SZENICSITE

A NEW COPPER MOLYBDATE FROM INCA DE ORO, ATACAMA, CHILE

Carl A. Francis, Lawrence C. Pitman,* and David E. Lange
Harvard Mineralogical Museum
24 Oxford Street
Cambridge, Massachusetts 02138

INTRODUCTION

In January 1993 Terry and Marissa Szenics of Santiago collected a beautiful green mineral, thought to be lindgrenite, at a small copper mine in northern Chile and through the Aurora Mineral Corporation submitted it to the Harvard Mineralogical Museum for identification. An X-ray diffraction pattern showed that the mineral is neither lindgrenite nor any other species in the Powder Diffraction File. Subsequent chemical study demonstrated it to be a copper molybdate new to science. The mineral was shown informally at the 1993 Tucson Gem and Mineral Show and the first notice of it, along with photographs, appeared three months later (Moore, 1993). However, the specimens were withheld from the market while a formal description was undertaken. The mineral and its name, which honors its finders, Terry Szenics (b. 1947) and Marissa Szenics (b. 1950), a husband and wife collecting team, were approved by the IMA Commission on New Minerals and Mineral Names. A suite of specimens documenting this find is preserved in the Harvard Mineralogical Museum under catalog numbers 133734–133773; szenicsite specimens 133734–133735 and 133738–133739 are the designated cotypes.

OCCURRENCE

Szenicsite was collected at the Jardinera No. 1 mine (69° 51.4′ W, 26° 4.44′ S), which exploits secondary copper ores. It is located in Chile's Atacama province 5 km east of Inca de Oro, which is 80 km north of Copiapo. To conceal the source, the specimens were originally mislabeled by Szenics as coming from Tierra Amarilla, a mining area 8 km southeast of Copiapo. Unfortunately our published abstract (Francis *et al.*, 1994) promulgated this disinformation and it was misquoted as "Tia Maria" by Moore (1993).

Szenicsite was discovered on an ore pile at the surface and was later found in place on the 60-meter level. The occurrence was only about 1 x 1 x 2 meters in extent and is now completely removed. Mining has progressed in 4 meter slices down to the 80 meter level but several visits over the past three years have failed to locate additional occurrences of szenicsite in the mine. The total quantity of szenicsite recovered is estimated to be on the order of 2 or 3 kilograms.

MORPHOLOGY

Szenicsite occurs primarily as bladed crystals in vugs but also fills fractures to about 5 mm in width. The {100} blades (habit 1) are elongated parallel to the *c*-axis and typically terminate with ragged edges. Crystals are typically about 1 cm in length, but may reach 1 x 3 cm in size. They may be intergrown in jackstraw fashion or in fans radiating like the pages of a partially opened book, often showing lustrous curved {010} cleavage faces. Terminated crystals are extremely rare. In addition to the most common habit, two specimens show crystals bladed parallel to the *b*-axis (habit 2), and three loose crystals consist of the dipyramid terminated by the brachypinacoid (habit 3).

PHYSICAL PROPERTIES

Szenicsite is transparent with an adamantine luster. Its color is dark green, reminiscent of the magnificent torbernites from Shinkolobwe, whereas its streak is malachite-green. Szenicsite does not fluoresce under shortwave or longwave ultraviolet radiation. Its Mohs hardness is $3^1/_2$ to 4. It is brittle with good cleavages on (100) and (010). The density measured using a Berman balance is 4.26(5) g/cm^3, which agrees well with the calculated values of 4.30 g/cm^3 (ideal composition), and 4.28 g/cm^3 based on the empirical formula and Z = 4.

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*Deceased, January 30, 1996

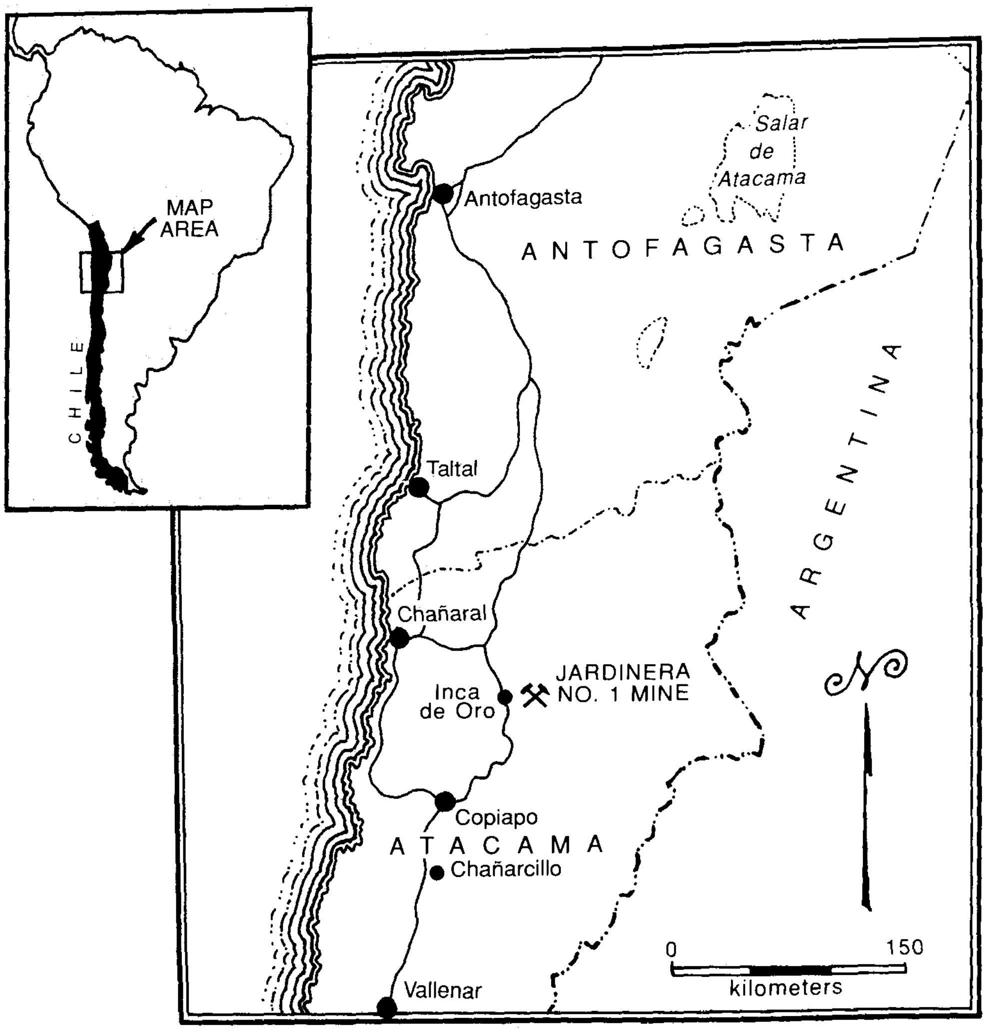

Figure 1. **Location map.**

Spindle-stage methods were used for the optical study. Szenicsite is biaxial positive with 2V = 74(3)° and the optical orientation is X = *b*, Y = *a*, and Z = *c*. The pleochroic scheme is X = yellow-green, Y and Z = green; dispersion is strong, with r > v. Its measured birefringence ($\gamma-\alpha = 0.017$) is low to moderate. The refractive indices are too high to measure with normal immersion fluids and our attempts using arsenic sulfide dissolved in methylene iodide were unsuccessful. The indices are probably greater than 1.8. The inadvisability of calculating optical data was pointed out in a review of this paper by J. A. Mandarino, and we advise readers to ignore the optical data presented earlier (Francis *et al.*, 1994), which were subsequently published in Mandarino (1997).

CHEMISTRY

Two chips of szenicsite were analyzed with a Cameca MBX electron microprobe using wavelength spectrometers. The average of 20 point analyses is reported in Table 1 along with details of the experimental conditions. A check for elements other than Cu, Mo, and O only showed a small amount of Al present. To be sure that this Al is not due to contamination introduced during polishing, the grain mount, which is free of other mineral species, was ground further using fresh SiC paper and polished on fresh diamond laps. In new analyses Al is still present in the same concentration. A grain mount of Jardinera No. 1 mine lindgrenite was made when the szenicsite samples were reground and its Al content is at the detection limit of 0.016 wt.% Al_2O_3. We conclude that the small quantity of Al in szenicsite is real. Water was determined by loss on ignition in air up to 800°C after drying the sample at 100°C. The

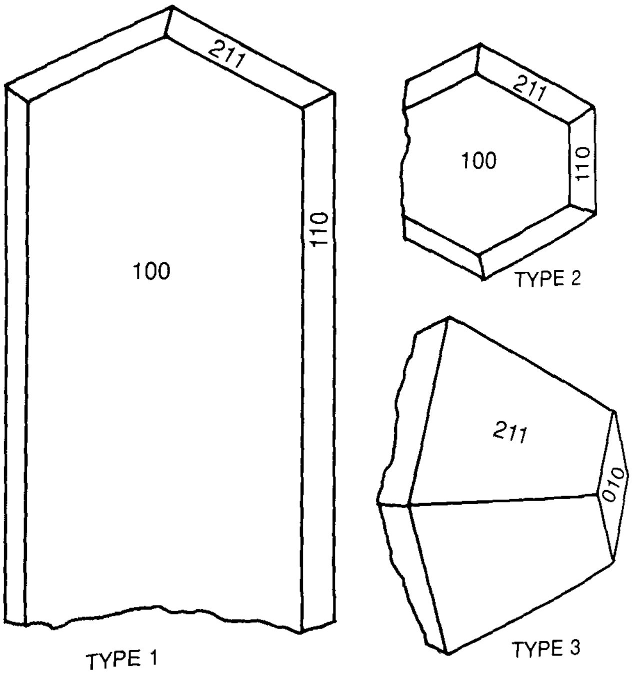

Figure 2. **Szenicsite crystal drawings (standard clinographic projections) illustrating the three known habits. Totally euhedral or doubly terminated crystals have yet to be found.**

oxygen content was also measured with the electron microprobe using $LiEuMo_2O_8$ as a standard. Calculating water from the measured oxygen content yields 8.91 wt.% H_2O versus 8.79 wt.% from the loss on ignition. On the basis of 8 oxygens the microprobe analysis gives a formula of $Cu_{2.97}Al_{0.01}(MoO_4)_{0.99}(OH)_{4.09}$ which is very close to $Cu_3MoO_4(OH)_4$. Chemical spot tests for Cu^{2+} and for Mo^{6+}, as described by Feigl and Anger (1972), confirmed the valences of the Cu and Mo in szenicsite.

Szenicsite joins ferrimolybdite, lindgrenite, powellite and wulfenite as a simple molybdate.

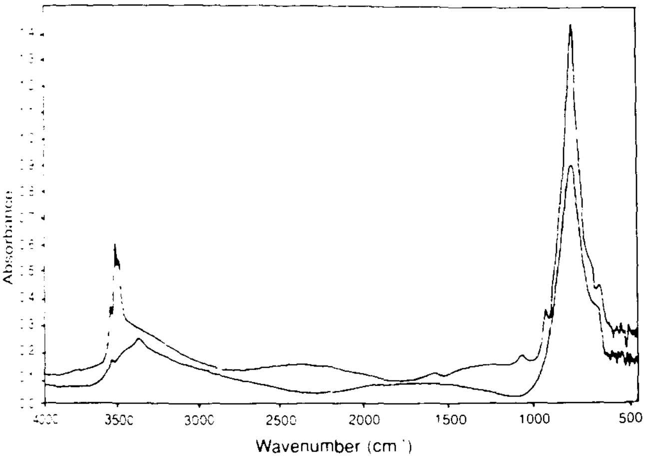

***Figure 3.* Infrared spectra of szenicsite (upper curve) and lingrenite (lower curve).**

SPECTROSCOPY

Infrared spectra of both szenicsite and type lindgrenite were recorded from single crystals mounted in a diamond cell on a Spectra Tech IR-Plan microscope attached to a Nicolet 510 FT-IR spectrometer by Eugene Farrell at the Harvard University Art Museums. The szenicsite pattern is more sharply resolved than the lindgrenite pattern. Absorption band positions are listed in Table 2. The very strong band in the 600–1000 cm⁻¹ region is due to the molybdate ion while the medium band near 3400 cm⁻¹ is due to hydroxyl. There is no evidence for molecular water in either mineral.

***Table 1.* Electron microprobe analysis of szenicsite.**

	Average	*Std. Dev.*	*Minimum*	*Maximum*	*Stoichiometric* $Cu_3MoO_4(OH)_4$
Al_2O_3	0.14	0.04	0.03	0.20	
CuO	56.26	0.25	55.88	56.69	57.01
MoO_3	34.00	0.50	33.00	34.72	34.38
H_2O	8.79				8.61
Total	99.19				100.00
Number of atoms on the basis of 8 Oxygens					
Al	0.01				0.00
Cu	2.97				3.00
Mo	0.99				1.00
H	4.09				4.00

Beam conditions: 15 KeV, 16 nanoamperes, 16 x 16 micrometer rastered beam. Ten analyses each on two chips. Sandia ZAF85 matrix correction progrram used. H_2O from loss on ignition. Microprobe gave 30.63% O which gives 8.91 % H_2O. Standards used: kyanite (Al), cuprite (Cu), $LiEuMo_2O_8$ (Mo, O). Other elements checked were below their detection limits: detection limit of 0.01 weight %: Cl; 0.06: F; 0.01 weight % oxide: Ca; 0.02 weight % oxide: Mg, Si, Ti, Cr, Mn, Zn, W; 0.03 weight % oxide: Fe, Co; 0.04: V, Ni; 0.09 weight % oxide: Pb.

***Table 2.* Infrared spectra of szenicsite and lindgrenite.**

Szenicsite		*Lindgrenite*	
Position	*Height*	*Position*	*Height*
3559	m	3526	m
3524	s	3420	m, shoulder
3505	s	3347	m
2409	w, broad	1633	w, broad
1089	w		
942	m	900	shoulder
795	vs	834	vs
690	shoulder	650	shoulder
625	m		

m medium, s strong, vs very strong, w weak

***Table 3.* X-ray powder diffraction data for szenicsite. (Recorded with CuKα radiation using a 114.6-mm diameter Debye-Scherrer camera.)**

I	$d_{meas.}$	$d_{calc.}$	*h*	*k*	*l*	*I*	$d_{meas.}$	$d_{calc.}$	*h*	*k*	*l*
w	6.270	6.263	0	2	0	m	2.125	2.125	4	0	0
s	5.471	5.460	0	1	1	vw	2.090	2.088	0	6	0
m	4.599	4.594	1	1	1	m	2.043	2.043	3	1	2
w	4.031	4.024	2	1	0	w	1.985	1.985	3	4	1
s	3.754	3.748	1	3	0	w	1.943	1.944	1	1	3
w	3.517	3.516	2	2	0	m	1.885	1.884	1	5	2
w	3.440	3.440	0	3	1	vw	1.856	1.855	3	3	2
w	3.121	3.131	0	4	0	vw	1.817	1.820	0	3	3
s	3.043	3.042	2	2	1	w	1.792	1.790	2	6	1
vw	2.981	2.978	2	3	0	w	1.758	1.758	4	4	0
m	2.759	2.763	3	1	0	w	1.742	1.740	4	0	2
w	2.641	2.645	1	4	1	w	1.719	1.720	0	6	2
vs	2.591	2.599	1	2	2	m	1.684	1.684	5	1	0
w	2.517	2.515	3	1	1	m	1.640	1.640	5	2	0
vw	2.470	2.469	2	0	2	w	1.594	1.594	2	6	2
m	2.415	2.422	2	1	2	m	1.566	1.566	4	5	1
m	2.357	2.358	1	3	2	s	1.519	1.517	0	0	4
w	2.295	2.297	2	2	2	vw	1.492	1.493	1	8	1
vw	2.235	2.234	1	5	1	w	1.472	1.473	5	1	2
m	2.180	2.179	0	4	2	w	1.453	1.452	1	2	4

CRYSTALLOGRAPHY

X-ray diffraction study by the precession method using MoKα radiation showed szenicsite to be orthorhombic, point group *mmm*, and space group *Pnnm* or *Pnn2*. The powder X-ray data reported in Table 3 were obtained using a 114.6-mm Debye-Scherrer camera with CuKα radiation. Refinement of all of the powder data using Burnham's program LCLSQ (version 8 adapted to run on personal computers) yielded a unit cell with $a = 8.499(3)$Å, $b = 12.526(5)$Å, $c = 6.067(2)$Å, and $V = 645.9(3)$Å³.

Eby and Hawthorne (1993) have published a structural classification of the copper oxysalts which is analogous to the familiar classification of the silicates. There is a systematic increase in the

Figure 4. **Szenicsite crystal cluster, 7.5 cm across, with yellow-green drusy powellite. Szenics specimen; Wendell Wilson photo.**

Figure 5. **Szenicsite sheaves to 2 cm on drusy yellow-green powellite. Szenics specimen; Wendell Wilson photo.**

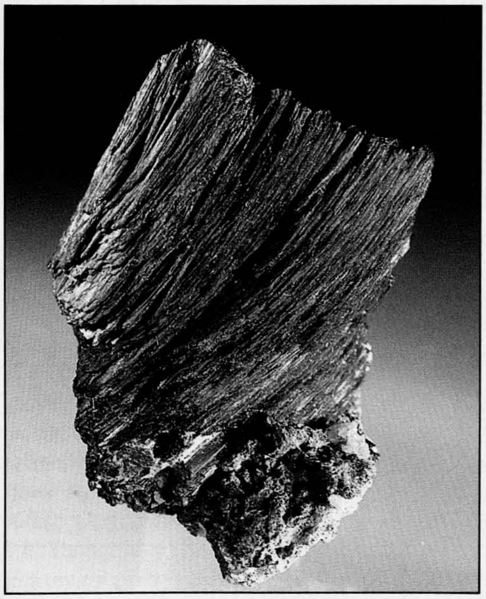

Figure 6. **Twisted parallel growth of szenicsite, 4 cm. Szenics specimen; Wendell Wilson photo.**

Figure 7. **Tabular szenicsite crystals to 1 cm. Szenics specimen; Wendell Wilson photo.**

Figure 8. Powellite pseudomorphs after blocky molybdenite crystals with minor dark green szenicsite, 7 cm. Szenics specimen; Wendell Wilson photo.

Figure 9. Steeply dipyramidal crystals of pale yellow powellite to 4 mm. Szenics specimen; Wendell Wilson photo.

Figure 10. **Powellite in thick bundles terminated by drusy-like surfaces, with dark green szenicsite at the base; 2.5 cm across. Szenics specimen; Wendell Wilson photo.**

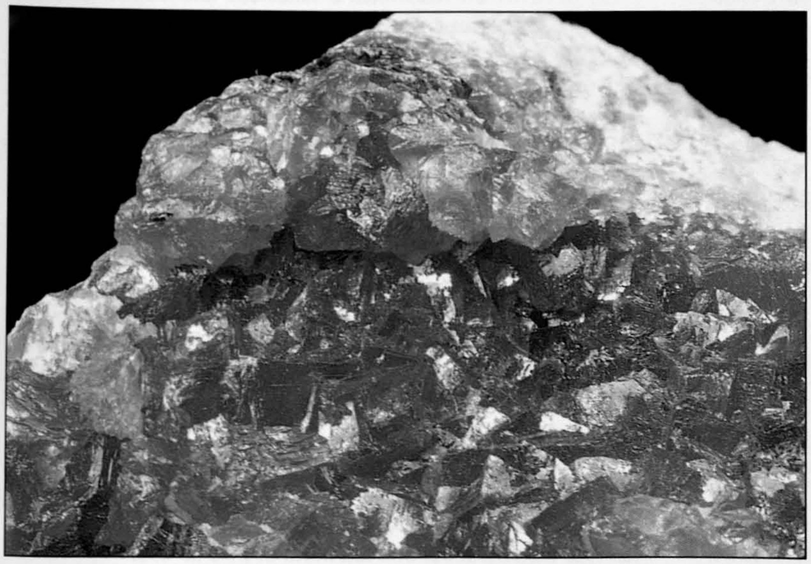

Figure 11. **Coarse druse of green powellite, 3 cm across. Szenics specimen; Wendell Wilson photo.**

average ratio of octahedral cations to tetrahedral cations as the degree of polymerization increases. Szenicsite has a ratio of 3:1, placing it among either the sheet structures or the framework structures. Its low birefringence implies that the bonding is fairly uniform in all directions and thus we predict that szenicsite has a framework structure. Significantly, lindgrenite with its lower Cu:Mo ratio of 3:2 is known to have a framework structure (Hawthorne & Eby, 1985).

PARAGENESIS

Szenicsite occurs as fracture fillings and as crystals in vugs closely associated with powellite. The granitic matrix has been hydrothermally altered. Feldspars have been completely converted to kaolinite, in some cases leaving quartz molds. Barite, brochantite, chalcocite, chalcopyrite, gold, hematite, lindgrenite and molybdenite-2H have also been identified in the specimen suite. All identifications except gold and quartz were verified by X-ray powder diffraction.

The primary ore assemblage is known from a single specimen which consists of a crystal of molybdenite embedded in a mass of chalcopyrite erroneously reported as bornite (Francis *et al.*, 1994). Chalcopyrite is veined and largely replaced by chalcocite which, in turn, is veined by an olive-brown, fine-grained material, and to a much lesser extent by veinlets of powellite and pulverulent red hematite. The olive-brown material is a mixture containing powellite. Small vugs contain dark dipyramidal millimeter-size crystals of powellite. Unlike the massive powellite veinlets, these crystals do not fluoresce.

Terry Szenics (personal communication, April 1996) asserts that the Jardinera No. 1 mine is very unusual among the mines in that area in having so much molybdenite present. The common *2H* polymorph of molybdenite occurs as isolated crystals to 2 cm in diameter and as masses of intergrown crystals. Hydrothermal breakdown of the molybdenite liberated molybdenum which oxidized in the solution forming the molybdate anion. According to Titley and Anthony (1961), the molybdate anion is stable in basic oxidizing solutions (Eh values > 0 and pH values > 6). Molybdate anions combined with calcium cations and precipitated as powellite. An influx of copper into the molybdate-bearing solution accounts for the green powellite and, more importantly, the subsequent precipitation of szenicsite. Lindgrenite occurs sparingly as seams in a white, altered rock in a zone beyond the szenicsite. Brochantite, the principal ore mineral, is a copper sulfate formed by oxidation of the copper sulfides. Brochantite and hematite form a colorful blue-green and dark red "spotted rock" which occasionally hosts szenicsite in cavities formerly occupied by molybdenite. The close association of powellite and szenicsite with molybdenite and its pseudomorphs suggests that molybdate ions are not very mobile in solution.

POWELLITE

The quality and variety of the powellite associated with szenicsite makes the Jardinera No. 1 mine a notable mineral locality regardless of the presence of copper molybdates! Worldwide, powellite typically occurs as inconspicuous pulverulent halos around molybdenite crystals, which are best observed under ultraviolet light. Crystals are known from several occurrences, including Houghton County, Michigan, and Tonopah, Nevada. The finest powellite crystals are from hydrothermal veins in the Deccan basalts at Nasik, India (Kothavala, 1982). In Chile, powellite crystals also occur sparingly at the nearby Tucumana mine, where Terry Szenics discovered them associated with chrysocolla and drusy quartz. In paragenetic order the three distinct types of powellite which occur at the Jardinera No. 1 mine are: pseudomorphs after molybdenite, massive vein-forming material and small, free-standing crystals in vugs.

Table 4. **Electron microprobe analyses of powellite.**

Color	yellow	green	brown	pale green	dark green
CaO	27.84	27.85	28.35	27.69	28.23
MoO_3	70.38	70.30	70.11	69.81	69.87
CuO	0.08	0.02	0.08	0.09	0.30
Total	98.30	98.17	98.53	97.59	98.40
Number of atoms on the basis of 4 oxygens					
Ca	1.01	1.01	1.03	1.01	1.03
Mo	1.00	1.00	0.99	1.00	0.99
Cu	0.002	0.001	0.02	0.02	0.008

Beam conditions: 15 KeV, 21 nanoamperes, 16 x 16 micrometer rastered beam. Five analyses on each sample. Sandia ZAF85 matrix correction progrram used. Standards: wollastonite (Ca), $LiEuMo_2O_8$ (Mo) and cuprite (Cu). W and Fe were also analyzed for but were below their detection limits of 0.19 and 0.04 weight % oxide, respectively.

Although powellite is said to be found frequently as pseudomorphs after molybdenite (Palache *et al.*, 1954), a catalog of pseudomorphs in the American Museum of Natural History (Frondel, 1935) lists only a specimen from Clifton, Utah, and the only examples in the Harvard University collection are undistinguished examples from the Black Mountain district and the Benton Range in California. In contrast, the Jardinera No. 1 mine pseudomorphs clearly show the rosette form typical of the molybdenite crystal clusters. Numerous isolated and intergrown rosettes 1 to 2 cm in diameter popped free of the altered matrix. Matrix specimens are less common but careful inspection of the matrix of szenicsite specimens shows that powellite pseudomorphs are common. Szenicsite sometimes grows directly on the pseudomorphs.

Much of the powellite consists of gray-green porous masses containing flakes of fresh molybdenite. This material takes a good polish, and some was cut into spheres that fluoresce in shortwave ultraviolet radiation. A specimen measuring about 40 cm in diameter and estimated to weigh 70 kg, collected from the ore pile, yielded some of the finest specimens of szenicsite. It was unique because, in addition to the gray quartz and massive powellite matrix, vugs are lined with a distinctive reddish granular rind up to 2 cm thick which resembles a sandstone and may actually be a hematite-stained powellite sediment. This material is veined and overgrown by a centimeter-thick crust of green powellite reminiscent of the classic green smithsonite from Tsumeb. The few existing specimens are unique for powellite.

Crystals to 5 mm commonly form druses lining vugs in gray quartz and massive powellite. The crystals are steep dipyramids with lustrous, slightly convex faces. They may have multiple terminations giving them a splintery appearance. Tabular and blocky habits are very rare. Colors range from paragenetically early yellow-green to paragenetically late pale yellow. A few specimens of dark brown color were also noted. Anticipating that color would correlate with their minor element chemistry, five samples of differing color were analyzed (Table 4). Surprisingly, the crystals are essentially pure calcium molybdate, and appear not to be colored green by copper.

LINDGRENITE

Lindgrenite, $Cu_3(MoO_4)_2(OH)_2$, is well known at Chuquicamata, the type locality about 500 km north of Inca de Oro, so lindgrenite

Figure 12. **Terry and Marissa Szenics at the type locality.**

was a logical provisional identification when the szenicsite was first found; a comparison of their properties, however, shows them to be distinctly different. They are easily distinguished by color. Lindgrenite is yellow-green, szenicsite is a deep green like malachite. A small quantity of lindgrenite was found on a subsequent visit to the Jardinera mine. Most of the samples are yellow-green veinlets cutting a chalky white altered igneous rock. One or two small vugs contain euhedral crystals. The single instance of szenicsite and lindgrenite being found in the same specimen suggests that lindgrenite formed only at a distance from the molybdenite and powellite, where the molybdate ion was depleted relative to copper.

For analytical comparison a sample of type lindgrenite (Palache, 1935) from Chuquicamata (H#97527) was mounted and analyzed with the szenicsite. Lindgrenite from the Jardinera No. 1 mine was later mounted and analyzed by electron microprobe as well. The results are compared in Table 5. Jardinera lindgrenite is very pure. Silicon is present in quantities just above its detetion limits. The Chuquicamata sample contains small amounts of silicon, iron and lead. The average value of PbO is 0.46 weight % but individual analyses vary from 0.17 to 0.67 weight %. A second type of lindgrenite which is brighter in reflected light is present in the Chuquicamata sample. It occurs as a porous mass between blades of lindgrenite. Compositionally it has a lower lead content, is tungsten-rich and occurs in patches up to 1 micrometer in size. The tungsten-rich patches are too small to be resolved with the electron microprobe. Analyses show up to 22 weight % WO_3 with copper and molybdenum in nearly a 3 (Cu) to 2 (Mo, W) ratio. Thus these patches may be cuprotungstite intimately intergrown with lindgrenite, or they may be some undescribed intermediate copper molybdate-tungstate.

Table 5. **Electron microprobe analysis of lindgrenite.**

# of Analyses	*Jardinera 10*	*Chuquicamata 10 blades*	*Chuquicamata 3 porous*	*Chuquicamata Palache (1935)*	*Stoichiometric $Cu_3MoO_4(OH)_4$*
SiO_2	0.02	0.10	0.10		
FeO	<0.04	0.08	0.13		
CuO	43.65	43.01	42.69	42.8	43.82
MoO_3	53.36	52.88	53.50	53.7	52.87
PbO	<0.10	0.46	0.22		
H_2O	3.33	3.30	3.32	3.5	3.31
Total	100.36	99.82	99.95	100.0	100.00
Number of atoms on the basis of 99 oxygens excluding the H_2O					
Si	0.002	0.01	0.01		
Fe		0.01	0.01		
Cu	2.97	2.95	2.91	2.92	3.00
Mo	2.01	2.01	2.02	2.03	2.00
Pb		0.01	0.01		
H	4.98	4.98	4.96	4.95	5.00

Beam conditions: 15 KeV, 22 nanoamperes, 16 x 16 micrometer rastered beam. For Pb (L-alpha line): 25 KeV, 17 nanoamperes, 30 x 30 micrometer rastered beam. Sandia ZAF85 matrix correction progrram used. H_2O calculated from stoichiometry. Standards used: fayalite (Si, Fe), cuprite (Cu), $LiEuMo_2O_8$ (Mo), $PbTiO_3$ (Pb). Other elements checked were below their detection limits: detection limit of 0.01 weight %: Cl; 0.07: F; and 0.01: Ca; 0.02: Mg, Al, Ti, Cr, Zn, W; 0.03: Mn, Co; 0.04: V, Ni as weight % oxide.

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