

SZYMAŃSKIITE, $\text{Hg}_{16}^{1+}(\text{Ni,Mg})_6(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_3\text{O})_8^{1+} \cdot 3\text{H}_2\text{O}$, A NEW MINERAL SPECIES FROM THE CLEAR CREEK CLAIM, SAN BENITO COUNTY, CALIFORNIA¹

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ABSTRACT

The new mineral species *szymańskiite*, $\text{Hg}_{16}^{1+}(\text{Ni,Mg})_6(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_3\text{O})_8^{1+} \cdot 3\text{H}_2\text{O}$, occurs as sprays of mm-sized crystals in vugs and cavities, and as disseminated single crystals and aggregates of crystals within massive quartz, at a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California. The mineral is most closely associated with cinnabar, montroydite, native mercury, edgarbaileyite and millerite in a matrix principally composed of quartz, chalcodony, opal, ferroan magnesite, goethite, chromite and minor chlorite and dolomite. It is hexagonal, $P6_3$, a 17.415(5), c 6.011(4) Å, V 1579(2) Å³, c/a 0.3452. The strongest eight lines of the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 14.9(100)(100), 5.60(100)(101), 3.299(80)(410), 3.201(50)(401), 2.704(60)(510,501), 2.665(60)(212), 2.476(50)(222) and 1.751(50)(702,532). The empirical formula, derived from crystal-structure analysis and electron-microprobe analyses, is $\text{Hg}_{16}^{1+}(\text{Ni}_{4.08}\text{Mg}_{1.92})_{\Sigma 6}(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_3\text{O})_8^{1+} \cdot 3\text{H}_2\text{O}$, based on $O = 59$. It requires MgO 1.67, NiO 6.59, Hg₂O 72.14, CO₂ 11.42, H₂O 8.18, total 100.00 wt.%. For the idealized formula with a Ni:Mg ratio of 2.125, the calculated density is 4.86 g/cm³ ($Z = 1$). Individual crystals of *szymańskiite* are acicular to prismatic, euhedral to subhedral, and do not exceed 0.4 mm in length by 0.05 mm in width. They are elongate [0001], with striations parallel to [0001] on {10 $\bar{1}$ 0}. Forms observed are {10 $\bar{1}$ 0} major and {0001} minor. Cleavage, on {10 $\bar{1}$ 0}, is poor. Freshly exposed crystals are transparent light blue-grey with a very pale blue streak and an irregular to conchoidal fracture. *Szymańskiite* is vitreous, brittle, nonfluorescent, and over an extended period of time, it is light-sensitive. It is uniaxial negative, ω 1.795(3), ϵ 1.786(3), and is pleochroic with O yellowish green, E bluish green, and $E > O$. The mineral name honors Dr. Jan T. *Szymański*, who determined the crystal structure.

Keywords: *szymańskiite*, new mineral species, hydrated hydronium mercurous nickel hydroxide-carbonate, X-ray data, Clear Creek mine, San Benito County, California.

SOMMAIRE

La *szymańskiite*, $\text{Hg}_{16}^{1+}(\text{Ni,Mg})_6(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_3\text{O})_8^{1+} \cdot 3\text{H}_2\text{O}$, nouvelle espèce minérale, forme des cristaux millimétriques dans des vacuoles ou disséminés ou en agrégats dans le quartz massif dans un puit de prospection près de la mine de mercure de Clear Creek, abandonnée depuis longtemps, du district de New Idria, comté de San Benito, en Californie. Ce minéral est étroitement associé à cinnabre, montroydite, mercure natif, edgarbaileyite et millerite dans une matrice composée surtout de quartz, calcédoine, opale, magnésite ferreuse, goethite et chromite, avec chlorite et dolomite accessoires. La *szymańskiite* est hexagonale, $P6_3$, a 17.415(5), c 6.011(4) Å, V 1579(2) Å³, c/a 0.3452. Les huit raies les plus intenses du cliché de poudre [d en Å(I)(hkl)] sont: 14.9(100)(100), 5.60(100)(101), 3.299(80)(410), 3.201(50)(401), 2.704(60)(510,501), 2.665(60)(212), 2.476(50)(222) et 1.751(50)(702,532). La formule empirique, déduite des résultats d'une structure cristalline et des analyses à la microsonde électronique, serait $\text{Hg}_{16}^{1+}(\text{Ni}_{4.08}\text{Mg}_{1.92})_{\Sigma 6}(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_3\text{O})_8^{1+} \cdot 3\text{H}_2\text{O}$, sur une base de 59 atomes d'oxygène. Cette formule correspond à MgO 1.67, NiO 6.59, Hg₂O 72.14, CO₂ 11.42, H₂O 8.18, total 100.00 % en poids. Pour la formule idéale, ayant un rapport de Ni à Mg de 2.125, la densité calculée est 4.86 g/cm³ ($Z = 1$). Les cristaux individuels de *szymańskiite* sont aciculaires à prismatiques, idiomorphes à sub-idiomorphes, et ne dépassent pas 0.4 mm en longueur et 0.05 mm en largeur. Ils sont allongés [0001] et striés parallèles à [0001] sur {10 $\bar{1}$ 0}. Les formes observées sont {10 $\bar{1}$ 0} dominante et {0001} secondaire. Le clivage, {10 $\bar{1}$ 0}, est de piètre qualité. Les cristaux nouvellement exposés aux éléments sont transparents et bleu-gris pâle, et montrent une rayure bleu très pâle et une cassure irrégulière à conchoïdale. La *szymańskiite* a un aspect vitreux; elle est cassante, non fluorescente, et sensible à la lumière après un certain temps. Elle est uniaxe négative, ω 1.795(3), ϵ 1.786(3), et pleochroïque, avec O vert jaunâtre, E vert bleuâtre, et $E > O$. Le nom honore Jan T. *Szymański*, qui en a déterminé la structure.

(Traduit par la Rédaction)

Mots-clés: *szymańskiite*, nouvelle espèce minérale, hydroxyde-carbonate hydraté de hydronium, mercure(I) et nickel, données de diffraction X, mine de Clear Creek, comté de San Benito, Californie.

¹Geological Survey of Canada, contribution number 44689.

INTRODUCTION

Szymańskiite, ideally $\text{Hg}_{16}^{1+}(\text{Ni},\text{Mg})_6(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_3\text{O})_{18}^{1+}\cdot 3\text{H}_2\text{O}$, is a newly recognized mineral species that was first encountered during megascopic examination and routine X-ray powder-diffraction characterization of mercury-bearing minerals collected in 1972 from a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California (lat. $36^\circ 22' 59''\text{N}$, long. $120^\circ 43' 58''\text{W}$). One of the authors (RCE) noticed what appeared to be small sprays of stibnite in a tiny vug in a hand specimen composed principally of blackish chert and white, well-crystallized quartz. Several of the black needles were lightly crushed under glass, which immediately revealed the megascopic misidentification, as they are nonopaque. Further grinding produced a very pale blue powder. Subsequent analysis by X-ray powder diffraction failed to produce a match with any inorganic compound listed in the JCPDS Powder Diffraction File, although the powder pattern does bear a superficial resemblance to that of faujasite (PDF 11-672), especially for several of the strongest powder lines. Further studies have shown that the

mineral is photosensitive and slowly darkens on prolonged exposure to light. The discovery specimen was housed in a mineral drawer and had been repeatedly subjected to light over a period of at least seventeen years.

Szymańskiite (SHĪ•MAN•SKĚ•AIT) is named in honor of Dr. Jan T. Szymański, X-ray crystallographer at CANMET (Canada Centre for Mineral and Energy Technology), Ottawa, Ontario, for his many outstanding structural contributions to mineralogy and crystallography. Dr. Szymański solved the crystal structure of this mineral prior to his knowledge of the mineral name. The new mineral species and mineral name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Holotype material, consisting of three small szymańskiite-bearing micromounts, are housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario under catalogue number NMC 65743.

OCCURRENCE AND ASSOCIATED MINERALS

Szymańskiite is a very rare constituent at the Clear

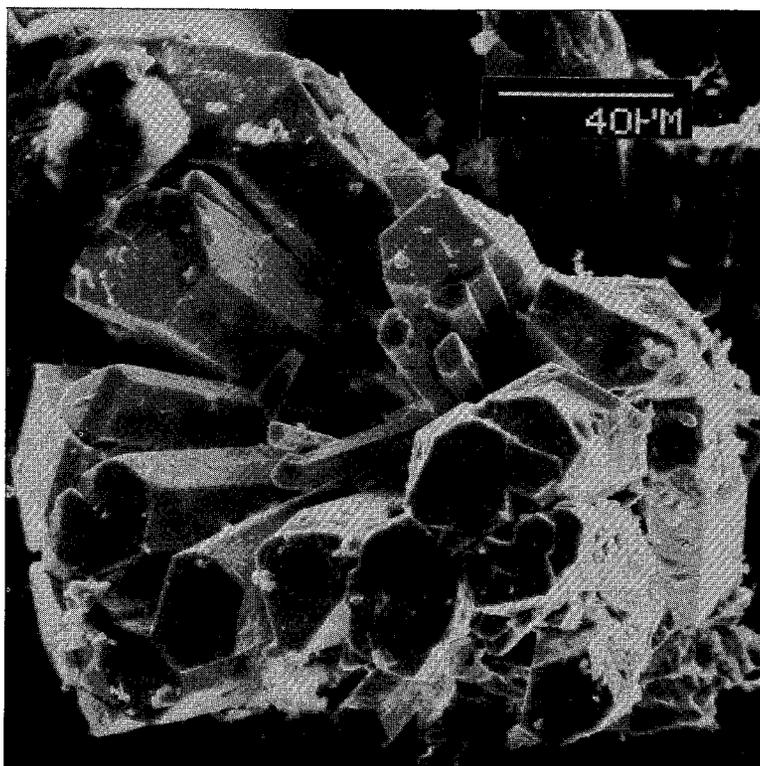


FIG. 1. SEM photomicrograph of a group of szymańskiite crystals. Scale bar: 40 μm .

Creek claim. Only three small micromounts, containing an estimated 20 mg of sample, have been identified to date. The mineral is found within mm-sized cavities of colorless to white, well-crystallized quartz and is surrounded by massive amber edgarbaileyite (Roberts *et al.* 1990a), which in turn has mm-size needles of red montroydite perched on it. In addition, disseminated single crystals and aggregates of szymańskiite and millerite have been identified within the surrounding massive quartz. The mineral appears to have formed at low temperature and pressure from CO₂-bearing residual fluids enriched in Hg and Ni. The mineral is most closely associated with montroydite, native mercury, edgarbaileyite, millerite and euhedral crystals of cinnabar in a matrix composed principally of quartz, chalcedony, opal, ferroan magnesite, goethite, chromite and minor chlorite and dolomite. Other mercury-bearing minerals at the Clear Creek claim, identified by X-ray powder diffraction, are metacinnabar, eglestonite, calomel, gianellaite, mosesite, edoylerite (Erd *et al.*, in preparation), wattersite (Erd *et al.*, in preparation) and four unidentified Hg-bearing phases that are currently under study.

PHYSICAL AND OPTICAL PROPERTIES

Szymańskiite occurs in vugs and cavities as sprays

of mm-size crystals, and is also found within massive quartz as disseminated single crystals and crystal aggregates. Individual acicular to prismatic crystals are euhedral to subhedral, up to 0.4 mm in length by 0.05 mm in width, and are elongate [0001], with striations parallel to [0001] on {10 $\bar{1}$ 0}. Forms observed are {10 $\bar{1}$ 0} major and {0001} minor, with a poor cleavage on {10 $\bar{1}$ 0}. An SEM photomicrograph of a spray of crystals is presented in Figure 1. The average size of a crystal is 0.1 mm long by 0.01 mm wide. Freshly exposed crystals are transparent light blue-grey in color; masses are a slightly deeper blue-green color. The mineral is light-sensitive and slowly turns darker on prolonged exposure to light. It has a very pale blue streak, an irregular to conchoidal fracture, a vitreous luster, is brittle, and is nonfluorescent under both long- and short-wave ultraviolet light. The crystals are too small for an accurate determination of hardness, and there is insufficient material available for a determination of density using the Berman balance. Szymańskiite turns white with a very pale blue cast in cold dilute HCl, but is otherwise unaffected. This same phenomenon occurs in cold concentrated HCl with some minor effervescence.

Optical measurements made with a spindle stage using sodium light (λ 589 nm) reveal that szymańskiite is uniaxial negative, ω 1.795(3), ϵ

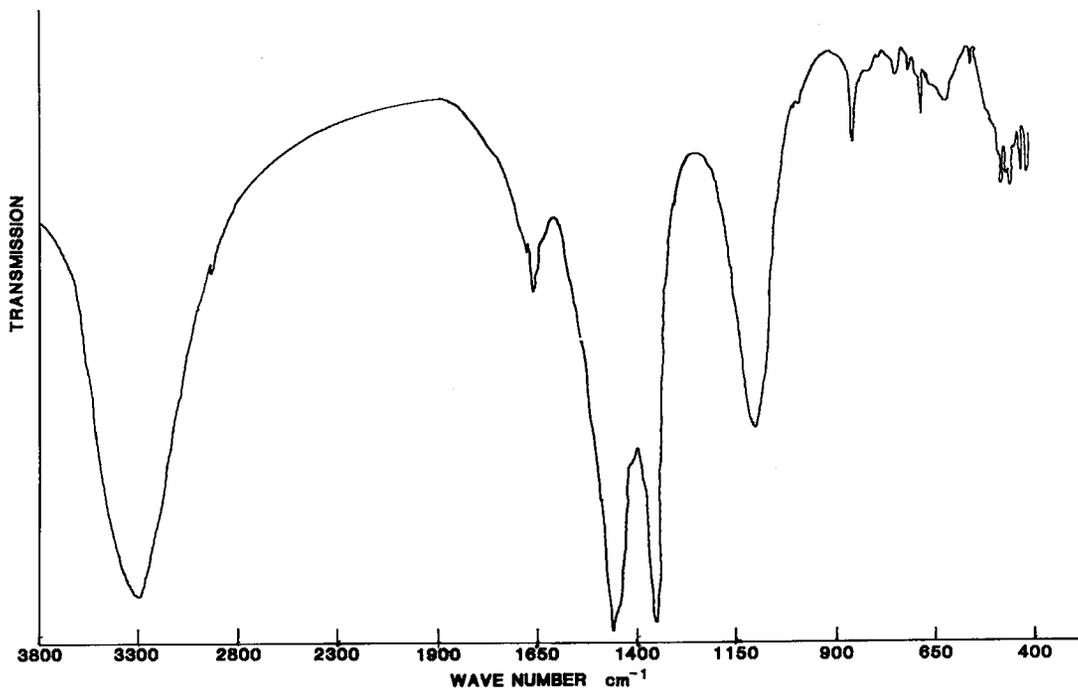


FIG. 2. Infrared-absorption spectrum for szymańskiite. The C-C interactions of the diamond-anvil cell in the range 1900–2200 cm⁻¹ have been removed from the spectrum.

1.786(3), and is pleochroic with *O* yellowish green, *E* bluish green, and with *E* > *O*. Material exposed to X radiation also is pleochroic, with *O* yellowish green, *E* lavender, and with *E* > *O*.

CHEMISTRY

Szymańskiite crystals were analyzed with a JEOL 733 electron microprobe at the Canadian Museum of Nature. The only elements detected were Ni, Hg, Mg and C. No other elements with *Z* greater than 11 were detected in energy-dispersion spectra; B, N and F were sought with wavelength spectrometers, but are absent. The elements Ni, Hg and Mg were sought at 15 kV, 25 nA with a 5- μ m beam spot. The maximum count-time in all cases was 15 seconds. Corrections to the sample and standard data for *CK* α X rays, generated by the carbon coating, proved to be identical; consequently the counts for C were not adjusted. Synthetic magnocolumbite (Mg), synthetic nichromite (Ni), montroydite (Hg), cerussite (C) and rhodochrosite (C) were used as standards. Data reduction was performed with a conventional ZAF routine in the Tracor Northern Task series of programs. The average of 3 analyses gave MgO 2.0(2), NiO 7.9(2), Hg₂O 75.8(9), CO₂ 6.0(4) using the cerussite standard, and CO₂ 10.7(9) using the rhodochrosite standard. The results for CO₂ vary dramatically depending upon which standard is used. This is due to the inability of ZAF theory to adequately deal with strong matrix effects (*i.e.*, the behavior of *CK* α X rays in the presence of Hg atoms). Thus without excellent standards, electron-

microprobe analyses for C in minerals that also contain very heavy elements are, at best, semiquantitative. The powder infrared absorption spectrum (Fig. 2) was collected at the Canadian Conservation Institute using a Nicolet FTIR (model 5DX) equipped with a diamond-anvil microsample cell. Crystals were crushed in the cell, minimizing the amount of adsorbed water. The spectrum is simple, and shows the presence of structural water (H₂O flex at 1650 cm⁻¹); the strong absorption at 3308 cm⁻¹ is due to OH stretching in the H₂O molecules and in hydroxyl groups. Internal modes for carbonate groups account for the rest of the large absorptions ν_1 1094, ν_2 844, ν_3 1452 and 1350, ν_4 669 cm⁻¹. The remainder of the spectrum is assigned to various lattice modes (*e.g.*, minor absorptions at 737, 702 cm⁻¹). Experimental flaws and artifacts have been removed from Figure 2 (sharp absorptions in the ranges 2300–2400 and 400–600 cm⁻¹ due to atmospheric CO₂ and instrument vibration, sharp absorptions in the range 1900–2200 cm⁻¹ due to C–C interactions in the diamond-anvil cell).

A dearth of pure material prevented the quantitative determination of H₂O. Consequently, quantitative values for CO₂ and H₂O were derived from the results of the crystal-structure analysis (Szymański & Roberts 1990a). The structure consists of a rigid framework surrounding large open hexagon-shaped tunnels. Application of heat, such as that produced by an electron-microprobe beam with a relatively high flux of current, drives out the disordered, loosely bound CO₂ and H₂O molecules from the structure. This, in turn, causes anomalously high MgO, NiO and Hg₂O values in the probe analyses. The same effect has been reported for voggite (Roberts *et al.* 1990b, Szymański & Roberts 1990b), which shows more pronounced differences between observed and calculated compositions determined on the electron microprobe. Using the results of the crystal-structure analysis and the Ni:Mg ratio of 2.125:1 derived from the electron-microprobe analyses, the chemical formula, based on O = 59, is Hg₁₆¹⁺(Ni_{4.08}Mg_{1.92})_{Σ6.00}(CO₃)₁₂(OH)₁₂(H₃O)₈⁺·3H₂O, which requires MgO 1.67, NiO 6.59, Hg₂O 72.14, CO₂ 11.42, H₂O 8.18, total 100.00 wt.%. This is yet another example of the use of crystal-structure analysis in order to determine the precise chemical formula of a complex mineral species (Hawthorne & Grice 1990).

The Gladstone–Dale constants of Mandarino (1981) and the oxide proportions determined from the crystal structure lead to a *K_C* value of 0.1635 if a Gladstone–Dale constant *k* of 0.134 is assumed for Hg₂O. *K_p*, calculated using the averaged indices of refraction and the calculated density, is 0.1630. Thus, 1–(*K_p*/*K_C*) is +0.003, indicating superior compatibility between the physical and chemical data (Mandarino 1981).

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR SZYMAŃSKIITE

<i>I</i> (est.)	<i>d</i> (\AA)(meas.)	<i>d</i> (\AA)(calc.)	<i>hkl</i>	<i>I</i> (est.)	<i>d</i> (\AA)(meas.)	<i>d</i> (\AA)(calc.)	<i>hkl</i>
100	14.9	15.1	100	50	2.476	2.473	222
30	8.72	8.71	110	5	2.415	2.415	520
10	7.56	7.54	200			2.300	610
5	5.74	5.70	210	30	2.295	2.292	431
100	5.60	5.58	101	30	2.242	2.241	521
30	4.71	4.70	201	25	2.155	2.155	700
5	4.35	4.35	220	15	2.089	2.088	332
		4.18	310	10	2.089	2.088	422
40	4.17	4.14	211	5	2.027	2.028	531
45	3.87	3.84	301	5	1.974	1.975	621
3	3.54	3.53	221	20	1.933	1.936	203
20	3.486	3.480	320			1.896	711
80	3.299	3.291	410	40	1.894	1.890	213
50	3.201	3.194	401	3	1.863	1.861	303
		3.016	500	15	1.811	1.812	631
30	3.015	3.006	002	15	1.798	1.799	801
		2.850	420	10	1.762	1.763	442
30	2.849	2.841	112			1.751	702
		2.709	510	50	1.751	1.751	532
60	2.704	2.696	501	3	1.716	1.717	622
60	2.665	2.659	212	10	1.697	1.697	730
		2.580	302	20	1.663	1.664	712
30	2.580	2.575	421	15	1.645	1.646	820
10	2.512	2.514	600				

114.6 mm Debye - Scherrer powder camera; Cu radiation, Ni filter (λ Cu K α 1.54178 \AA)
intensities estimated visually; not corrected for film shrinkage
indexed on *a* 17.415, *c* 6.011 \AA

X-RAY STUDIES

A single, untwinned crystal of *szymańskiite* was examined by single-crystal precession methods employing Zr-filtered $\text{MoK}\alpha$ radiation. It was initially mounted such that a^* is parallel to the dial axis, then remounted such that 110^* is parallel to the dial axis. The following levels were collected: $hk0 \rightarrow hk2$, $h0l \rightarrow h3l$ and hhl . Precession films indicate hexagonal symmetry, and measured unit-cell parameters a 17.36 and c 6.00 Å. The $hk0 \rightarrow hk2$ precession films display only 6 as the diffraction symmetry, and the only systematic absence is $00l$ with $l \neq 2n$. The permissible space-groups are $P6_3/m$ (176) and $P6_3$ (173) (diffraction aspect $P6_3/*$). The correct space-group is $P6_3$, as determined from crystal-structure studies (Szymański & Roberts 1990a). There is a pseudo-absence, hhl with $l \neq 2n$; nodes of the type hhl and l odd are very weak to absent on single-crystal precession films. The refined unit-cell parameters, a 17.415(5), c 6.011(4) Å, V 1579(2) Å³ and c/a 0.3452, are based on 20 X-ray powder lines between 3.466 and 1.645 Å for which unambiguous indexing was possible. A fully indexed powder pattern is presented in Table 1. All indexed reflections were checked on single-crystal precession films. The powder pattern is unique, but it does bear a superficial resemblance to that of *faujasite* (PDF 11-672), especially for several of the stronger reflections. With $Z = 1$, the calculated density for $\text{Hg}_{16}^{1+}(\text{Ni},\text{Mg})_6(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_2\text{O})_8^+ \cdot 3\text{H}_2\text{O}$ and a Ni:Mg ratio of 2.125:1 is 4.86 g/cm³.

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