 1.595 Å, in the X-ray powder pattern for which unambiguous indexing was possible. The unconventional setting of $c < b < a$ conforms to the cell setting reported by Pring *et al.* (1990). With the conventional setting of $c < a < b$, the refined unit-cell parameters are: a 9.000(3), b 9.294(3), c 5.133(2) Å, V 429.3(3) Å³, and $a:b:c$ 0.9684:1:0.5523.

Chemical composition

Two aggregates of shannonite were mounted in polished section and chemically analysed with a Cameca SX-50 electron microprobe utilizing an operating voltage of 10 kV, a beam current of 20 nA, a beam diameter of 20 µm, and a counting time of 20 s. An energy-dispersive spectrum indicated the absence of elements with an atomic number greater than 9, other than Pb. The standard employed for Pb was natural cerussite from Namibia. The X-ray counts were processed with the PAP procedure (Pouchou and Pichoir, 1985). Shannonite is very stable under the electron beam and does not show any evidence of cathodoluminescence. The average of eight analyses on both aggregates gave PbO 89.9(5) wt.%. The presence of C was also confirmed by electron-microprobe analyses, but quantitative analyses for CO₂ gave inconsistently high results and are not reported here.

The CO₂ was determined on 10.685 mg of pure hand-picked sample using a Perkin Elmer model 240 CHN elemental analyser. The sample was heated to

approximately 1000°C in O/He, followed by purification of evolved gases and measurement of CO₂ by thermal conductivity detectors. Calibration against cerussite and blanks were run both before and after the sample. The results give 9.70 wt.% CO₂ in shannonite.

Combining the electron microprobe and CHN elemental analyser results give PbO 89.9(5), CO₂ 9.70, total 99.60 wt.%. With O = 4, the empirical formula is Pb_{1.91}C_{1.05}O_{4.00} or, ideally, Pb₂CO₄. This idealized formula may be better written as Pb₂OCO₃ and requires PbO 91.03, CO₂ 8.97, total 100.00 wt.%.

Shannonite is soluble in concentrated HCl and in dilute HNO₃ and H₂SO₄.

Calculations using the Gladstone-Dale relationship, and using constants reported by Mandarino (1981), yield $1 - (K_p/K_C) = -0.64$ if the empirical formula and corresponding calculated density are used, and yield -0.26 if the idealized formula and corresponding calculated density are used. These values indicate a fair compatibility between the empirical, and an excellent compatibility between the idealized, physical and chemical data (Mandarino, 1981).

Optical properties

Two fragments of shannonite, mounted in epoxy resin and polished, were buffed with a suspension of MgO in distilled water and cleaned before examination with the reflecting microscope. The mineral is unusual in its appearance in reflected light. In plane-polarized light, in air, it appears almost uniformly white, an appearance unchanged between crossed polars regardless of orientation, i.e. the mineral is 'flooded' by white internal reflections. At least these are the observations when using ×16 objectives. With ×4 objectives there is little evidence of internal reflection; indeed, the mineral is dull, dark grey to a slightly lighter grey in plane-polarized light. Between crossed polars, 'sectors' of similar, nondescript shades are apparent though the mineral does not extinguish. Re-examination with ×16 objectives, adjusted so that their effective numerical apertures were at a minimum, revealed a modest change in its appearance in plane-polarized light, such that fractures and traces, perhaps of grain boundaries, were visible. Between crossed polars, again there was little change from this appearance; however, when the analyser was rotated from extinction, subtle details of a very fine scale granularity were revealed. The conclusion may be drawn, therefore, that the mineral is very finely crystalline, if not microcrystalline. Further, that it is essentially transparent throughout the visible spectrum, and that the explanation for the discrepancy between its appearance with the two objectives is

SHANNONITE

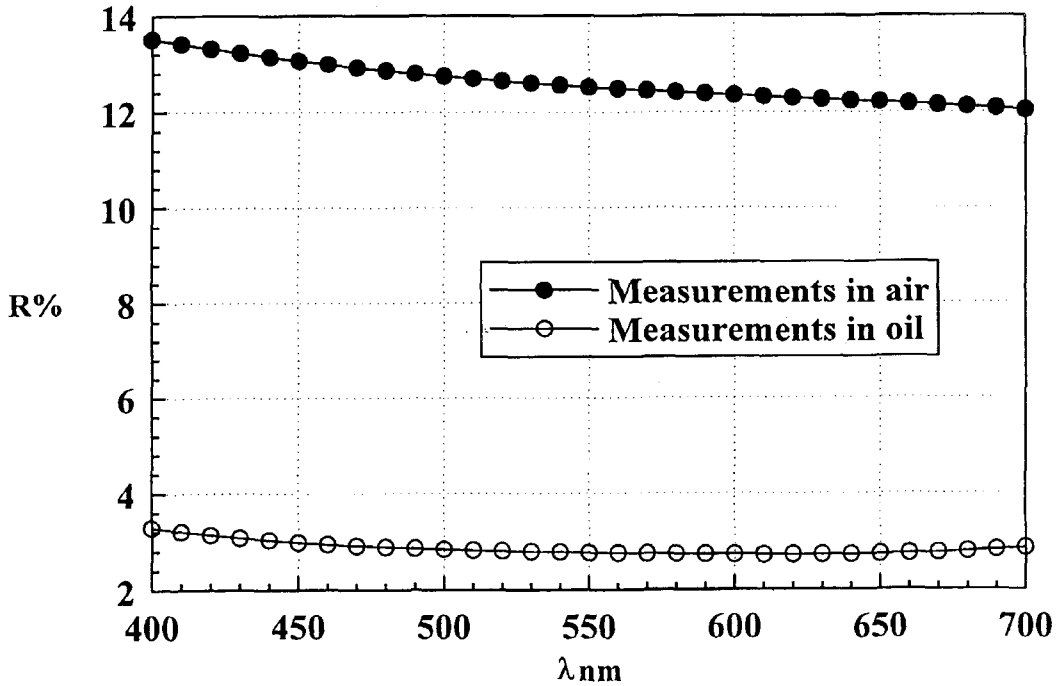


FIG. 1. Reflectance spectra measured in air and in oil ($N_D = 1.515$) for two aggregates of shannonite ($\times 4$ objectives).

found in the larger cone angle of the $\times 16$ objective as compared with the $\times 4$ objective. To summarize, the mineral is weakly anisotropic, displays no pleochroism, and has barely detectable bireflectance.

From the foregoing, it is evident that measurement of the reflectance of this mineral was particularly problematic. It was clearly impossible to isolate and orientate individual grains; instead, areas of the

mineral were selected for measurement which appeared to contain a number of randomly orientated grains. Measurements were made with both $\times 4$ and $\times 16$ objectives. The same field-stop was used for both objectives, resulting in the diameter of the measured field for the former of 80 μm and for the latter, of 20 μm . Reflectance measurements were made with a Zeiss SiC (#472) reflectance standard in air and in Zeiss immersion oil ($N_D 1.515$); the effective semi-angular apertures were adjusted to 1° for the $\times 4$ objectives and to 6° for the $\times 16$ objectives. Measurement of a general, or integrated, specular reflectance, free from a significant component from diffuse reflectance caused by internal reflection, proved impossible with the $\times 16$ objectives. With the $\times 4$ objectives, though the R and mR values are not exactly compatible (mR undoubtedly being more seriously affected by internal reflection than R), the R values are as good an approximation of an integrated or average reflectance as is currently obtainable. The results for the $\times 4$ objectives are presented in Table 2 and are graphically represented in Fig. 1. The refractive indices calculated from the reflectance spectra descend monotonically from 2.16 at 400 nm, through 2.09 at 590 nm, to 2.06 at 700 nm.

TABLE 2. Reflectance data ($\times 4$ objectives) and colour values for shannonite

λ nm	R	mR	λ nm	R	mR
400	13.6	3.27	560	12.45	2.74
420	13.3	3.13	580	12.4	2.73
440	13.1	3.02	589	12.4	2.72
460	12.95	2.94	600	12.35	2.71
470	12.9	2.91	620	12.3	2.71
480	12.85	2.88	640	12.2	2.72
500	12.75	2.84	650	12.2	2.73
520	12.6	2.80	660	12.15	2.74
540	12.5	2.77	680	12.1	2.77
546	12.5	2.76	700	12.0	2.82

Unnamed $\text{PbCO}_3\cdot 2\text{PbO}$

This unnamed phase, identical to PDF 17-731, has been identified by X-ray powder diffraction on three of the shannonite-bearing specimens. In all cases, it is intermixed with either shannonite or litharge, and occurs as a light to dark yellow-brown porcellanous crust on the host rock. The colour is usually indicative of the 'contaminant'; a light yellow-brown crust usually means a mixture with shannonite, a dark yellow-brown crust usually means a mixture with litharge. The further characterization of this phase must await the discovery of pure, uncontaminated material.

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- [Manuscript received 8 June 1994;
revised 27 July 1994]