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# ATHENEITE, $[Pd_2][As_{0.75}Hg_{0.25}]$, FROM ITABIRA, MINAS GERAIS, BRAZIL: CRYSTAL STRUCTURE AND REVISION OF THE CHEMICAL FORMULA

LUCA BINDI[§]

*Museo di Storia Naturale, Sezione di Mineralogia – Università di Firenze, via La Pira 4, I–50121 Firenze,*
*and C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via La Pira 4, I–50121 Firenze, Italy*

## ABSTRACT

The crystal structure of the rare mineral atheneite was solved using intensity data collected from a crystal from Itabira, Minas Gerais, Brazil. The structure is hexagonal, space group $P\bar{6}2m$, with $a$ = 6.813(1), $c$ = 3.4892(5) Å and $V$ = 140.26(4) Å$^3$. The refinement of an anisotropic model led to an $R$ index of 7.26% for 261 independent reflections. The crystal structure strongly resembles that of synthetic MM'As compounds, with M = Ru, Rh, Pd, and M = 3$d$ transition element. There are two fully occupied Pd sites: site Pd1 has a ten-fold coordination, and Pd2, an eleven-fold coordination. The two As atoms in the structure have a tricapped trigonal prismatic coordination; As1 is filled by arsenic only, whereas As2 has an occupancy of 0.60 As and 0.40 Hg. The presence of Hg at the As2 site accounts for the longer distances observed. On the basis of information gained from this characterization, the crystal-chemical formula was revised according to the structural results, yielding $Pd_2[As_{0.75}Hg_{0.25}]$ ($Z$ = 3) instead of $(Pd,Hg)_3As$ ($Z$ = 2) as previously reported. A recalculation of the chemical data listed in the scientific literature for atheneite according to the structural results obtained here leads to an excellent agreement.

*Keywords*: atheneite, Pd arsenides, structure solution, crystal-structure refinement, chemical analysis.

## SOMMAIRE

La structure cristalline de l'athénéite, minéral rare, a été résolue en utilisant les intensités prélevées sur un cristal provenant d'Itabira, Minas Gerais, Brésil. La structure est hexagonale, groupe spatial $P\bar{6}2m$, avec $a$ = 6.813(1), $c$ = 3.4892(5) Å et $V$ = 140.26(4) Å$^3$. L'affinement d'un modèle anisotrope fondé sur 261 réflexions indépendantes a mené à un résidu $R$ de 7.26%. La structure ressemble fortement à celle des composés synthétiques MM'As, avec M = Ru, Rh, Pd,et M = élément de transition 3$d$. Il y a deux sites Pd complètement remplis. Le site Pd1 possède une coordinence 10, et Pd2, une coordinence 11, Les deux atomes de As dans la structure possèdent une coordinence trigonale prismatique à trois sommets; As1 contient uniquement l'arsenic, tandis que As2 possède une population de 0.60 As et 0.40 Hg. La présence de Hg au site As2 explique les distances plus longues qui sont observées. Compte tenu de l'information structurale acquise suite à cette nouvelle caractérisation, la formule cristallochimique a été révisée; elle serait $Pd_2[As_{0.75}Hg_{0.25}]$ ($Z$ = 3) plutôt que $(Pd,Hg)_3As$ ($Z$ = 2), comme on le croyait auparavant. Un recalcul des données chimiques déjà dans la littérature concorde très bien avec cette nouvelle formule.

(Traduit par la Rédaction)

*Mots-clés*: athénéite, arséniures de Pd, solution structurale, affinement de la structure cristalline, analyse chimique.

## INTRODUCTION

Atheneite was established as a mineral species by Clark *et al*. (1974) during a study of old samples from Itabira, Minas Gerais, Brazil, in the collections of the former British Museum. These authors supplied a detailed chemical and physical characterization of the mineral, and described it as the first naturally occurring Pd–Hg arsenide with the formula $(Pd,Hg)_3As$ (with Pd ≈ 2.67 and Hg ≈ 0.33 *apfu*) and Z = 2. Clark *et al*. (1974) were able to index the diffraction pattern they obtained by means of a Gandolfi camera using the parameters of a hexagonal unit-cell (*i.e., a* 6.80, *c* 3.48 Å, space group *P*6/*mmm*) given by Claringbull & Hey (1957) for the mineral arsenopalladinite, $Pd_3As$. Clark *et al*. then stated "The density of atheneite (given by Claringbull and Hey 1957) is 10.2, comparing very favourably with the calculated value of 10.16 based on two formula units per unit cell". It is important to note that Clark *et al*. (1974) erroneously interpreted the measured

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[§] *E-mail address*: luca.bindi@unifi.it density for the mineral atheneite [given by Claringbull & Hey (1957)], which they used to estimate the *Z* of the atheneite formula. Actually, Claringbull & Hey (1957) measured a value of 10.2 g/cm$^3$ for arsenopalladinite (with only Pd and As, without Hg), and not for atheneite. This does mean that the density of atheneite is definitely higher than that measured for arsenopalladinite, and that the *Z* of the formula given by Clark *et al.* (1974) is likely wrong. The mistake of Clark *et al.* (1974) persisted in the mineralogical literature (*e.g.*, Anthony *et al.* 1990), in several mineralogical databases (*e.g.*, www.webmineral.com; www.mindat.org), as well as in successive studies on Pd-bearing arsenides (Cabral *et al.* 2008, and references therein).

To help resolve the concerns relating to the mineral atheneite, crystal-structure data for the mineral from its type locality, the Itabira deposit, are presented here, together with physical and chemical data.

## OCCURRENCE AND PHYSICAL AND OPTICAL PROPERTIES

The sample (catalogue number 45433/G) containing the mineral atheneite used in this study was obtained from the mineralogical collection of the Natural History Museum of the University of Florence. The sample, a small metal placer, consists of 2.34 g of residual concentrate from the gold washing at Itabira, Minas Gerais, Brazil, the type locality for the mineral atheneite. Geological and metallogenic data for this deposit are given by Kwitko *et al.* (2002). The associated minerals are arsenopalladinite and gold (Fig. 1). The mineral occurs as anhedral to subhedral grains up to 200 μm across. It does not show any inclusions of other minerals or intergrowths.

Atheneite is gray-black (under a binocular microscope), and has a metallic luster. The micro-indentation measurements carried out with a VHN load of 100 g gave a mean value of 427 kg/mm$^2$ (range: 415–435). This value is in excellent agreement with that found by Clark *et al.* (1974) for the type atheneite (431 kg/mm$^2$).

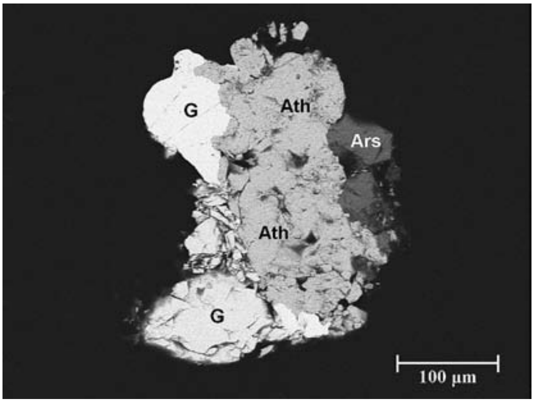

FIG. 1. Back-scattered electron SEM photograph of atheneite (Ath), associated with arsenopalladinite (Ars) and gold (G). Scale bar is indicated.

In plane-polarized light, the separate grains of atheneite appear to be the same color as arsenopalladinite. Neither bireflectance nor reflectance pleochroism are visible in air. No evidence of growth zonation or twinning is observed. Under crossed polars, the mineral does not extinguish. It displays a range of bright anisotropic tints, from purple brown through light grey to a metallic dark grey.

Reflectance measurements were performed in air using a MPM–200 Zeiss microphotometer equipped with a MSP–20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for the specimen and a standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages for $R_{\min}$ and $R_{\max}$ are 47.2, 54.3 (471.1 nm), 50.1, 57.8 (548.3 nm), 53.0, 60.7 (586.6 nm), and 55.2, 62.9 (652.3 nm), respectively. The reflectance percentages obtained for atheneite in this study are in excellent agreement with those measured by Clark *et al.* (1974).

## CRYSTAL-STRUCTURE SOLUTION AND REFINEMENT

A small fragment was selected from the Museum sample for the single-crystal X-ray-diffraction study. Unit-cell parameters, determined by centering 25 high-θ (25–33°) reflections, on an automated diffractometer (Bruker P4), are shown in Table 1. To check for the possible presence of diffuse scattering or weak superlattice peaks, the crystal was also mounted (exposure time of 200 s per frame; 40 mA × 45 kV) on a CCD-equipped diffractometer (Oxford Xcalibur™ 3), but no additional reflections were detected. Intensity data were collected using Mo*K*α radiation monochromatized by a flat graphite crystal in ω scan mode. Intensities were corrected for Lorentz-polarization effects and subsequently for absorption following the semi-empirical method of North *et al.* (1968). The values of the equivalent pairs were averaged. The merging *R* for the Ψ-scan data set decreased from 13.71% before absorption correction to 7.18% after this correction. No systematic absences were observed, and the statistical tests on the distribution of |E| values strongly indicate the absence of an inversion center ($|E^2 - 1| = 0.677$). After several trials in different space-groups, the best solution was found in the space group $P\overline{6}2m$.

The position of most of the atoms (Pd1, Pd2, As2) was determined from the three-dimensional Patterson synthesis (Sheldrick 1997a). A least-squares refinement using these heavy-atom positions and isotropic temperature-factors yielded an *R* factor of 12.44%.

Three-dimensional difference-Fourier synthesis yielded the position of the remaining As atom (*i.e.,* As1). The full-matrix least-squares program SHELXL–97 (Sheldrick 1997b) was used for the refinement of the structure. The Pd1 and Pd2 positions were found to be fully occupied by palladium. The As1 position was found fully occupied by arsenic, whereas the As2 position showed a mean number of 51.8 electrons which, taking into account a Hg → As substitution, yielded a site population of 0.60 As + 0.40 Hg. The introduction of anisotropic temperature-factors for all the atoms led to $R$ = 7.26% for all 261 independent reflections. Neutral scattering curves for Pd, As and Hg were taken from the *International Tables for X-ray Crystallography* (Ibers & Hamilton 1974). Inspection of the difference-Fourier map revealed that maximum positive and negative peaks were 1.36 and 1.25 $e^-/Å^3$, respectively.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR THE ATHENEITE CRYSTAL SELECTED

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $Pd_{2.00}As_{0.73}Hg_{0.27}$ |
| Temperature (K) | 298 |
| Space group | $P\bar{6}2m$ (#189) |
| Cell parameters | |
| *a* (Å) | 6.813(1) |
| *c* (Å) | 3.4892(5) |
| *V* (Å$^3$) | 140.26(4) |
| Z | 3 |
| Crystal color | black |
| Crystal shape | block |
| Crystal size (mm) | 0.02 × 0.03 × 0.04 |
| **Data Collection** | |
| Diffractometer | Bruker P4 |
| Radiation | Mo*K*α (λ = 0.71073 Å) |
| Scan mode | ω |
| sin θ / $\lambda_{max}$ (Å$^{-1}$) / $\theta_{max}$ (°) | 0.807 / 35.00 |
| *hkl* range | $-9 \le h \le 9$, $-10 \le k \le 10$, $-5 \le l \le 5$ |
| Number of reflections | 2419 |
| **Data Reduction** | |
| Absorption correction | ψ scan (North *et al.* 1968) |
| No. of independent reflections | 261 |
| Criterion for observed reflections | $Fo > 4\sigma(Fo)$ |
| No. of observed reflections | 261 |
| $R_{int}$ | 0.0718 |
| **Refinement** | |
| Refinement coefficient | $F^2$ |
| Number of refined parameters | 15 |
| Weighting scheme | $w = 1 / [\sigma^2(I) + (0.044 \times I)^2]$ |
| R (obs) / R (all) | 0.0726 / 0.0726 |
| Difference-Fourier ($e^-/Å^3$) | [−1.25, 1.36] |

It is important to note that the Pd atoms are at the Wyckoff positions 3*f* and 3*g*, the As1 atom at 1*b*, and the As2 atom (mixed As,Hg site) at 2*c*. This leads to a number of atoms equals to 9. If we assume $Z = 2$, as reported by Clark *et al.* (1974), we obtain the general formula $Pd_3(As_{1.10}Hg_{0.40})$, whereas if we assume $Z = 3$, the formula $Pd_2(As_{0.73}Hg_{0.27})$ is obtained. The assumption of $Z = 2$ adopted by Clark *et al.* (1974) is clearly wrong, as it gives rise to a number of atoms in the structure equals to 4.5 and, moreover, it does not correspond to the stoichiometry obtained from the electron-microprobe data by the authors themselves.

Experimental details and $R$ indices are given in Table 1. Fractional atomic coordinates are shown in Table 2, and anisotropic-displacement parameters, in Table 3.

A list of the observed and calculated structure-factors is available from the Depository of Unpublished Data on the MAC website [document Atheneite CM48_1149].

## CHEMICAL COMPOSITION

The fragment of atheneite used for the structural study was analyzed with a JEOL JXA–8600 electron microprobe. Major and minor elements were determined at 20 kV accelerating voltage and 40 nA beam current, with variable counting times: 30 s were used for As, Pd and Hg, and 60 s for the minor elements Fe, Cu, Se, Sn, Sb, Pt, Au and Bi. For the wavelength-dispersion analyses, the following lines were used: As*L*α, Pd*L*α, Hg*L*α, Fe*K*α, Cu*K*α, Se*L*α, Sn*L*α, Sb*L*α, Pt*L*α, Au*M*α, Bi*M*α. The estimated analytical precision (in wt.%) is: ±0.40 for Pd, ±0.25 for Hg and As, ±0.10 for Pt, ±0.07 for Au, ±0.05 for Sb, ±0.02 for Fe, Cu, Sn, Se and Bi. The standards employed were: synthetic AsGa (As), Pd pure element (Pd), synthetic HgS (Hg), pure Fe (Fe), synthetic CuSe (Cu, Se), pure Sn (Sn), pure Sb (Sb), pure Pt (Pt), pure Au (Au), and pure Bi (Bi). The

TABLE 2. WYCKOFF POSITIONS, SITE-OCCUPANCY FACTORS, FRACTIONAL ATOMIC COORDINATES, AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å$^2$) FOR ATHENEITE

| Atom | Wyckoff | s.o.f. | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|---|---|
| Pd1 | 3*f* | 1.000 | 0.7424(4) | 0 | 0 | 0.0203(8) |
| Pd2 | 3*g* | 1.000 | 0.3984(5) | 0 | 1/2 | 0.028(1) |
| As1 | 1*b* | 1.000 | 0 | 0 | 1/2 | 0.018(1) |
| As2 | 2*c* | 0.598(3) | 1/3 | 2/3 | 0 | 0.029(1) |
| Hg2 | 2*c* | 0.402 | 1/3 | 2/3 | 0 | 0.029(1) |

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS $U_{ij}$ (Å$^2$) FOR ATHENEITE

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Pd1 | 0.0126(9) | 0.020(1) | 0.031(1) | 0.0099(6) | 0 | 0 |
| Pd2 | 0.022(1) | 0.058(2) | 0.016(1) | 0.029(1) | 0 | 0 |
| As1 | 0.022(2) | 0.022(2) | 0.011(2) | 0.0108(8) | 0 | 0 |
| As2 | 0.0066(7) | 0.0066(7) | 0.073(3) | 0.0033(4) | 0 | 0 |
| Hg2 | 0.0066(7) | 0.0066(7) | 0.073(3) | 0.0033(4) | 0 | 0 |

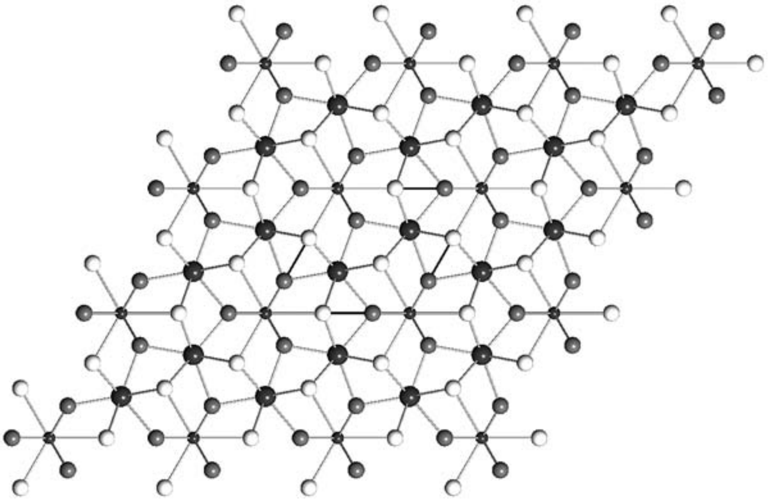

FIG. 2. The crystal structure of atheneite projected down [001]. Black, gray and white circles refer to As, Pd1 and Pd2 atoms, respectively. The size of the circle for As2 is greater than that for As1.

crystal fragment was found to be homogeneous within the analytical error. The average chemical composition (six analyses on different spots), together with other analytical data reported in literature (Clark *et al.* 1974, Cabral *et al.* 2002, 2008, Kwitko *et al.* 2002), are shown in Table 4. On the basis of three atoms (see above), the empirical formula of atheneite is [$Pd_{1.98}Pt_{0.01}As_{0.01}$] [$As_{0.75}Hg_{0.25}$], ideally $Pd_2$[$As_{0.75}Hg_{0.25}$]. In Table 4, the analytical results are given either on the basis of both three and four atoms.

## RESULTS AND DISCUSSION

The crystal structure of atheneite (Figs. 2, 3) strongly resembles that of synthetic MM'As compounds, with M = Ru, Rh, Pd, and M = 3*d* transition element (Roy-Montreuil *et al.* 1968, Deyris *et al.* 1979). The two Pd positions show a different crystal-chemical environment (Table 5). Of these, Pd1 coordinates four As atoms (with a mean bond distance of 2.522 Å) and six Pd2 atoms, which form a trigonal prism around Pd1. On the other hand, Pd2 coordinates one As1 at a distance of 2.715 Å and other four As2 (mixed As,Hg) at 2.719 Å. The coordination sphere is completed by six Pd1 atoms (forming a trigonal prism around Pd2). The most interesting crystal-chemical feature observed in the structure of atheneite, however, concerns the environment of the arsenic atoms. Both the As atoms have a tricapped trigonal prismatic coordination (Figs. 4, 5) but with some differences. For As1, the six distances forming the trigonal prism are the shortest (2.452 Å), whereas for As2 such distances are the longest (2.719 Å). The overall mean bond-distance for As1 (2.555 Å) in atheneite is in good agreement with the <As1–Pd1,2> in the crystal structure of synthetic AsCrPd (2.547 Å; Deyris *et al.* 1979). The As2 position (with an occupancy of 0.60 As and 0.40 Hg) shows the three short distances with Pd1 (2.568 Å), much longer with respect to those observed for the As2 position (fully occupied by As) in the crystal structure of synthetic AsCrPd (2.444 Å; Deyris *et al.* 1979). This accounts for a longer overall <As2–Pd1,2> bond, which is 2.669 Å in atheneite and

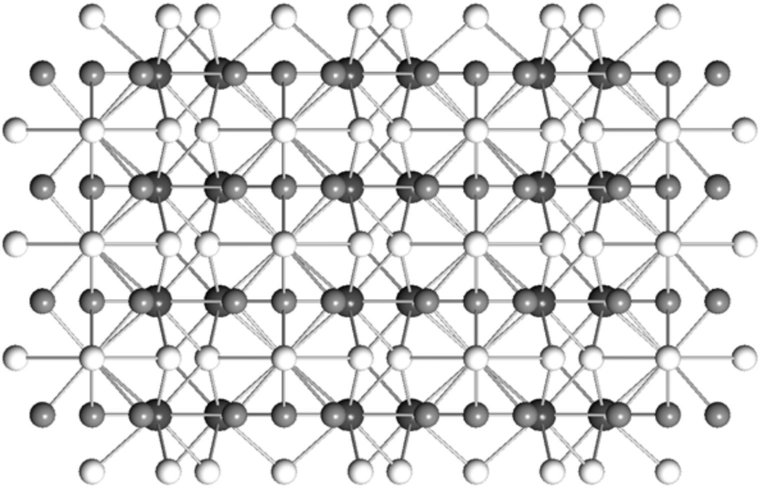

FIG. 3. The crystal structure of atheneite projected down [100]. Symbols as in Figure 1.

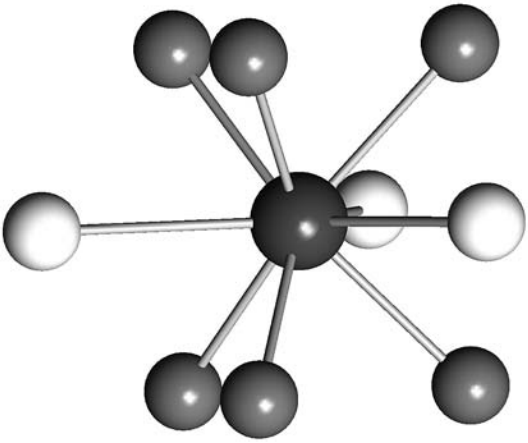

FIG. 4. Coordination polyhedron of the As1 atom. Colors of atoms as in Figure 1.

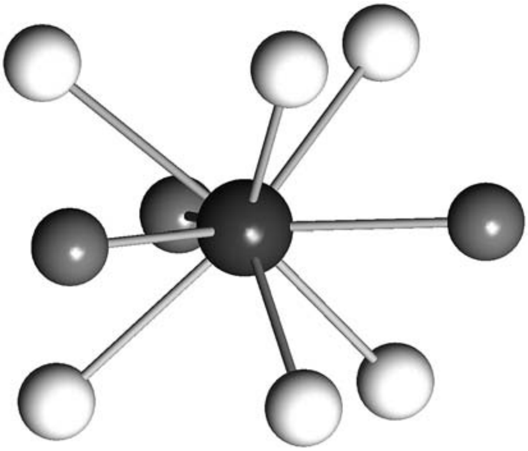

FIG. 5. Coordination polyhedron of the As2 atom. Colors of atoms as in Figure 1.

2.547 Å in synthetic AsCrPd (Deyris *et al*. 1979). The strong enlargement of the As2 site is obviously due to the presence of the larger Hg replacing As.

The crystal structure obtained here indicates that there are nine atoms in the unit cell. Assuming $Z = 3$, the atheneite formula is revised to $Pd_2[As_{0.75}Hg_{0.25}]$ instead of $(Pd,Hg)_3As$ as previously reported. The chemical data reported for atheneite (Table 4) are in keeping with this assumption. Hence, the density for atheneite is 11.36 g/cm$^3$, calculated taking into account the molecular weights of the overall mean given in Table 4 and the unit-cell volume (140.26 Å$^3$) obtained in this study.

Table 6 compares the X-ray powder pattern reported by Clark *et al*. (1974) with that calculated using the structural parameters obtained in this study. Calculated and observed data are in excellent agreement.

TABLE 4. ELECTRON-MICROPROBE DATA (MEANS IN Wt% OF ELEMENTS) AND ATOM RATIOS (ON THE BASIS OF 3 ATOMS AND 4 ATOMS) FOR ATHENEITE

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Pd wt% | 66.00 | 65.60 | 67.15 | 68.18 | 67.90 | 67.04 | 65.33 | 67.11 | 67.76 | 66.90 |
| Pt | n.a. | n.a. | 1.96 | <0.30 | <0.30 | 1.62 | 0.83 | 1.98 | <0.20 | 0.80 |
| Hg | 14.90 | 16.10 | 13.79 | 13.99 | 13.77 | 13.22 | 15.69 | 15.99 | 16.34 | 14.87 |
| Au | 0.50 | 0.30 | 0.47 | 1.10 | 2.06 | 0.39 | 0.23 | n.a. | <0.30 | 0.59 |
| Ag | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | <0.20 | 0.02 |
| Fe | n.a. | n.a. | 0.08 | 0.05 | 0.07 | 0.22 | 0.03 | n.a. | <0.07 | 0.06 |
| Cu | 0.10 | 0.10 | <0.07 | <0.07 | <0.07 | <0.07 | 0.02 | 0.84 | <0.10 | 0.16 |
| As | 19.00 | 19.00 | 17.48 | 16.94 | 16.90 | 18.30 | 17.64 | 15.86 | 15.64 | 17.42 |
| Sb | 0.10 | 0.30 | <0.03 | <0.03 | <0.03 | <0.03 | 0.10 | 0.00 | 0.43 | 0.12 |
| Sn | n.a. | n.a. | <0.03 | <0.03 | <0.03 | <0.03 | 0.03 | 0.00 | n.a. | 0.02 |
| Se | n.a. | n.a. | <0.07 | <0.07 | <0.07 | 0.13 | 0.04 | 0.00 | <0.05 | 0.05 |
| Bi | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 0.03 | n.a. | n.a. | 0.00 |
| Total | 100.60 | 101.40 | 101.13 | 100.76 | 101.20 | 101.05 | 99.97 | 101.78 | 101.09 | 101.01 |
| $\Sigma_{atoms} = 3$ | | | | | | | | | | |
| Pd *apfu* | 1.96 | 1.93 | 1.99 | 2.03 | 2.02 | 1.97 | 1.98 | 2.00 | 2.04 | 1.99 |
| Pt | - | - | 0.03 | 0.00 | 0.00 | 0.03 | 0.01 | 0.03 | 0.00 | 0.01 |
| Hg | 0.23 | 0.25 | 0.23 | 0.22 | 0.23 | 0.21 | 0.25 | 0.26 | 0.26 | 0.24 |
| Au | 0.01 | 0.01 | 0.01 | 0.02 | 0.03 | 0.01 | 0.00 | - | 0.00 | 0.01 |
| Ag | - | - | - | - | - | - | - | - | 0.01 | 0.00 |
| Fe | - | - | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | - | 0.00 | 0.00 |
| Cu | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.01 | 0.01 |
| As | 0.80 | 0.80 | 0.74 | 0.73 | 0.72 | 0.76 | 0.76 | 0.67 | 0.67 | 0.74 |
| Sb | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |
| Sn | - | - | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | - | 0.00 |
| Se | - | - | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Bi | - | - | - | - | - | - | 0.00 | - | - | 0.00 |
| $\Sigma_{atoms} = 4$ | | | | | | | | | | |
| Pd *apfu* | 2.60 | 2.57 | 2.66 | 2.72 | 2.70 | 2.63 | 2.62 | 2.67 | 2.71 | 2.65 |
| Pt | - | - | 0.04 | 0.01 | 0.01 | 0.03 | 0.02 | 0.04 | 0.00 | 0.02 |
| Hg | 0.32 | 0.34 | 0.30 | 0.29 | 0.29 | 0.28 | 0.33 | 0.34 | 0.35 | 0.32 |
| Au | 0.01 | 0.01 | 0.01 | 0.03 | 0.04 | 0.01 | 0.00 | - | 0.01 | 0.01 |
| Ag | - | - | - | - | - | - | - | - | 0.01 | 0.00 |
| Fe | - | - | 0.01 | 0.00 | 0.01 | 0.02 | 0.01 | - | 0.01 | 0.01 |
| Cu | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.01 |
| As | 1.06 | 1.06 | 0.98 | 0.95 | 0.95 | 1.02 | 1.02 | 0.90 | 0.89 | 0.98 |
| Sb | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 |
| Sn | - | - | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | - | 0.00 |
| Se | - | - | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Bi | - | - | - | - | - | - | 0.00 | - | - | 0.00 |

Notes: n.a.: not analyzed. Columns: 1–2: Clark *et al.* (1974), 3–6: Cabral *et al.* (2002), 7: this study (mean of six determinations on different spots), 8: Kwitko *et al.* (2002), 9: Cabral *et al.* (2008), 10: overall mean.

TABLE 5. THE MAIN INTERATOMIC DISTANCES (Å) IN ATHENEITE

| | | | | | |
|---|---|---|---|---|---|
| Pd1 | – As1 (×2) | 2.475(2) | Pd2 | – As1 | 2.715(3) |
| | – As2 (×2) | 2.568(2) | | – As2 (×4) | 2.719(1) |
| | – Pd2 (×2) | 2.922(3) | | – Pd1 (×2) | 2.922(3) |
| | – Pd2 (×4) | 2.954(2) | | – Pd1 (×4) | 2.954(2) |
| As1 | – Pd1 (×6) | 2.475(2) | As2 | – Pd1 (×3) | 2.568(2) |
| | – Pd2 (×3) | 2.715(3) | | – Pd2 (×6) | 2.719(1) |

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TABLE 6. X-RAY POWDER-DIFFRACTION PATTERNS FOR ATHENEITE

| | | | 1 | | 2 | |
|---|---|---|---|---|---|---|
| h | k | l | $d_{calc}$ (Å) | $I/I_o$ | $d_{obs}$ (Å) | $I/I_o$ |
| 0 | 0 | 1 | 3.4892 | 5.38 | - | - |
| 1 | 1 | 0 | 3.4065 | 2.08 | - | - |
| 1 | 0 | 1 | 3.0033 | 1.03 | - | - |
| 1 | 1 | 1 | 2.4375 | 100.00 | 2.423 | vvs |
| 2 | 0 | 1 | 2.2528 | 72.44 | 2.246 | vs |
| 2 | 1 | 0 | 2.2301 | 44.18 | 2.221 | m |
| 3 | 0 | 0 | 1.9667 | 42.29 | 1.958 | w |
| 2 | 1 | 1 | 1.8791 | 28.89 | 1.871 | ms |
| 0 | 0 | 2 | 1.7446 | 20.79 | 1.738 | mw |
| 3 | 0 | 1 | 1.7133 | 2.28 | 1.708 | vw |
| 2 | 2 | 0 | 1.7033 | 3.11 | - | - |
| 3 | 1 | 0 | 1.6364 | 6.58 | 1.632 | w |
| 2 | 2 | 1 | 1.5306 | 3.52 | 1.526 | vvw |
| 3 | 1 | 1 | 1.4816 | 6.01 | 1.477 | mw |
| 4 | 0 | 0 | 1.4751 | 1.30 | - | - |
| 2 | 1 | 2 | 1.3741 | 14.77 | 1.371 | s |
| 4 | 0 | 1 | 1.3586 | 1.45 | - | - |
| 3 | 2 | 0 | 1.3536 | 2.41 | 1.352 | vw |
| 3 | 0 | 2 | 1.3051 | 18.56 | 1.302 | s |
| 4 | 1 | 0 | 1.2875 | 5.07 | 1.286 | m |
| 3 | 2 | 1 | 1.2620 | 22.26 | 1.259 | s |
| 2 | 2 | 2 | 1.2187 | 1.88 | 1.215 | vvw |
| 4 | 1 | 1 | 1.2079 | 6.76 | 1.205 | m |
| 3 | 1 | 2 | 1.1935 | 3.82 | 1.191 | mw |
| 5 | 0 | 0 | 1.1800 | 1.50 | - | - |
| 3 | 3 | 0 | 1.1355 | 2.15 | 1.134 | vvw |
| 5 | 0 | 1 | 1.1178 | 5.51 | - | - |
| 4 | 2 | 0 | 1.1150 | 3.74 | 1.113 | mw |
| 1 | 1 | 3 | 1.1007 | 5.60 | 1.098 | mw |
| 2 | 0 | 3 | 1.0820 | 5.21 | 1.080 | w |
| 3 | 2 | 2 | 1.0695 | 2.05 | 1.067 | w |
| 4 | 2 | 1 | 1.0621 | 2.81 | 1.059 | w |
| 5 | 1 | 0 | 1.0597 | 2.47 | - | - |
| 4 | 1 | 2 | 1.0360 | 5.03 | 1.034 | ms |
| 2 | 1 | 3 | 1.0312 | 3.49 | - | - |
| 5 | 1 | 1 | 1.0140 | 5.01 | 1.012 | mw |
| 5 | 0 | 2 | 0.9774 | 1.77 | 0.9750 | vw |
| 3 | 3 | 2 | 0.9517 | 2.87 | - | - |
| 3 | 1 | 3 | 0.9480 | 1.39 | 0.9444 | vw |
| 5 | 2 | 0 | 0.9448 | 3.59 | 0.9422 | mw |
| 4 | 2 | 2 | 0.9395 | 5.19 | 0.9364 | w |
| 5 | 2 | 1 | 0.9120 | 1.32 | 0.9094 | w |
| 5 | 1 | 2 | 0.9057 | 3.97 | 0.9030 | mw |
| 6 | 1 | 0 | 0.8998 | 1.21 | - | - |
| 3 | 2 | 3 | 0.8822 | 10.15 | 0.8795 | ms |
| 0 | 0 | 4 | 0.8723 | 2.79 | - | - |
| 6 | 1 | 1 | 0.8713 | 6.48 | 0.8692 | vw |
| 4 | 1 | 3 | 0.8631 | 3.80 | 0.8608 | vw |
| 5 | 2 | 2 | 0.8308 | 8.57 | 0.8288 | mw |
| 5 | 0 | 3 | 0.8284 | 4.65 | 0.8265 | m |
| 4 | 4 | 1 | 0.8273 | 2.97 | 0.8248 | mw |
| 5 | 3 | 1 | 0.8193 | 1.43 | 0.8168 | vvw |
| 2 | 1 | 4 | 0.8124 | 6.44 | 0.8106 | mw |
| 4 | 2 | 3 | 0.8049 | 3.39 | 0.8030 | vvw |
| 6 | 1 | 2 | 0.7997 | 3.89 | 0.7979 | w |
| 3 | 0 | 4 | 0.7974 | 12.26 | 0.7958 | m |
| 6 | 2 | 1 | 0.7966 | 2.70 | 0.7946 | mw |
| 5 | 1 | 3 | 0.7833 | 10.60 | 0.7817 | ms |
| 7 | 1 | 0 | 0.7815 | 3.15 | 0.7799 | mw |
| 2 | 2 | 4 | 0.7764 | 3.43 | - | - |

*Note*: 1: Calculated powder-pattern and indexing for atheneite of this study. The *d* values are calculated on the basis of *a* = 6.813(1) Å, *c* = 3.4892(5) Å, and with the atom coordinates reported in Table 2. Intensities are calculated using the XPOW software, version 2.0 (Downs *et al.* 1993). 2: Observed powder-pattern originally reported by Clark *et al.* (1974).

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