

THE NEW MINERAL SPECIES BRODTKORBITE, Cu_2HgSe_2 , AND THE ASSOCIATED SELENIDE ASSEMBLAGE FROM TUMINICO, SIERRA DE CACHO, LA RIOJA, ARGENTINA

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ABSTRACT

Brodtkorbite, ideally Cu_2HgSe_2 , a new mineral species, occurs in a telethermal selenide vein-type assemblage at the Tuminico la selenium deposit, Sierra de Cacho (Sierra de Umango) district, La Rioja, Argentina. The selenide assemblage also contains berzelianite, bellidoite, cadmoselite (mercurian, cuprian), chaméanite, crookesite, eskebornite, eucairite, ferroselite, hakite, klockmannite, a luanheite-type phase, trogtalite-krutaité, tiemannite, tyrrellite, umangite and uraninite. Minor constituents are undefined phases that belong to the Cd-(Cu)-Hg-Se and (Co,Ni,Cu)-As-Se systems. The selenides occur as veinlets, as impregnations and as massive ores in calcite veins, and are hosted by altered (hematite-stained) amphibolites of the Sierra de Pampeanas, the Precambrian basement of the Precordillera terrane. Brodtkorbite was observed as anhedral grains; they range in size from 10×20 up to 50×100 μm and as aggregates of composite grains up to 150×250 μm , commonly intergrown with berzelianite, tiemannite and (rarely) umangite and clausthalite. The mineral is dark grey, opaque, has a metallic luster, and a dark grey streak. VHN_{10} ranges from 91.4 to 131 (mean 118) kg/mm^2 , which corresponds to a calculated Mohs hardness of about $2\frac{1}{2}$ to 3. The density is 7.77 g/cm^3 and was calculated for the ideal formula with $Z = 2$. In plane-polarized reflected light, the mineral is white, is weakly to moderately pleochroic from pinkish to bluish white, and lacks internal reflections. It has a weak to strong birefractance; the anisotropy is weak to strong with rotation tints from mauve-grey to yellowish grey. The reflectance spectra and color values in air and in oil are tabulated. The chemical composition, which was obtained with an electron microprobe, shows very little variation within individual grains and between grains. The average composition is: Cu 26.2, Hg 40.7, Se 32.9, total 99.8 wt%. This leads to an empirical formula (total atoms = 5) of $\text{Cu}_{2.00}\text{Hg}_{0.98}\text{Se}_{2.02}$. Brodtkorbite is monoclinic, a 7.492(5), b 4.177(1), c 7.239(4) Å, β 114.20(5)°, V 206.6(2) Å³, $a:b:c$ 1.7936:1.17330, space group $P2_1/n$ (14). The strongest seven X-ray powder-diffraction lines [d in Å (hkl)] are: 3.991(70)(101), 3.576(50)(110), 3.534(50)(011), 3.414(50)(200), 2.731(100)(112), 2.223(70)(211) and 2.072(50)(113,312). The mineral name honors Milka Kronegold de Brodtkorb, Professor at the universities of Buenos Aires and La Plata, Argentina, for her outstanding contributions to the mineralogy and economic geology of Argentina. The selenide mineralogy at Tuminico is discussed on the basis of an extensive electron-microprobe study. The conditions of formation for brodtkorbite and the associated selenides are inferred from mineral stabilities and fluid-inclusion studies.

Keywords: brodtkorbite, copper mercury selenide, new mineral species, selenide association, electron-microprobe analyses, X-ray data, reflectance data, Tuminico, Sierra de Cacho (Cerro Cacho), Sierra de Umango, La Rioja Province, Argentina.

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SOMMAIRE

La brodtkorbite, dont la composition idéale est Cu_2HgSe_2 , est une nouvelle espèce minérale découverte dans une association de sélénures téléthermaux en veines au gisement de sélénium de Tuminico Ia, district de Sierra de Cacho (Sierra de Umango), La Rioja, Argentine. L'assemblage de sélénures contient berzélanite, bellidoïte, cadmosélie (mercurefère, cuprifère), chaméanite, crookesite, eskébornite, eucairite, ferrosélie, hakite, klockmannite, un minéral ressemblant à la luanhéite, trogtalite-kruitaïte, tiémannite, tyrrellite, umangite et uraninite. Les constituants accessoires sont des phases méconnues des systèmes Cd–(Cu)–Hg–Se et (Co,Ni,Cu)–As–Se. Les sélénures se présentent sous forme de veinules, imprégnations et amas de minéral massif dans des veines de calcite, dans un encaissant d'amphibolite altérée et imprégnée d'hématite, faisant partie de la Sierra de Pampeanas, le socle précambrien de la Précordillère. La brodtkorbite se présente en grains xénomorphes allant de 10×20 jusqu'à $50 \times 100 \mu\text{m}$ et en agrégats de grains composés atteignant $150 \times 250 \mu\text{m}$, généralement en intercroissances avec berzélanite, tiémannite et (plus rarement) umangite et clausthalite. Il s'agit d'un minéral gris foncé, opaque, ayant un éclat métallique et une rayure gris foncé. La dureté VHN₁₀ varie de 91.4 à 131 (118, en moyenne) kg/mm², ce qui correspond à une dureté de Mohs de 2½ à 3. La densité, égale à 7.77 g/cm³, a été calculée pour la formule idéale, avec $Z = 2$. En lumière réfléchie non polarisée, le minéral est blanc, légèrement à modérément pléochroïque du blanc rosâtre à bleuâtre, sans réflexions internes. Sa biréfractance est faible à intense; l'anisotropie est faible à intense, avec des teintes de rotation allant de mauve-gris à gris jaunâtre. Les spectres de réflectance et les valeurs de la couleur dans l'air et dans l'huile sont présentés. La composition chimique, établie avec une microsonde électronique, varie très peu d'un grain à l'autre et à l'intérieur d'un même grain. La composition moyenne est: Cu 26.2, Hg 40.7, Se 32.9, total 99.8% (poids), ce qui mène à une formule empirique (nombre d'atomes égal à 5) de $\text{Cu}_{2.00}\text{Hg}_{0.98}\text{Se}_{2.02}$. La brodtkorbite est monoclinique, a 7.492(5), b 4.177(1), c 7.239(4) Å, β 114.20(5)°, V 206.6(2) Å³, $a:b:c$ 1.7936:1:1.7330, groupe spatial $P2_1/n$ (14). Les sept raies les plus intenses du spectre de diffraction, méthode des poudres [d en Å (hkl)] sont: 3.991(70)(101), 3.576(50)(110), 3.534(50)(011), 3.414(50)(200), 2.731(100)(112), 2.223(70)(211) et 2.072(50)(113,312). Le nom honore Milka Kronegold de Brodtkorb, Professeur aux universités de Buenos Aires et La Plata, en Argentine, et souligne ses contributions très importantes à la minéralogie et à la géologie économique de l'Argentine. Nous discutons de la minéralisation en sélénures à Tuminico à la lumière de notre étude poussée des compositions suite aux analyses à la microsonde électronique. La reconstruction des conditions de formation de la brodtkorbite et des sélénures associés repose sur une évaluation des champs de stabilité des minéraux et des inclusions fluides piégées.

(Traduit par la Rédaction)

Mots-clés: brodtkorbite, sélénure de cuivre et de mercure, nouvelle espèce minérale, association de sélénures, analyses à la microsonde électronique, données de diffraction X, données de réflectance, Tuminico, Sierra de Cacho (Cerro Cacho), Sierra de Umango, province de La Rioja, Argentine.

INTRODUCTION

Selenide mineralization has been known to occur in several provinces of northwestern Argentina since the 19th century. The most important occurrences are located within the province of La Rioja (Fig. 1); silver, copper, selenium and mercury were periodically sought and mined on a small scale in the Sierra de Umango (districts of Sierra de Cacho and Las Asperzas), in Los Llanenes and the Sierra de Famatina (Guerrero 1969, Angelelli 1984, de Brodtkorb *et al.* 1993, Paar *et al.* 1996 a, b, 1998 a, b, 2000). Despite the fact that this Argentinian province hosts one of the most significant concentrations of selenides or selenium on Earth, very little is known about the geology of the various deposits, and in particular, the mineralogy of the numerous occurrences. As part of an ongoing bilateral project between the Austrian (FWF) and Argentinian (CONICET) research councils, a thorough mineralogical investigation of the selenium province of La Rioja is currently being carried out. In this paper, we describe the complex ore mineralogy of the Tuminico selenium deposit, which hosts several unnamed species collected during field work in 1998 and 2001 by the senior author. *Brodtkorbite* is one of these new species. It is named in honor

of Dr. Milka Kronegold de Brodtkorb (b. 1932), Professor at the universities of Buenos Aires and La Plata, Argentina, for her fundamental and numerous contributions to the economic geology and mineralogy of Argentina. The mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (99–023). The holotype material is deposited under catalog numbers 14600 – 14602 in the systematic mineral collection of the Institute of Mineralogy, University of Salzburg, Austria, and cotype material is deposited in the mineral collections of The Natural History Museum, in London, where it is registered as BM 1998, 173.

LOCATION AND GEOLOGY

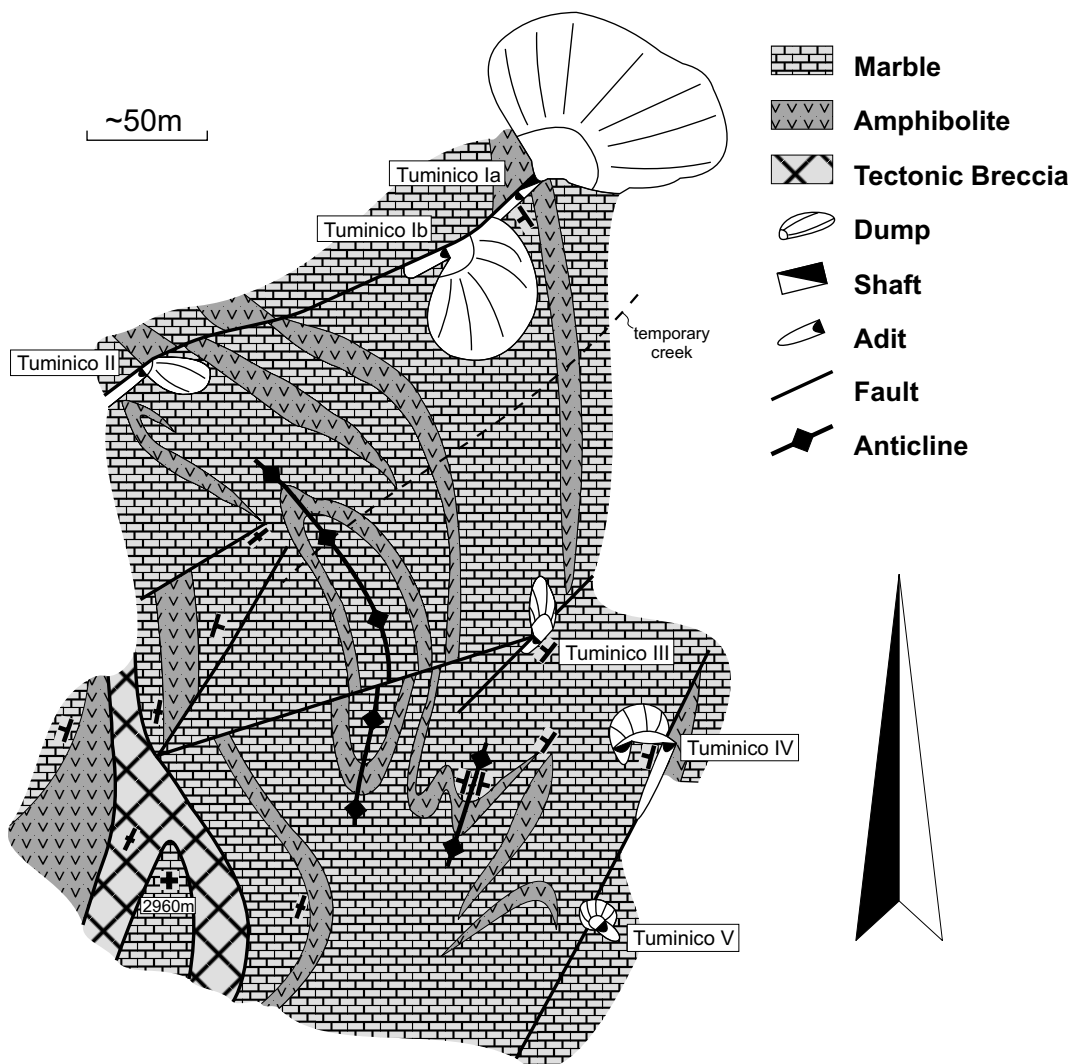
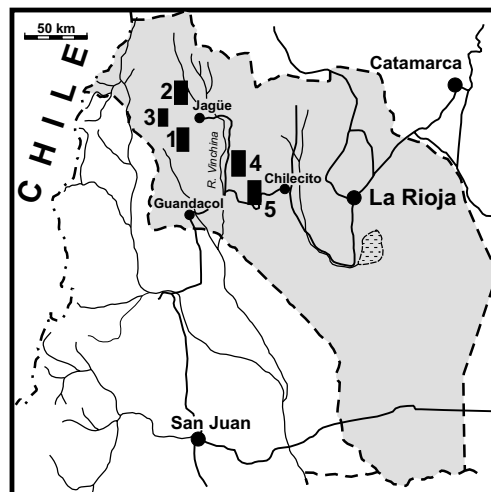
The mining area of Tuminico is located in the northern part of the Sierra de Cacho mountain range, 25 to 30 km southwest of the village Bajo (= Lower) Jagüe,

FIG. 1. Location map of selenide districts and geology of the Tuminico selenide mineralization.



Selenide Districts of La Rioja:

- 1 Cerro Cacho y La Asperzas
- 2 Los Llantenes
- 3 El Chire
- 4 Famatina
- 5 Sañogasta



which is the closest settlement. The dump of Tuminico Ia (Fig. 1), which is the source of the brodtkorbite-bearing specimens, is located at 28°49.9' S (longitude), 68°38.04' W (latitude), at an altitude of 2820 m above sea level, in an extremely remote area that lacks infrastructure and is very difficult of access. The Sierra de Cacho, which is northwest of the Sierra de Umango, after which the copper selenide mineral umangite was named, is part of the Sierras Pampeanas, which belong to the Precambrian basement of the Precordillera terrane. The host rocks of the selenide mineralization consist of marble intercalated with thin layers of amphibolite. The latter are intensely stained with hematite in the vicinity of the selenium-bearing ores. The host-rock schistosity is parallel to the lithologic boundaries and cylindrically folded around NNE-trending axes. Near the crest of the slope (Fig. 1), this structure is disturbed by a N-trending zone of tectonic brecciation up to several tens of meters wide. Large shear lenses, not affected by tectonic crushing, form small peaks along a broad and rather smooth ridge. Related to this shear zone are several NE- to NNE-trending faults to the east of the crest. All five adits of the Tuminico mining area are arranged along these faults. The mineralization is contained within NE-trending calcite veins, which formed during NE-SW compressive strike-slip movements (Amann *et al.* 1999, Amann & Paar 2002).

THE SELENIDE MINERALIZATION

The selenide mineralization occurs as a network of veinlets and disseminations with a calcite gangue. Angular to slightly rounded graphite-bearing fragments of altered (hematite-stained) country rock (amphibolite) also are present in the veins. The accumulations of selenide minerals do not only delineate the boundaries of the calcite grains, but are also irregularly dispersed throughout the calcite matrix. Massive selenide-bearing veins or pods must have been present in the early days of mining in the 20th century, but are now very rarely encountered. Most of the samples used in this study were collected from the dumps, especially from an ore pile at the Tuminico Ia dump (Fig. 1). A few specimens were mined from underground exposures of the Tuminico Ib gallery.

As interpreted from our observations of the mineral textures, the first stage of selenide mineralization involved the formation of Fe, Cu–Fe as well as Co–Cu–Ni selenides and arsenides. The crystallization of ferroselite was followed by tyrrellite and Co-rich members of the trogtalite–krutaite solid-solution series and ended with several as yet undefined (Co,Ni,Cu)–As–Se mineral species.

The second stage commenced with the formation of hakite, cadmoselite and several as-yet undefined Cd–Hg–Se phases, and terminated with the deposition of bukovite and chaméanite. The latter two minerals replace the earlier-formed cadmoselite, but, in turn, were

replaced by umangite, the dominant copper selenide of the third stage.

The third stage involves the precipitation of various copper selenides, which represent more than 90% of the total selenide assemblage. Umangite is the most widespread species and is generally associated with klockmannite. Berzelianite and bellidoite are less common, and their intergrowth textures with umangite point to an overlapping period of crystallization. Crookesite is very rare and is commonly found embedded within berzelianite. Brodtkorbite is generally intimately associated with berzelianite, but their intergrowth textures are not indicative of the sequence of crystallization. Cross-cutting veinlets of tiemannite in brodtkorbite grains mark the beginning of the fourth stage of mineralization, during which Ag–(Cu) and Hg selenides were deposited. These include eucairite, naumannite and the bulk amount of the tiemannite. A very rare Ag–Hg compound, probably related to luanheite, is assumed to have formed during this stage.

The fifth and last stage of ore formation involved the precipitation of sulfides in negligible amounts, particularly chalcopyrite, bornite, chalcocite and covellite. Secondary minerals, such as malachite in reniform and radiating masses, chalcomenite, schmiederite and connellite, are usually observed in vugs and cavities of the calcite gangue.

BRODTKORBITE

Appearance and physical properties

Brodtkorbite is a fairly common species at Tuminico, where it was discovered in specimens stored on the plateau of the Tuminico Ia dump (Fig. 1). It has, as yet, not been encountered in any of the other selenide occurrences of the Sierra de Umango and Los Llantenes districts of La Rioja. The new species occurs as individual anhedral grains that range in size from 10 × 20 µm (rarely up to 50 × 100 µm), and as aggregates of composite grains approaching 150 × 250 µm in size. The most common associated phase is berzelianite, followed by tiemannite, umangite and clausthalite (Figs. 2a–d). Brodtkorbite is dark grey in color, has a metallic luster, a dark grey streak and is brittle. Neither cleavage nor parting is evident in polished sections. The fracture is uneven. The density calculated on the basis of the ideal formula and $Z = 2$ is 7.77 g/cm³.

The Mohs hardness could not be determined because suitable material was not available. The calculated Mohs hardness is about 2½ to 3 based on the equation of Young & Millman (1964) and an average VHN₁₀ of 118 kg/mm². Microhardness measurements were performed with a Leitz Miniload 2 hardness tester using loads of 10 and 25 g. The hardness varies between 91.4 and 131 kg/mm² (10 indentations) for a 10 g load, and between 123 and 136 kg/mm² (four indentations) for a 25 g load.

Electron-microprobe analyses

Thirteen polished sections prepared from the holotype specimen and other samples collected at Tuminico Ia were analyzed with a JEOL Superprobe JXA-8600, equipped with an ELX-LINK system, utilizing an operating voltage of 25 kV and a beam current of 30 nA. Natural Cu_3Se_2 (umangite) ($\text{CuK}\alpha$), natural HgS (cinnabar) ($\text{HgL}\alpha$), and synthetic Bi_2Se_3 ($\text{SeK}\alpha$) were used as standards. The raw data were then corrected with the LINK ZAF-4 program. The results from ten grains in five different sections indicate only minor variation of the chemical constituents (Table 1). The average result of seven point analyses is Cu 26.2, Hg 40.7, Se 32.9, total 99.8 wt%, which corresponds to $\text{Cu}_{2.00}\text{Hg}_{0.98}\text{Se}_{2.02}$ or, ideally, Cu_2HgSe_2 , on the basis of total atoms = 5. Trace amounts of Fe (0.11–0.16 wt.%) were detected in several grains.

Qualitative optical properties

In plane-polarized reflected light (~3200 K), the specular reflectance of brodtkorbite is white and, depending on optical orientation, is weakly to strongly bireflectant and weakly to moderately pleochroic from pinkish to bluish white (Figs. 2a–c). Internal reflections were not observed. It is weakly to strongly anisotropic (polars crossed), and its rotation tints vary from a mauve-grey to a yellowish grey. As usual, these properties are enhanced upon immersion in oil (Fig. 2d).

Quantitative optical properties

The dispersion of the specular reflection of brodtkorbite was measured within the visible spectrum (400–700 nm) at intervals of 10 nm using a Zeiss MPM800 microscope-spectrophotometer. A WTiC reflectance standard (Zeiss 314) was used as reference for the air and oil (Zeiss $N_D = 1.515$) measurements. These were made with $\times 50$ objectives, the effective numerical apertures of which were confined to 0.28, and the diameters of the measured discs were 10 μm .

Table 2 summarizes the data collected from the most bireflectant grain of the mineral. This, and Figure 3, confirm the qualitative observations. From 400 to 500 nm, the reflectance values for R_1 and R_2 are parallel,

descending rapidly from the shorter wavelength. The absolute bireflectance in both media is about 7%, whereas the relative bireflectance is 24% in air and 44% in oil. The reflectance values for the two vibration directions then diverge, and the bireflectance increases to a maximum at about 640 nm (in air, 8% absolute, 31% relative, and in oil, 7% absolute, 57% relative). From there to 700 nm, the bireflectance decreases again (in air, 7% absolute, 26% relative, and in oil, 6% absolute, 47% relative). These points are labored because they provide a partial explanation for the observed reflectance-pleochroism, that the differences and separation in the dispersion of the reflectance values for R_1 and R_2 with the peak at 640 nm provide physical evidence for what is seen by eye. However, the color values for both illuminants (CIE A at 2856 K and CIE C at 6774 K) in Table 2 show insignificant differences in hue (dominant wavelength, λ_d) for the two vibration directions in air and in oil. Similarly, the differences in saturation (excitation purity, P_e %), of the hues are small. Under these circumstances, the most probable explanation for the perceived differences in color is a combination of physiological (eye-brain) and physical factors. The combination of the lower reflectance and slightly higher saturation for the bluish white (R_1) vibration direction provides a visual complement to the higher reflecting, but less saturated pinkish white (R_2) vibration direction.

TABLE 2. REFLECTANCE DATA AND COLOR VALUES FOR BRODTKORBITE

λ nm	R_1	R_2	mR_1	mR_2
400	30.70	38.10	16.50	23.75
420	30.60	38.20	16.30	23.65
440	30.40	37.90	16.00	23.20
460	29.90	37.30	15.50	22.50
470	29.60	37.10	15.15	22.00
480	29.30	36.60	14.90	21.70
500	28.65	36.00	14.30	21.00
520	28.05	35.60	13.80	20.55
540	27.50	35.20	13.40	20.25
546	27.40	35.10	13.30	20.15
560	27.10	35.00	13.15	20.15
580	26.80	34.80	12.80	19.95
589	26.60	34.60	12.70	19.80
600	26.40	34.50	12.50	19.65
620	26.15	34.30	12.35	19.55
640	26.10	34.20	12.25	19.30
650	26.10	34.10	12.30	19.25
660	26.10	33.90	12.40	19.05
680	26.30	33.60	12.60	18.85
700	26.40	33.30	12.70	18.65

CIE: A				
x	0.438	0.442	0.431	0.438
y	0.404	0.405	0.401	0.403
λ_d	27.0	34.9	13.0	20.0
A_p	489	488	488	486
P_e %	2.4	1.5	4.2	2.6

CIE: C				
x	0.300	0.304	0.292	0.299
y	0.306	0.309	0.297	0.303
λ_d	27.3	35.1	13.25	20.2
A_p	478	476	476	474
P_e %	5.1	3.2	8.7	5.8

TABLE 1. ELECTRON-MICROPROBE DATA FOR BRODTKORBITE

	1	2	3	4	5	6	7	$A_v(1-7)^1$
Cu, wt. %	25.8	26.0	26.1	26.2	26.3	26.5	26.2	(0.25)
Hg	41.0	40.8	40.8	40.6	40.9	40.2	40.7	(0.33)
Se	33.5	33.0	32.5	32.5	32.8	32.6	32.9	(0.35)
Total	100.3	99.8	99.4	99.3	100.0	99.3	99.8	

¹ standard deviation in brackets.

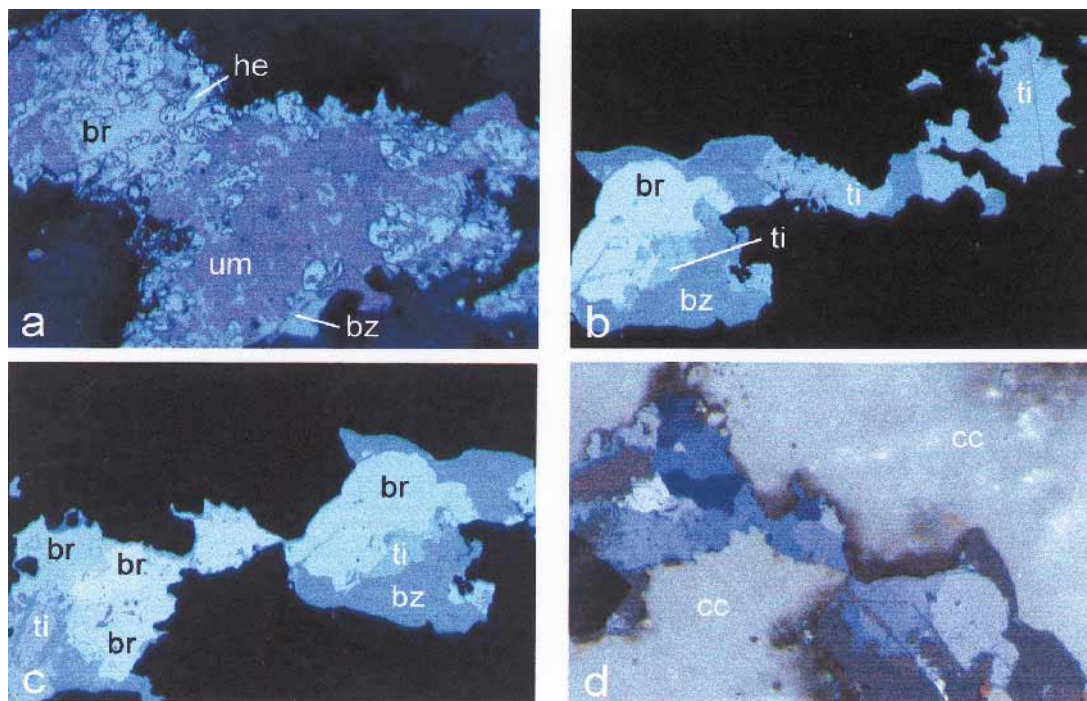


FIG. 2. a) Brodtkorbite (br) in association with umangite (um), berzelianite (bz) and hematite (he) (sample 17/3). b) Brodtkorbite in association with tiemannite (ti) and berzelianite (sample 99/65A). c) Brodtkorbite showing moderate birefringence and pleochroism in the left "half" of the butterfly-shaped aggregate. d) Same as c) with partially crossed polars to show the vivid anisotropic colors of brodtkorbite. Area of images is 0.2×0.14 (a) and 0.5×0.35 mm (b–d).

Calculation of optical constants

Although we have no way of knowing, from the randomly oriented grains in the polished section, whether the extreme values for R_1 and R_2 were measured on principal sections, it was decided to calculate the optical constants corresponding to these vibration directions using the two-media method. This serves two purposes; firstly, to see how the indices of refraction and absorption coefficients vary with wavelength and, secondly, to assess the reliability of the measured reflectance data using techniques derived by Embrey & Criddle (1978). Figure 4 is a graphical representation of the dispersion of the indices of refraction and absorption coefficients where n_1 and k_1 are the number couple corresponding to the vibration direction for $R_1/^{im}R_1$. Even a cursory inspection of Figure 4 shows that the dispersion of the absorption and the reflectance follow nearly identical trends, thus demonstrating that the observed behavior of the mineral is determined by its absorption and not by its indices of refraction. The fact that the absorption coefficients do not drop below 0.8 explains why no internal reflections are seen in this mineral. The serrations in the curves between 520 and 660 nm follow differ-

ences in the second decimal place in the calculated constants, *i.e.*, they are physically insignificant given that the original data on reflectance had been rounded to a single decimal place. All of the data plot well within the envelope for real values for the constants as described by Embrey & Criddle (1978).

Finally, the spectral reflectance data for brodtkorbite are currently unique: they do not match any of the data in the reference works of Picot & Johan (1982) or Criddle & Stanley (1993). The qualitative description of imiterite, Ag_2HgS_2 , shows similarities (Guillou *et al.* 1985), but imiterite is far less birefractant (1–3%) than brodtkorbite (7–9%), although its two reflectance curves are bracketed by those of brodtkorbite.

X-ray powder and single-crystal study

A small fragment, dug out of polished section 17/1 c.2, was mounted and studied by single-crystal precession methods employing unfiltered Mo radiation. The fragment was oriented with a^* parallel to the dial axis. The reciprocal lattice levels collected were: $h0l$, $h1l$, $hk0$, $hk1$, $011/a^*$, $012/a^*$ and $013/a^*$. The fragment is composed of two nearly overlapping individual crystals

(in roughly 80:20 ratio) and is probably not suitable for crystal-structure analysis. Brodtkorbite is monoclinic, space group $B2_1/a$, with the following systematic absences: hkl with $h + l = 2n$; $h0l$ with $h = 2n$ and $l = 2n$; $0k0$ with $k = 2n$. The refined unit-cell parameters: a 12.370(6), b 4.177(1), c 8.004(4) Å, β 92.16(3)°, V 413.2(3) Å³ and $a:b:c = 2.961:1:1.916$, are based on 23 reflections between a d of 3.991 and 1.689 Å in the X-ray powder pattern for which unambiguous indexing was possible. However, this B -lattice cell, so clearly obvious in precession single-crystal photographs, is not, unfortunately, in its reduced crystallographic form; the correct space-group is $P2_1/n$, which has systematic absences: $h0l$ with $h + l = 2n$ and $0k0$ with $k = 2n$, and the following refined unit-cell parameters: a 7.492(5), b 4.177(1), c 7.239(4) Å, β 114.20(5)°, V 206.6(2) Å³ and $a:b:c = 1.7936:1:1.7330$.

All possible reflections down to 1.689 Å were visually examined on single-crystal precession films. Fully indexed X-ray powder data acquired with a 114.6 mm Debye–Scherrer camera, and based on the primitive reduced cell, are presented in Table 3. The data are unique and do not bear resemblance to any mineral or inorganic compound listed in the PDF up to and including Set 47.

The mineral is not structurally related to imiterite (Guillou *et al.* 1985), and appears to belong to a unique prototype structure.

MINERALOGY OF THE ASSOCIATED SELENIDES

A thorough investigation of the selenide species at Tuminico was undertaken using the same electron microprobe, same analytical conditions and same correction procedures as previously given for brodtkorbite. The following elements were systematically sought in most of the selenide species: Ag, As, Cd, Co, Cu, Fe, Hg, Ni, Sb, Se, Tl and Zn. The standards and measured lines were as follows: natural Cu₃Se₂ (umangite; CuK α , SeK α), natural CuFeS₂ (chalcopyrite; FeK α , SK α), CdTe (CdL β), natural HgS (cinnabar; HgL α), natural NiAs (nickeline; NiK α , AsK α), ZnS (ZnK α), natural TlAsS₂ (lorandite; TlL α), natural Sb₂S₃ (stibnite; SbL α), Ag metal (L α) and Co metal (CoK α). The selenide assemblages are discussed in their general sequence of crystallization.

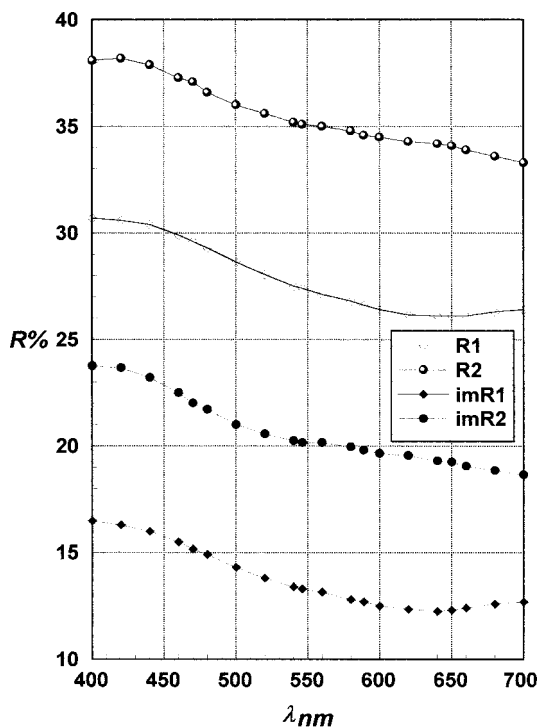


FIG. 3. Reflectance spectra in air (R_1 , R_2) and immersion oil (n_D 1.515; $^{im}R_1$, $^{im}R_2$) for brodtkorbite.

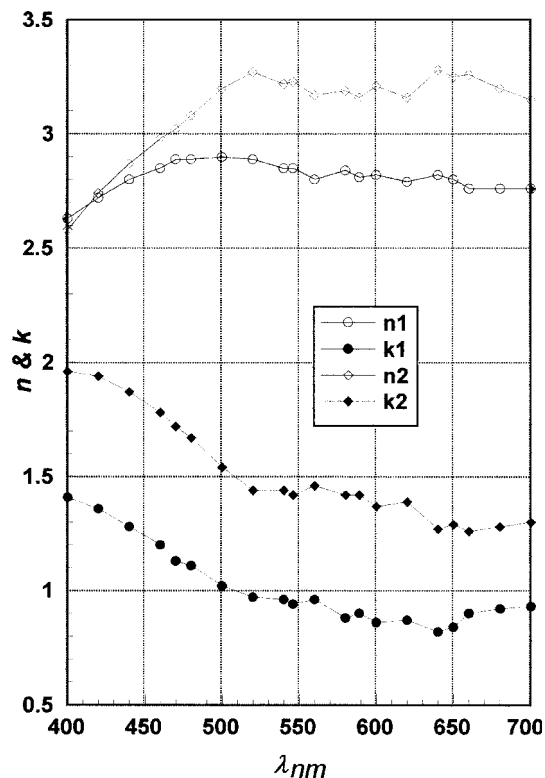


FIG. 4. Brodtkorbite: n and k values derived from reflectance measurements.

Ferroselite – tyrrellite – trogtalite-krutaite

Ferroselite, FeSe_2 , is present as rare veinlets not exceeding a few mm in width and several cm in length, composed of both euhedral grains and grain aggregates (Figs. 5a, b). It is commonly associated with umangite, klockmannite and tiemannite. The chemical composition is very close to stoichiometry (Table 4).

Eskebornite (Fig. 5c), CuFeSe_2 , occurs as small inclusions in umangite and may be associated with members of the trogtalite-krutaite solid-solution series. The chemical composition shows no deviation from stoichiometry (Table 4).

Tyrrellite, $(\text{Co,Cu,Ni})_3\text{Se}_4$, occurs as anhedral crystals and aggregates, not exceeding $20 \times 30 \mu\text{m}$ in size, which are enclosed in umangite. In a few cases, euhedral crystals ($10 \times 10 \mu\text{m}$) (Fig. 5h) similar to those observed at the selenide occurrence of Sierra de Cacheuta in Mendoza Province are present. The empirical formula, based on results of four analyses (Table 4), $(\text{Co}_{1.41}\text{Cu}_{0.95}\text{Ni}_{0.67})_{\Sigma 3.03}\text{Se}_{3.97}$, is similar to that reported for the mineral from the Beaverlodge District, Saskatchewan, Canada (Robinson & Brooker 1952).

Members of the trogtalite – krutaite – penroseite series, CoSe_2 – CuSe_2 – NiSe_2 , are sparsely distributed throughout, either in umangite or in the calcite matrix (Figs. 5c, d). A Co-dominant phase of this series occurs in association with eskebornite, and Fe-rich krutaite has been observed rimmed by small laths of ferroselite. The chemical composition of members of this series (Table 4) varies in each of the analyzed grains, even in the same polished section. Most of the analyses were done on trogtalite with $\text{Co} > \text{Cu} > \text{Ni}$ or intermediate members of the krutaite – trogtalite series with $\text{Cu} \approx \text{Co} > \text{Ni}$.

Two arsenoselenides were detected in trace amounts as inclusions in umangite (Figs. 5e, f). The grains are usually less than $10 \times 20 \mu\text{m}$, i.e., too small to be ex-

tracted for X-ray studies. The chemical compositions (Table 4) are close to $(\text{Co,Ni,Cu})\text{AsSe}$ and $(\text{Cu,Cu,Ni})_{\sim 4}\text{As}_3\text{Se}_6$. The former composition is chemically and optically very similar to “unnamed CoAsSe ” from Lake Athabasca, Saskatchewan, Canada (Cabri *et al.* 1991). The copper content makes it a Cu-bearing variety of this unnamed phase.

Hakite – bukovite – chaméanite

Hakite, ideally $(\text{Cu,Ag})_{10}(\text{Hg,Cd,Zn,Fe})_2(\text{Sb,As})_4\text{Se}_{13}$, was originally described as a new mineral species from the Předbořice deposit, Czech Republic, and later

TABLE 4. ELECTRON-MICROPROBE DATA FOR FERROSELITE, ESKEBORNITE, TYRRELLITE, TROGTALITE-KRUTAITE AND UNNAMED PHASES IN THE SYSTEM (Co,Ni,Cu) – As – Se

wt. %	Fe	Co	Ni	Cu	As	Se	Total Sample
Ferroselite	25.9 25.0			0.5 0.3		72.8 74.0	99.2 99.3
Eskebornite	18.9 19.0 19.9			23.2 22.8 22.5		57.0 57.4 56.3	99.1 99.2 99.28
Tyrrellite		18.7 16.7 15.9 15.3	4.2 8.0 9.5 9.9	14.4 12.3 11.0 11.2		63.3 62.8 63.7 62.4	100.6 99.9 100.1 98.9
Trogtalite-krutaite	2.2 2.4 1.2 0.7	17.6 17.0 11.2 10.4	0.9 0.9 4.3 5.7	8.3 8.7 12.7 12.3		71.4 69.4 71.9 70.1	100.4 98.4 101.3 99.2
Ferroan krutaite	11.7			15.2		72.2	99.1
$(\text{Fe,Cu})\text{Se}_2$	21.6			4.0		72.5	98.1
(Co,Ni,Cu) – As – Se	0.1	13.7 19.4	9.8 7.0	6.4 2.5	30.3 30.3	39.3 40.9	99.5 100.2
(Cu,Cu,Ni) – As – Se	0.3	10.6	4.5	21.4	20.5	41.4	98.7
apfu	Fe	Co	Ni	Cu	As	Se	basis
Ferroselite	0.99 0.97			0.03 0.01		1.98 2.02	$\Sigma M + \text{Se} = 3$
Eskebornite	0.95 0.95 1.00			1.02 1.01 0.99		2.02 2.04 2.0	$\Sigma M + \text{Se} = 4$
Tyrrellite		1.57 1.41 1.34	0.35 0.67 0.81	1.12 0.96 0.85		3.96 3.95 3.99	$\Sigma M + \text{Se} = 7$
Trogtalite-krutaite	0.09 0.09 0.05 0.03	0.65 0.64 0.41 0.39	0.03 0.03 0.16 0.21	0.28 0.30 0.43 0.42		1.96 1.94 1.96 1.94	$\Sigma M + \text{Se} = 3$
Ferroan krutaite	0.46			0.52		2.01	
$(\text{Fe,Cu})\text{Se}_2$	0.84			0.14		2.01	
(Co,Ni,Cu) – As – Se		0.50 0.70	0.36 0.26	0.22 0.08	0.86 0.86	1.07 1.10	$\Sigma M + \text{Se} = 3$
(Cu,Cu,Ni) – As – Se	0.05	2.06	0.88	3.86	3.14	6.00	$\Sigma M + \text{Se} = 16$

Elements not reported for the respective minerals were below the limit of detection. apfu: atoms per formula unit.

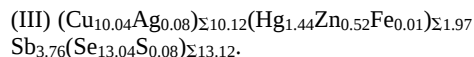
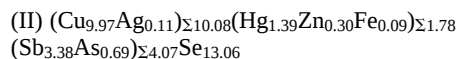
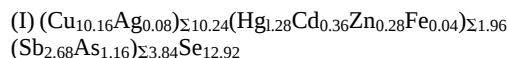
TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR BRODTKORBITE

I_{cal}	$d \text{ \AA}$ meas.	$d \text{ \AA}$ calc.	hkl	I_{cal}	$d \text{ \AA}$ meas.	$d \text{ \AA}$ calc.	hkl
10	6.259	6.180	101	50	2.072	2.082	113
* 70	3.991	3.999	101			2.073	312
* 50	3.576	3.564	110	* 20	1.989	1.991	021
* 50	3.534	3.530	011	* 10	1.947	1.947	013
* 30	3.476	3.461	211	5	1.922	1.924	301
* 50	3.414	3.417	200	* 20	1.883	1.882	103
* 20	3.095	3.090	202	* 15	1.851	1.851	121
* 10	2.887	2.889	111	3	1.823	1.821	221
* 20	2.784	2.778	211	* 20	1.803	1.804	204
* 100	2.730	2.730	112	3	1.782	1.782	220
* 10	2.644	2.645	210	* 10	1.765	1.765	022
* 30	2.495	2.491	301	3	1.746	1.747	311
* 30	2.401	2.402	103	* 10	1.731	1.730	222
* 30	2.223	2.224	211	5	1.711	1.708	400
* 30	2.199	2.199	112	* 20	1.689	1.690	411
* 40	2.140	2.140	311				

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter ($\lambda \text{ CuK}\alpha = 1.54178 \text{ \AA}$). The intensities were estimated visually. The pattern was not corrected for shrinkage and no internal standard was added. * Reflection used for unit-cell refinement. The pattern was indexed with $a \ 7.492$, $b \ 4.177$, $c \ 7.239 \text{ \AA}$, $\beta \ 114.20^\circ$.

observed at Bukov and Petrovice within the same country, in association with uranium mineralization (Johan & Kvacek 1971, Johan *et al.* 1978). Giraudite, the As-dominant analogue of hakite, was described as a new species found associated with uranium mineralization at Chaméane, Puy-de-Dôme, France (Johan *et al.* 1982). At Tuminico, both As-bearing and As-free hakite (hakite I, II; hakite III: Table 5) occur, in grain sizes ranging between 10×10 and 30×60 μm . The As-bearing variety has As values between 0.6 and 5.0 wt.%, which correspond to a Sb:As ratio between 19.1 and 2.3. This variety is typically associated with chaméanite (Figs. 5g, h), whereas the As-free hakite is typically intergrown with berzelianite or a combination of umangite, klockmannite and eskebornite. Hakite from Tuminico is Ag- and Hg-poor in comparison to the samples from the type locality at Předbořice. Amongst the minor elements, Zn, Fe and locally high Cd are

present. The chemical formulae of hakite I, II, III are fairly close to being stoichiometric:



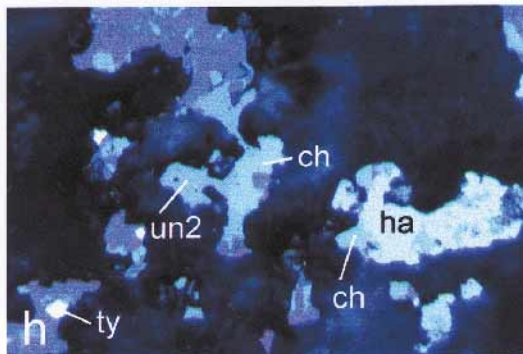
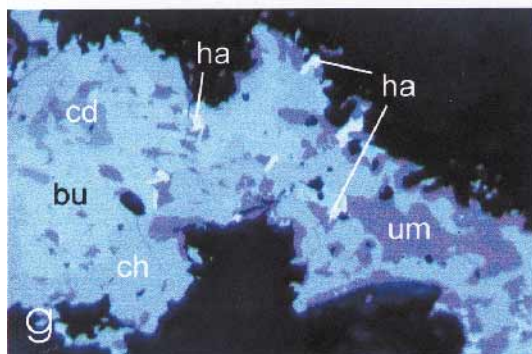
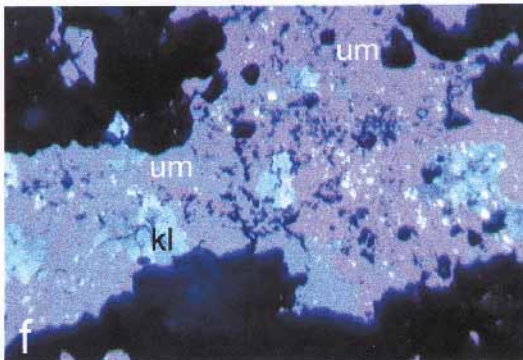
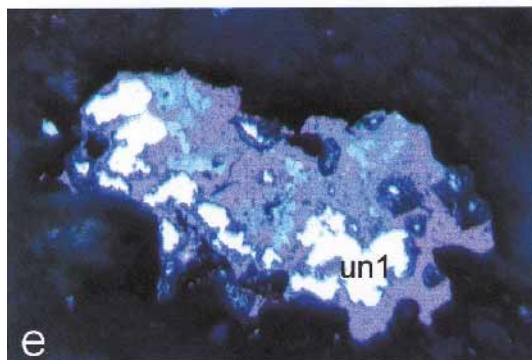
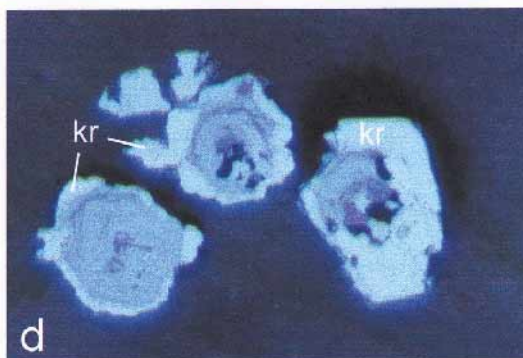
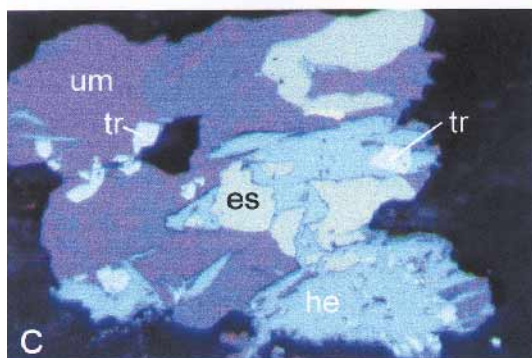
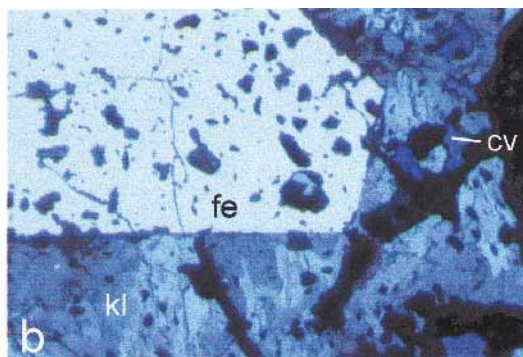
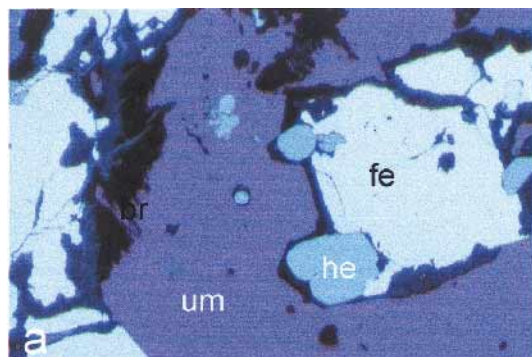
Bukovite, $\text{Cu}_3\text{Ti}_2\text{FeSe}_4$, which is one of two Ti-bearing selenides identified at Tuminico, was observed in association with hakite, cadmoselite, chaméanite and umangite (Fig. 5g). It also occurs as composite grains (40×60 μm) embedded in berzelianite. The average chemical composition (Table 5) is $\text{Cu}_{3.10}\text{Ti}_{1.89}\text{Fe}_{0.90}$

TABLE 5. ELECTRON-MICROPROBE DATA¹ FOR HAKITE, BUKOVITE, CHAMÉANITE, CADMOSELITE AND UNNAMED Cd-Hg-Se PHASES

wt. %	Cu	Ag	Fe	Zn	Cd	Hg	As	Sb	Ti	Se	S	Total	Sample
Hakite (5) ² range	26.8 26.4 27.3	0.4 0.1 0.5	0.1 0.0 0.1	0.8 0.5 1.8	1.6 0.8 1.8	10.8 9.5 11.6	3.7 3.2 5.0	13.5 11.7 14.4		42.3 41.6 43.1		100.0	99/7
Hakite (3) range	25.8 25.6 26.0	0.3 0.3 0.4	0.0 0.0 0.1	1.4 1.3 1.5		11.8 11.3 12.2		18.6 18.5 18.7		41.6 41.4 41.8	0.1 ³	99.6	4/1
Hakite (4) range	25.7 25.3 25.9	0.5 0.3 0.6	0.2 0.1 0.3	0.8 0.7 0.9		11.4 10.9 12.0	2.1 0.6 3.0	16.7 15.1 19.2		41.9 41.5 42.5		99.3	99/67
Bukovite (5) range	20.1 19.8 20.6		5.6 5.5 5.7						41.2 ⁴	33.0 32.7 33.2		99.9	17/3
Chaméanite (2)	34.8		1.9				12.2			50.0		98.9	17/3
Cadmoselite (2)	1.6	0.1			51.7	5.3				40.7		99.4	99/9
Cd-Hg-Se I (2)	0.3				49.4	10.2				39.0		98.9	99/67C
II (4)	0.2				42.8	18.1				38.8		99.9	99/67A
III (4)	0.4				41.5	19.8				38.1		99.8	99/7
IV (6)	0.6				33.2	29.3				36.0		99.1	99/67B
V (5)	1.4	0.3			24.2	37.6				34.7		98.2	99/67C
VI (4)	0.1				18.2	46.2				31.4		95.9 ⁵	99/67B
apfu	Cu	Ag	Fe	Zn	Cd	Hg	As	Sb	Ti	Se	S	basis	
Hakite	10.16 10.04 9.97	0.08 0.08 0.11	0.04 0.01 0.09	0.28 0.52 0.30	0.36	1.28 1.44 1.39	1.16 1.44 0.69	2.68 3.76 3.38		12.92 13.04 13.06	0.08	$\Sigma M + \text{Se}, S = 29$	
Bukovite	3.10		0.90						1.89	4.04		$\Sigma M + \text{Se} = 10$	
Chaméanite	3.58		0.23				1.06			4.13		$\Sigma M + \text{Se} = 9$	
Cadmoselite	0.05				0.90	0.05				1.00		$\Sigma M + \text{Se} = 2$	
Cd-Hg-Se I	0.01				0.89	0.10				0.99		$\Sigma M + \text{Se} = 2$	
II	0.00				0.79	0.19				1.02			
III	0.01				0.77	0.21				1.01			
IV	0.02				0.65	0.32				1.01			
V	0.06				0.49	0.43				1.02			
VI	0.01				0.40	0.58				1.01			

¹ Elements not given for the respective minerals were below the limit of detection. *apfu*: atoms per formula unit.

² Number of analyses made. ³ Range 0.1–0.3. ⁴ Range 40.6–42.6. ⁵ Very fine grain-size (5 μm).



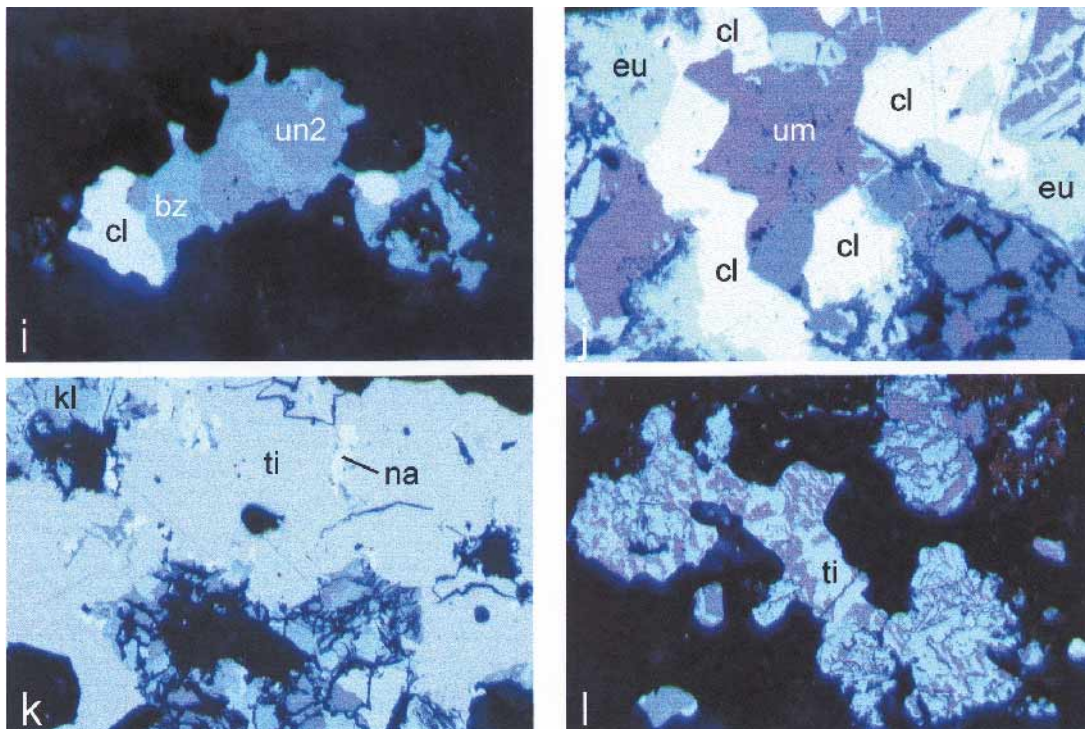


FIG. 5. Selenide associations at Tuminico (calcite is the gangue in all cases). a) Euhedral grains of ferroselite (fe) as inclusions in umangite (um) and associated with hematite (he) (s.98/10R). b) Euhedral grains of ferroselite with numerous inclusions of hematite, embedded in klockmannite (kl); covellite (cv) occurs as aggregates of tiny grains (s.98/9–1). c) Eskebornite (es) and trogtalite (tr) are replaced by umangite (s. 17/3). d) Rhythmically intergrown umangite – berzelianite is replaced by krutaite (kr), which occurs as an overgrowth on euhedral crystals (s. 99/3). e, f) Co–As–Se (un1) as composite grains (e) and as dust-like inclusions (f) in umangite – klockmannite (s. 99/64C). g) Complex association of cadmoselite (cd) – hakite (ha) – bukovite(bu) – chaméanite (ch) and umangite (s. 99/9). h) An undefined Cd–Hg–Se compound (V; un2) intergrown with chaméanite and berzelianite (not discernible); hakite is randomly replaced by chaméanite. Tyrrellite (ty) occurs in euhedral crystals embedded in umangite (s. 99/67C). i) A second undefined Cd–Hg–Se compound (III; un2) is associated with berzelianite and clausenthalite (cl) (s. 99/7). j) Eucairite (eu), in irregularly shaped grains and lamellae, and clausenthalite, both found as inclusions in umangite (s.99/65A). k) Naumannite (na) occurs as tiny inclusions in tiemannite (ti), which is associated with klockmannite (s. 98/9–2). l) Tiemannite – umangite intergrowth, which replaces hematite. A Cd–Hg–Se mineral associated with berzelianite is also present (composite grain close to the lower edge of the image) (s. 17/3). Areas of images are 0.2×0.14 (c–j, l) and 0.5×0.35 mm (a, b, k).

Se_{4.04}, which is very close to bukovite from Předbořice, Czech Republic (Johan 1989). Hg, S and Ag were not detected in the grains of bukovite analyzed.

Chaméanite, (Cu,Fe)₄AsSe₄, is fairly common, and is frequently associated with hakite – eskebornite, bukovite – cadmoselite or clausenthalite. The grain sizes are usually quite small, and attain 30 µm. Electron-microprobe analyses of several grains do not indicate chemical zoning. The Cu:Fe ratio is about 15.6, which is significantly higher than the value reported for the strongly zoned chaméanite (6–13) from the type locality (Johan *et al.* 1982). Co, Ni, Zn, Sb and S were sought but not detected.

A Hg-bearing variety of cadmoselite, CdSe, was detected as inclusions less than 30 µm across in bukovite (Fig. 5g, Table 5). Several other phases of the system Cd–(Cu)–Hg–Se were observed in association with umangite, berzelianite, clausenthalite and the ubiquitous hematite. The anhedral grains of these unidentified phases attain sizes up to 50×50 and 30×60 µm, but are typically smaller and usually penetrated by the associated phases. The optical properties (brownish color, very weak anisotropism with rose-brown to bluish grey rotation-tints, broad twin lamellae) for the various compositions (Cd–Hg–Se I to VI; Table 5) are virtually identical and do not allow a distinction. The reflectances of

the compositional varieties Cd–Hg–Se III and V for the standard wavelengths (470, 546, 589, 650 nm) are (III, V; in air, %): 22.4, 24.4; 22.0, 23.0; 21.8, 23.1; 21.7, 22.5. A distinct increase of the reflectances toward the compound richer in Hg, i.e., composition V, can be noted.

Twenty-five point analyses were carried out on eight different grains in five polished sections, prepared from the single specimen found to contain these minerals (Table 5). The individual grains are chemically homogeneous, except for one that shows a weak zonation from core to rim. Five different compositions with varying but distinct Cd:Hg ratios were observed: 9:1, 4:1, 2:1, 1:1 and 2:3. No intermediate compositions were detected. The only minor element is Cu, which varies between 0.1 and 1.4 wt.%, corresponding to 0.01 and 0.06 atoms per formula unit, *apfu*. These compositions may either represent cadmoselite in which Cd is systematically substituted by Hg, or a suite of new mineral species in the system CdSe–HgSe. Their further characterization is inhibited by grain-size limitations and intergrowth features.

Umangite – klockmannite – berzelianite – brodtkorbite – crookesite

The Cu selenides umangite, Cu_3Se_2 , klockmannite, CuSe, and berzelianite, Cu_{2-x}Se , are the dominant selenide species at Tuminico and are generally intergrown with each other. Bellidoite, tetragonal Cu_2Se , is rare and usually found in assemblages dominated by berzelianite. Electron-microprobe analyses of umangite show that it is close to being stoichiometric. Minor elements substituting for Cu are Fe (0.36–0.59 wt.%) where it is associated with eskebornite and ferroselite, and Co (0.1 wt.%) where it is intergrown with Co-bearing sulfarsenides, respectively. Hg (0.3–0.5 wt.%) was detected where umangite is intergrown with brodtkorbite. Klockmannite, CuSe, occurs as late-stage roundish inclusions, composed of radiating tablets or single flakes, either in umangite or in the gangue. The chemical composition of berzelianite varies slightly between $\text{Cu}_{1.75}\text{Se}$ and $\text{Cu}_{1.91}(\text{Se},\text{S})$. Sulfur (up to 0.16 wt.%) may substitute for Se.

Bellidoite, described as a new mineral species by de Montreuil (1975), occurs as composite grains ranging in size from 10 to 40 μm . They are found embedded in calcite and are commonly intergrown with berzelianite or umangite (or both). Bellidoite shows all the optical properties (creamy white color, weak anisotropism, grey rotation tints, reflectance spectrum) and microhardness that were described for the type material from Habri, near Tisnov, Czech Republic (de Montreuil 1975). The chemical composition corresponds exactly to Cu_2Se with only a minor amount of S (0.1 wt.%) substituting for Se. Tuminico is therefore the second reported world-wide occurrence of this very rare selenide species.

Crookesite, Cu_7TlSe_4 , the second known Tl-bearing mineral at Tuminico, is rare and is associated with

berzelianite or the aforementioned Cd–Hg–Se phases. Electron-microprobe analyses gave no variation in the chemical composition ($\text{Cu}_{7.1}\text{Tl}_{0.97}\text{Se}_{4.03}$).

Eucairite – naumannite – tiemannite

The Ag-bearing selenides (Fig. 5k) are eucairite, AgCuSe , which can be traced as worm-like and spindle-shaped inclusions in umangite, and naumannite, Ag_2Se . No deviation from stoichiometry was observed for either mineral.

Tiemannite, HgSe, and brodtkorbite are commonly associated with berzelianite, but also occur as isolated grains in the calcite gangue (Figs. 5k, l). Tiemannite has a composition close to stoichiometry. Trace elements are Cu (0.13–0.17 wt.%) and Cd (0.15 wt.%).

A Hg–Ag compound, probably related to luanheite, occurs as isolated inclusions along the grain boundaries of calcite. The grains, which average a few μm in diameter, have a composition $\text{Ag}_{0.7-0.8}\text{Hg}_{0.2-0.3}$ and are assumed to be of supergene origin.

DISCUSSION AND CONCLUSIONS

Tuminico is a unique occurrence of selenides in the Sierra de Umango and Sierra de Cacho districts of La Rioja, Argentina. Apart from the dominance of the copper selenide species, which are also the most common selenide species in the other deposits of this region, a wide spectrum of additional selenide minerals was also observed. This variability in selenides may be explained by a local and unique availability of numerous minor elements in the mineralizing fluids, such as Ag, As, Cd, Co, Fe, Hg, Ni, Sb, Tl and Zn, which led to the formation of “exotic” mineral associations, not present in other deposits. Amongst these “exotic” minerals are the new mineral species brodtkorbite and several other undefined, potentially new phases. Silver-bearing selenides are scarce and at Tuminico, Au- and Pd-bearing mineral species (such as native gold, fischesserite, christianite, oosterboschite, merenskyite), which are more common in other deposits of Sierra de Cacho and Los Llanes (Paar *et al.* 1996b, 1998a, 2000), are absent.

The Tl-bearing selenides are reported herein for the first time from Argentina, and the high Cd compounds (Cd–Hg–Se) represent compositions not known from any other occurrence of selenides. The dominance of Co over Ni, which is reflected by the presence of trogtalite – krutaite, Co-enriched tyrellite and Co-bearing arsenoselenides, is typical for La Rioja and is also documented from the other selenium occurrences at Sierra de Cacheuta, Mendoza Province (Angelelli 1984).

The presence of umangite is indicative of a temperature of formation below 112°C. This is very close to the temperature at which decomposition to berzelianite and high klockmannite takes place (Chakrabarti & Laughlin 1981). However, intergrowth textures that would provide evidence of such a disintegration were not ob-

served. The assemblage berzelianite – bellidoite – umangite, which is only stable below 112°C, is another indication of the low temperature of deposition. This is the same environment in which brodtkorbite was precipitated. Preliminary fluid-inclusion studies, carried out on calcite intergrown with the selenides, show homogenization temperatures in the range between 60 and 130°C, which support the data on mineral stability.

The selenide mineralization at Tuminico and the other selenide deposits of the Sierra de Umango (Sierra de Cacho) and Los Llantenes districts shows variations in $\text{Se}_{2(g)}$ and $\text{S}_{2(g)}$ fugacities, which are very similar to those for “telethermal selenide vein-type” deposits described in detail by Simon *et al.* (1997). An increasing trend of the $f(\text{Se}_{2(g)})$ during deposition of the selenide minerals is obvious from the sequence of crystallization of the copper selenides, which form volumetrically more than 90% of the total selenide assemblage. The increase of the $f(\text{Se}_{2(g)})$ reached the stability field of krutaite (berzelianite → umangite → klockmannite → krutaite; Fig. 5d). The presence of krutaite and klockmannite requires high $f(\text{Se}_{2(g)})$, which has permitted the formation of widespread ferroselite.

These deposits have been formed from Se-rich oxidizing fluids within the stability field of hematite. The source of the metals is, as yet, unknown, but is the subject of ongoing research in northwestern Argentina.

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