

## ISHIHARAITE, (Cu,Ga,Fe,In,Zn)S, A NEW MINERAL FROM THE CAPILLITAS MINE, NORTHWESTERN ARGENTINA

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### ABSTRACT

Ishiharaite is a new sulfide mineral, (Cu,Ga,Fe,In,Zn)S, discovered at the Nueva Esperanza vein, Capillitas mine (27°20'43" S, 66°23'17" W, 3290 m osl) an epithermal ore deposit belonging to the Farallón Negro Mining District, northwestern Argentina. The mineral occurs as subhedral, equidimensional, individual grains (20 to 50 µm in size) included in tennantite. It is a dark gray metallic mineral, opaque and non-fluorescent. Under polarizing-reflected light, it is an isotropic mineral, and its color is burgundy brown with a faint violet hue in air and violet-burgundy in oil. The main reflectance values are ( $R_{air}, R_{oil} - \lambda/nm$ ): 18.27, 6.77 – 470; 20.10, 7.91 – 546; 21.74, 8.96 – 589; and 23.94, 10.44 – 650. Ishiharaite is cubic, space group  $F\bar{4}3m$ ,  $a$  5.368(1) Å,  $V$  154.68(1) Å<sup>3</sup>,  $Z$  = 4. The strongest five X-ray powder-diffraction lines [ $d$  in Å (I)( $hkl$ )] are: 3.096 (100) (111); 1.897 (60) (220); 1.620 (40) (311); 2.684 (20) (200); 1.097 (15) (422). Electron-microprobe analyses of the natural grains ( $n$  = 22) give an average composition (wt.%) of: S 30.77, Cu 33.61, Ga 13.31, In 9.48, Zn 5.74, Fe 6.13; the average ( $n$  = 6) chemical composition of the synthetic phase is: S 30.73, Cu 28.05, Ga 15.99, In 11.86, Zn 7.37, Fe 6.13. The empirical formulae of ishiharaite and the synthetic analogue, based on 2 *apfu*, are: (Cu<sub>0.55</sub>Ga<sub>0.19</sub>Fe<sub>0.13</sub>In<sub>0.08</sub>Zn<sub>0.08</sub>) $\Sigma$ 1.03S<sub>0.97</sub>, and (Cu<sub>0.45</sub>Ga<sub>0.24</sub>Fe<sub>0.11</sub>In<sub>0.11</sub>Zn<sub>0.11</sub>) $\Sigma$ 1.02S<sub>0.98</sub>, respectively. The mineral (IMA No. 2013-119) is named in honor of Dr. Shunso Ishihara (b. 1934), Emeritus Advisor of AIST (Advanced Industrial Science and Technology), Tsukuba, Japan.

**Keywords:** ishiharaite, (Cu,Ga,Fe,In,Zn)S, indium, gallium, epithermal, Capillitas mine, Farallón Negro Mining District, Argentina.

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## INTRODUCTION

Ishiharaite is a new sulfide mineral with the chemical composition  $(\text{Cu,Ga,Fe,In,Zn})\text{S}$ . It was found in the Nueva Esperanza vein of the Capillitas mine, an epithermal ore deposit from northwestern Argentina (Fig. 1). Among several samples collected from this vein, only one hosted this new mineral.

The mineral ishiharaite and its name were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA (2013-119). Type material is deposited at the Mineralogical Museum "Alfred Stelzner" of the Facultad de Ciencias Exactas Físicas y Naturales of the Universidad Nacional de Córdoba, Argentina, under the catalog number MS003280.

The name is in honor of Dr. Shunso Ishihara (born in 1934 in Hiroshima, Japan). Dr. Ishihara has contributed widely to geological sciences and his numerous manuscripts, published in English and Japanese, are highly significant. He introduced the extensively applied classification of granites in the Magnetite and Ilmenite series based on the content of magnetite linked with the redox state of the magma. Since 2005, he has spent most of his time in indium research and exploration and, at present, is an Emeritus advisor at AIST, Japan.

## OCCURRENCE

The Capillitas mine is an epithermal precious- and base-metal vein deposit, genetically linked to the other mineralizations of the Farallón Negro Volcanic

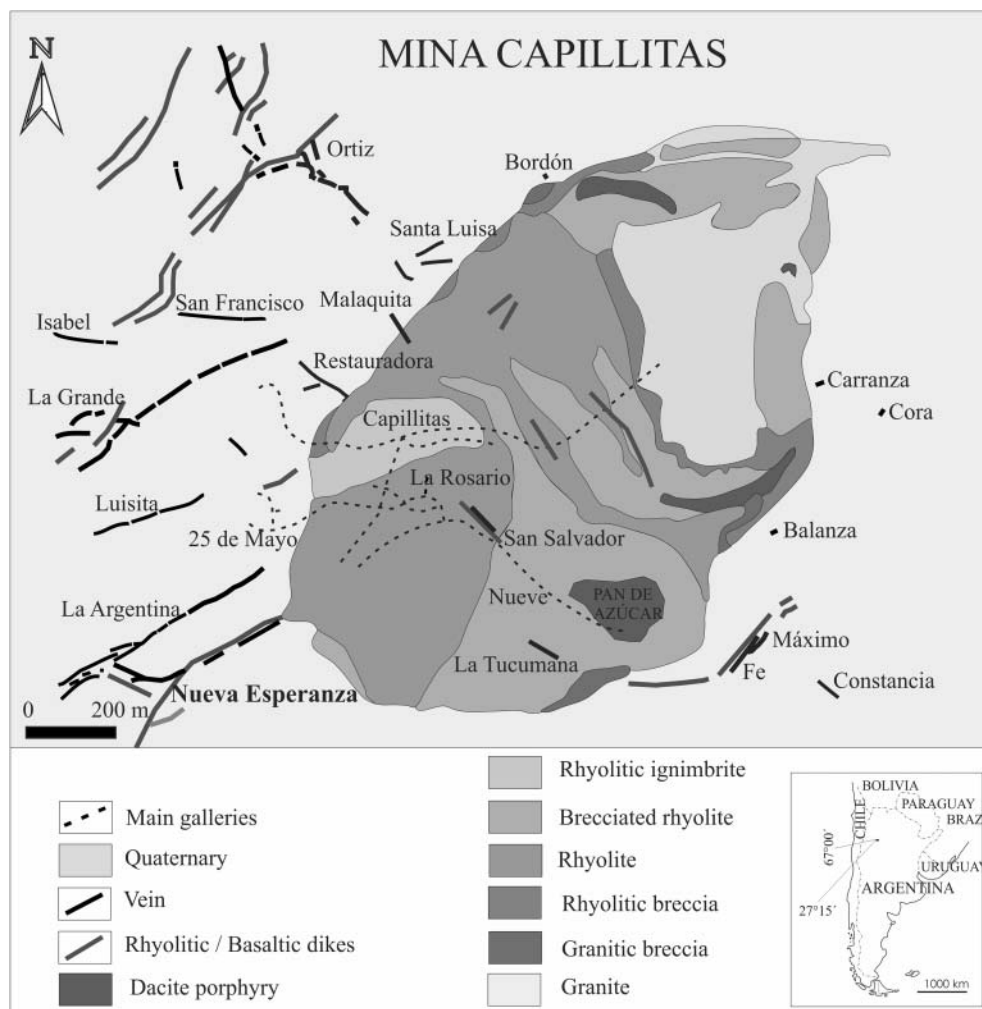


FIG. 1. Schematic geology of Mina Capillitas (modified from Márquez-Zavalía & Craig 2004).

Complex. It is located along the eastern slope of the Capillitas Range, in Catamarca province, northwestern Argentina (Fig. 1). The deposit has been discontinuously mined for gold since pre-Colombian times. During the last two centuries extensive workings in the oxidation zone were developed, interspersed with episodic attempts to recover copper which were discontinued after encountering metallurgical problems. Since the second part of the last century, mining has been restricted to the extraction of pink banded rhodochrosite, the main gangue mineral in some of the veins, and for which the Capillitas mine is internationally known.

The volcanism from which the mineralization of the Capillitas mine and the other deposits of the region (*e.g.*, Farallón Negro, La Alumbra, Agua Tapada, Cerro Atajo, Agua Rica) are derived is located 500 km east of the actual Pacific trench and 300 km east of the present-day volcanic front in the flat-slab region of the Central Andes (*e.g.*, Sillitoe 1976, Isaaks *et al.* 1982, Jordan *et al.* 1983). It developed in a back-arc position of the Miocene-Recent volcanic arc, along the Carachipamapa-Farallón Negro transversal volcanic chain of the Central Andes, and has dominant high-K calcalkaline to shoshonitic affinities (Viramonte *et al.* 1984). The volcanism occurred in a geological setting belonging to the Pampean Ranges of Northwestern Argentina. The geological column comprises upper Precambrian to lower Cambrian folded pelites and mica schists of the Suncho and Buey Muerto Formations, respectively, intruded by the late orogenic Capillitas granite in the Ordovician to the lower Silurian during the Famatinian Orogenic Cycle. Andean-age deformation reactivated NE-striking structural fabrics in the Neoproterozoic – early Cambrian Pampean basement, forming a tilt-block province.

The Capillitas granite is unconformably overlain by Cenozoic units: the El Morterito Formation (conglomerates, sandstones, and claystones), the Farallón Negro Volcanic Complex (rhyolites, brecciated rhyolites, rhyolitic and granitic breccias, dacite porphyries, and rhyolitic, trachytic, and basaltic dikes), and undifferentiated Quaternary deposits. In the area of the Capillitas mine, locally the Farallón Negro Volcanic Complex rocks form an ellipsoidal diatreme (1500 m × 900 m), with the long axis striking northeast. Hydrothermal alteration is widespread at Capillitas, but varies laterally depending upon the type of the host rock; 20 veins are hosted by the volcanic and granitic rocks in ENE and WNW directions (Márquez-Zavalía 1999).

The precious and base metal vein mineralization has a very diversified mineralogy, with more than 100 minerals among primary and secondary species described by Márquez-Zavalía (1999, 2006 and references therein), Márquez-Zavalía & Craig (2004), Márquez-Zavalía *et al.* (1999), and Putz *et al.* (2009). The Capillitas mine is the type locality for two other minerals: catamarcaite (Putz *et al.* 2006) and putzite (Paar *et al.* 2004).

Ishiharaite was found in one sample from the Nueva Esperanza vein (27°20'43" S, 66°23'17" W, 3290 m asl), one of the veins in the Capillitas mine (Fig. 1). This vein strikes N80°E, dips 45°S, is approximately 100 m long, 0.30 m thick, and is hosted in granite. It is mainly composed of sphalerite, pyrite, tennantite, chalcopyrite, enargite, galena, gold, stannoidite, stannite, and hübnerite, with chalcocite and covellite as secondary minerals in a quartz gangue (Fig. 2). Sphalerite and tennantite from this vein have chemical variations from In-free to In-rich compositions. One exploratory drill hole (JICA 1978–81) cut the Nueva

Minerals	Hypogene minerals				Supergene minerals
	Stage I	Stage II	Stage III	Stage IV	
Quartz	-----	-----	-----		
Pyrite	-----	-----	-----	-----	
Enargite		-----	-----		
Tennantite			-----	-----	
Sphalerite			-----	-----	
Chalcopyrite			-----		
Ishiharaite			-----		
Galena			-----		
Gold			-----		
Stannoidite			-----		
Stannite			-----		
Hübnerite			-----		
Chalcocite					-----
Covellite					-----

FIG. 2. Paragenetic sequence of the Nueva Esperanza vein.

Esperanza vein at 372 m and gave impoverished grades (0.77 g/t Au, 39.5 g/t Ag, 0.3% Cu) compared with the average grades obtained from the old galleries (6.2 g/t Au, 2413 g/t Ag, 13.83% Cu).

The primary mineral ishiharite occurs as subhedral, equidimensional, individual grains (20 to 50 µm in size), included in tennantite (Fig. 3), associated

with sphalerite, pyrite, chalcopyrite, and galena in a quartz gangue. One of the grains has very small (<1 µm) inclusions of chalcopyrite, while the other is surrounded by a discontinuous rim of that mineral. The optical properties were the first indication of the possibility of a new mineral, which was subsequently confirmed with additional studies.

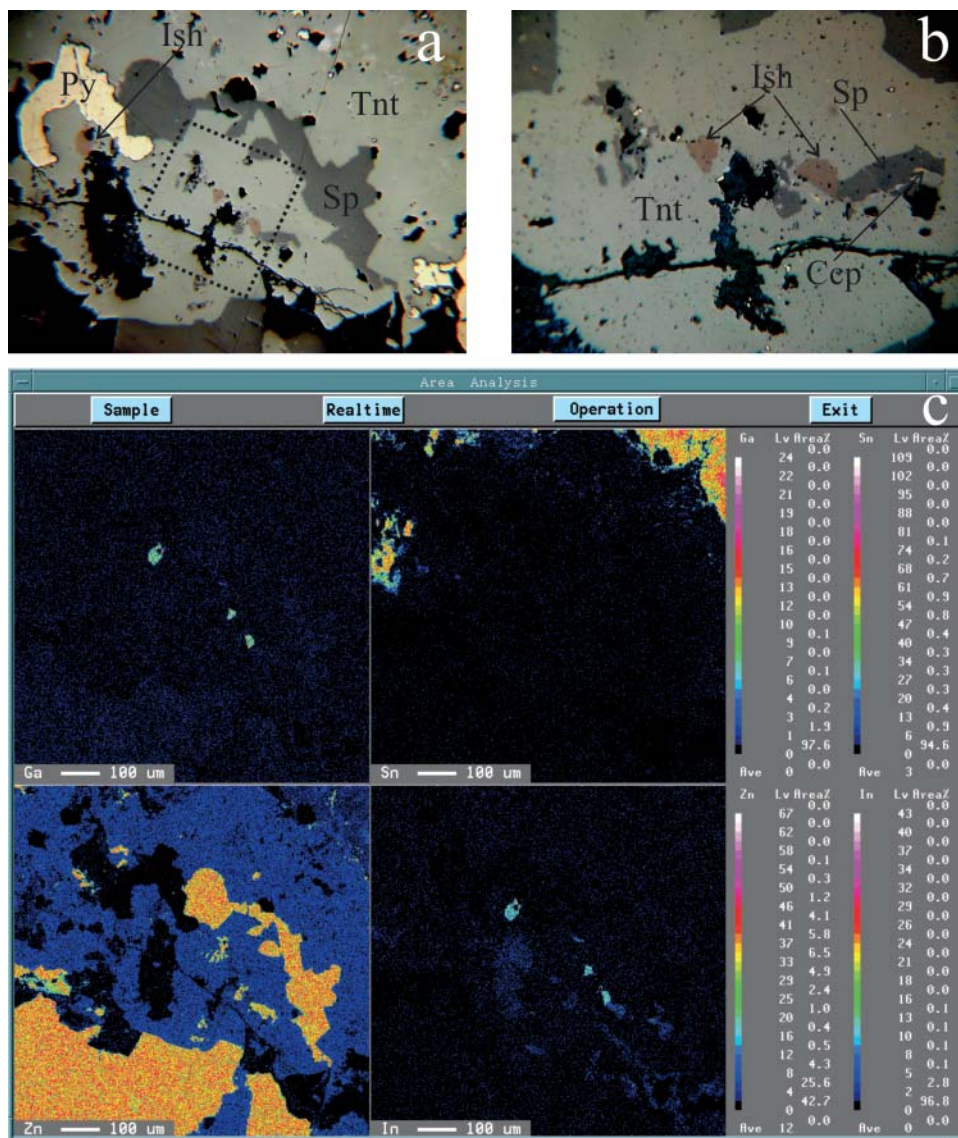


FIG. 3. (a, b) Photomicrographs of section NE-1176. Ishiharaite (Ish) hosted by tennantite (Tnt) is associated with pyrite (Py) and sphalerite (Sp) and minor chalcopyrite (Ccp), scale bar 50 µm; (c) WDS mapping of the section showing that ishiharite is the only mineral rich in In and Ga in the area of the photograph. Abbreviations for most minerals after Whitney & Evans (2010).

## PHYSICAL PROPERTIES

Under the stereomicroscope ishiharaite is dark with metallic luster and is non-fluorescent. Observed under the reflected light microscope the mineral is completely opaque without external reflections. Its color is burgundy brown with a faint violet hue in air and violet-burgundy in oil. As expected for a cubic mineral, neither bireflectance nor pleochroism were observed, and the mineral is isotropic in crossed polarizers. The relative hardness is higher than tennantite and the mineral acquires a good polish. Due to the small grain size, the Vickers hardness could not be measured. The reflectance values were determined using a Leitz Orthoplan microscope attached to a Hamamatsu solid state mini-spectrometer via optical fiber, with dry and immersion 20× objectives (effective NA: 0.2 in air and oil) using SiC No. 878 as standard; the oil conforms to the German standard DIN 58.884, now ISO 8036, with  $n = 1.5180$ . About 700 reflectance values for one spectrum were obtained; these were subsequently reduced to the required wavelength (400 to 700 nm) in steps of 20 nm, plus the four COM standard wavelengths. The obtained values ( $R_{\text{air}}$ ,  $R_{\text{oil}}$ ,  $\lambda/\text{nm}$ ) are shown in Table 1. The density, calculated using the empirical formula, is  $4.343 \text{ g/cm}^3$ .

DIFFRACTION PROPERTIES AND CRYSTAL  
STRUCTURE DESCRIPTION

Ishiharaite occurs as tiny grains and it was not possible to extract or isolate sufficient material for crystallographic investigations. Therefore, these measurements were performed on synthetic (Cu,Fe,Ga,In,Zn)S.

Synthetic (Cu,Fe,Ga,In,Zn)S was prepared using the evacuated silica glass tube method in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague, Czech Republic. High purity sulfur, iron, copper, zinc, indium, and gallium were used as starting materials. The weighed charge sealed in an evacuated silica glass tube was annealed at 300 °C for 20 days. After cooling, the charge was repeatedly (four times) reground under acetone and reheated at 600 °C for one week. The temperature was controlled electronically ( $\pm 4$  °C). The reaction product was examined by X-ray powder diffraction, reflected light microscopy, and with an electron microprobe. Synthetic (Cu,Fe,Ga,In,Zn)S forms irregular grains, <40  $\mu\text{m}$  in size (Fig. 4). In addition to ishiharaite, traces of inclusions of bornite were detected in the product.

X-ray powder diffraction data were collected using a Philips X'Pert MPD system with a vertical PW3020 goniometer in the Bragg-Brentano reflecting geometry, copper radiation (40 kV and 40 mA), secondary graphite monochromator, and a proportional counter. The samples were placed on a low-background silicon

TABLE 1. ISHIHARAITE REFLECTANCE AND COLOR VALUES FOR ILLUMINANT C IN AIR AND OIL

$\lambda$ (nm)	$R_{\text{air}}$	$R_{\text{oil}}$
400	19.86	8.67
420	18.89	7.21
440	18.37	6.78
460	18.30	6.70
<b>470</b>	18.27	6.77
480	18.37	6.85
500	18.92	7.11
520	19.25	7.46
540	19.88	7.80
<b>546</b>	20.10	7.91
560	20.67	8.24
580	21.28	8.73
<b>589</b>	21.74	8.96
600	22.31	9.25
620	22.87	9.67
640	23.79	10.17
<b>650</b>	23.94	10.44
660	24.45	10.55
680	25.13	10.97
700	25.77	11.11
	Color values C	
x	0.3295	0.3411
y	0.3268	0.3337
Y(%)	20.66	8.27
$\lambda_d$ (nm)	586	585
$P_e$ (%)	8	13

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC (Cu,Fe,Ga,In,Zn)S

<i>hkl</i>	Synthetic (Cu,Fe,Ga,In,Zn)S			Sphalerite (ICDD 5-566)	
	$l_r$	$d_m$	$d_c$	$l_r$	$d_m$
111	100	3.096	3.099	100	3.123
200	20	2.684	2.684	10	2.705
220	60	1.898	1.897	51	1.912
311	40	1.620	1.618	30	1.635
222	5	1.549	1.550	2	1.561
400	10	1.344	1.342	6	1.351
331	10	1.231	1.231	9	1.240
422	15	1.097	1.095	9	1.103
511	10	1.035	1.033	5	1.043
440	5	0.948	0.949	3	0.9557
531	5	0.907	0.907	5	0.9138
620	5	0.850	0.849	3	0.8548

holder. Step-scanned data were collected in the angular range 20–145° 2 $\theta$ , with a step size of 0.02° and 7 seconds exposure per step. The data are compared with those for sphalerite in Table 2.

Structural identity between the synthetic and the natural material was confirmed by electron backscattering diffraction (EBSD) using a TESCAN Vega scanning electron microscope combined with an EBSD system (HKL NordlysNano, Oxford Instruments).

Synthetic ishiharaite was identified as an isostructural analogue of sphalerite. The unit cell parameters were calculated using the "Unit cell" program (Holland & Redfern 1997). The structure of sphalerite and ishiharaite is based on inscribed tetrahedra in a face-centered cube [a face-centered cubic arrangement of sulfur and zinc (Cu, Fe, Ga, In) in the center of each tetrahedron]. No diffraction maxima corresponding to  $hkl$  indices not allowed in the  $F\bar{4}3m$  space group were observed; consequently, we present our data in the usual sphalerite setting.

The natural sample was prepared for investigation by etching the mechanically polished surface with colloidal silica (OP-U) for 10 minutes to reduce surface damage. EBSD patterns were collected and processed using the proprietary computer program AZteca Channel 5. The center of six Kikuchi bands was automatically detected using the Hough transform routine (Schmidt *et al.* 1991) with a resolution of 50 (internal Hough resolution parameter in the HKL software). The solid angles calculated from the patterns were compared with synthetic (Cu,Fe,Ga,In,Zn)S. The EBSD patterns (Fig. 5) obtained from the natural material (seven measurements from different spots on natural

ishiharaite) were found to match the patterns generated from the structure of the synthetic sample. The values of the mean angular deviation (MAD, *i.e.*, goodness of fit of the solution) between the calculated and measured Kikuchi bands ranged between  $0.57^\circ$  and  $0.21^\circ$ . These values reveal a very good match; as long as values of mean angular deviation are less than  $1^\circ$ , they are considered as indicators of an acceptable fit.

The EBSD study, chemical identity, and optical properties confirmed the identity of the natural and synthetic materials and consequently render legitimate the use of the synthetic phase for the complete characterization of ishiharaite.

Ishiharaite is isostructural with sphalerite and therefore belongs in Strunz group 2.CB.05a.

#### CHEMICAL COMPOSITION

The first nine analyses given in Table 3 (labeled US-xx) were obtained using a Cameca SX-50 electron microprobe at the Department of Geological Sciences, Virginia Polytechnic Institute & State University, Blacksburg, Virginia, US (WDS mode, 15 kV, 20 nA, 2  $\mu\text{m}$  beam diameter). The other 13 analyses (JP-xx) were obtained with a JEOL JXA-8900R electron microprobe at the National Institute of Advanced Industrial Science and Technology (AIST), Geological Survey of Japan, Tsukuba, Japan (WDS mode, 15 kV, 20 nA, 2  $\mu\text{m}$  beam diameter). The standards and

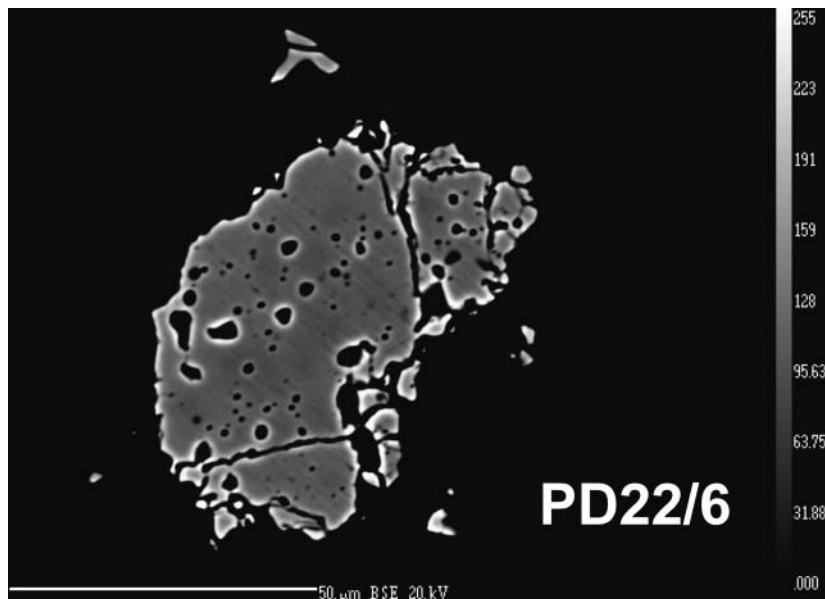


FIG. 4. BSE image of ishiharaite synthesized at  $600^\circ\text{C}$ .

TABLE 3. CHEMICAL COMPOSITION OF ISHIHARAITE

No.	US-1	US-2	US-3	US-4	US-5	US-6	US-7	US-8	US-9	JP-1	JP-2	JP-3	JP-4
wt.%													
S	29.72	29.86	30.27	30.30	30.36	30.15	29.90	30.42	30.30	31.37	30.95	31.25	30.91
Cu	34.00	34.77	34.47	34.47	34.48	31.72	34.64	35.09	34.59	33.69	33.92	33.73	33.74
In	9.34	9.65	9.39	9.81	10.33	9.94	9.57	8.94	9.52	9.25	9.80	8.46	8.89
Ga	12.69	12.62	13.26	13.17	12.76	12.16	13.45	12.28	12.67	14.13	13.56	14.21	13.47
Fe	7.05	7.12	7.13	7.09	7.07	6.34	6.78	7.07	7.01	6.96	6.84	6.78	6.48
Zn	6.79	5.60	4.73	4.54	4.78	9.27	4.80	5.55	4.93	4.83	5.08	4.82	5.43
Ge	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.05	0.14	0.12	0.01
As	0.28	0.04	0.06	0.00	0.00	0.00	0.00	0.05	0.05	0.03	0.00	0.01	0.12
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.12	0.16	0.15
Total	99.87	99.66	99.31	99.38	99.78	99.58	99.14	99.40	99.07	100.51	100.52	99.55	99.21
<i>apfu</i>													
S	0.946	0.952	0.964	0.965	0.965	0.962	0.957	0.965	0.965	0.982	0.974	0.984	0.980
Cu	0.546	0.559	0.554	0.554	0.553	0.510	0.560	0.561	0.561	0.532	0.539	0.536	0.540
In	0.083	0.086	0.083	0.087	0.092	0.089	0.086	0.079	0.079	0.081	0.086	0.074	0.079
Ga	0.186	0.185	0.194	0.193	0.187	0.178	0.198	0.179	0.179	0.203	0.196	0.206	0.196
Fe	0.129	0.130	0.130	0.130	0.129	0.116	0.125	0.129	0.129	0.125	0.124	0.123	0.118
Zn	0.106	0.088	0.074	0.071	0.075	0.145	0.075	0.086	0.086	0.074	0.078	0.074	0.084
Ge	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002	0.002	0.000
As	0.004	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.002
Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
No.	JP-5	JP-6	JP-7	JP-8	JP-9	JP-10	JP-11	JP-12	JP-13	Avr.	Max.	Min.	St.Dev.
wt.%													
S	31.29	31.19	31.39	30.82	31.50	31.43	31.39	31.18	30.98	30.77	31.50	29.72	0.58
Cu	32.16	33.74	33.96	32.21	33.96	32.17	33.39	31.90	32.61	33.61	35.09	31.72	1.02
In	8.19	9.62	9.59	10.93	9.08	9.56	9.83	9.06	9.88	9.48	10.93	8.19	0.59
Ga	13.39	13.60	14.20	10.41	14.57	13.93	14.39	14.23	13.78	13.31	14.57	10.41	0.95
Fe	6.69	6.75	7.16	6.22	7.07	6.28	6.78	6.88	6.41	6.82	7.16	6.22	0.30
Zn	7.43	4.84	5.22	7.94	5.41	7.26	5.28	5.40	6.41	5.74	9.27	4.54	1.25
Ge	0.13	0.05	0.00	0.28	0.00	0.00	0.01	0.04	0.00	0.06	0.28	0.00	0.08
As	0.15	0.02	0.00	0.03	0.04	0.06	0.07	0.29	0.00	0.06	0.29	0.00	0.08
Sb	0.15	0.02	0.07	0.08	0.02	0.05	0.09	0.15	0.08	0.06	0.16	0.00	0.06
Total	99.68	99.84	101.59	99.04	101.72	100.73	101.28	99.19	100.14				

ISHIHARAITE, (Cu,Ga,Fe,In,Zn)<sub>5</sub>, A NEW MINERAL FROM THE CAPILLITAS MINE

TABLE 3. (CONTINUED)

No.	US-1	US-2	US-3	US-4	US-5	US-6	US-7	US-8	US-9	JP-1	JP-2	JP-3	JP-4
<i>apfu</i>													
S	0.984	0.983	0.974	0.986	0.975	0.983	0.979	0.988	0.978	0.972	0.988	0.946	0.012
Cu	0.510	0.537	0.532	0.520	0.531	0.508	0.525	0.510	0.519	0.536	0.561	0.508	0.018
In	0.072	0.085	0.083	0.098	0.078	0.084	0.086	0.080	0.087	0.083	0.098	0.072	0.006
Ga	0.194	0.197	0.203	0.153	0.207	0.200	0.206	0.207	0.200	0.193	0.207	0.153	0.013
Fe	0.121	0.122	0.128	0.114	0.126	0.113	0.121	0.125	0.116	0.124	0.130	0.113	0.005
Zn	0.115	0.075	0.079	0.125	0.082	0.111	0.081	0.084	0.099	0.089	0.145	0.071	0.019
Ge	0.002	0.001	0.000	0.004	0.000	0.000	0.000	0.001	0.000	0.001	0.004	0.000	0.001
As	0.002	0.000	0.000	0.000	0.001	0.001	0.001	0.004	0.000	0.001	0.004	0.000	0.001
Sb	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.000	0.001
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

analytical lines selected were as follows: S (CuFeS<sub>2</sub>, K $\alpha$ ), Cu (CuFeS<sub>2</sub>, K $\alpha$ ), Ga (GaAs, K $\alpha$ ), In (In, L $\alpha$ ), Fe (CuFeS<sub>2</sub>, K $\alpha$ ), and Zn (ZnS, K $\alpha$ ). A counting time of 20 s, with background count-time of 10 s, was used for all elements. Germanium, As, Se, Ag, Cd, Sn, Sb, Te, Au, Pb, and Bi were also analyzed, but all results were below detection limits. The ZAF method was employed for matrix corrections.

The synthetic material was analyzed using a Cameca SX-100 instrument (WDS mode, 15 kV, 20 nA, 1–2  $\mu$ m beam diameter) at the Institute of Geology AS CR. The standards and analytical lines selected were as follows: S (ZnS, K $\alpha$ ), Cu (Cu, K $\alpha$ ), Ga (GaAs, L $\alpha$ ), In (InP, L $\alpha$ ), Fe (Fe, K $\alpha$ ), and Zn (Zn, K $\alpha$ ). Data were reduced using the PAP routine of Pouchou & Pichoir (1985).

A total of 22 chemical analyses (Table 3) were obtained from ishiharaite via electron probe microanalyzer. The averages (standard deviations) expressed in wt.% are: S 30.44 (0.52), Cu 34.10 (0.84), Ga 13.11 (0.65), In 9.45 (0.50), Fe 6.90 (0.25), and Zn 5.47 (1.29).

The structural formula, calculated from the average of the 22 chemical analyses and based on two atoms per formula unit (*apfu*), is (Cu<sub>0.55</sub>Ga<sub>0.19</sub>Fe<sub>0.13</sub>In<sub>0.08</sub>Zn<sub>0.08</sub>) $\Sigma$ 1.03S<sub>0.97</sub>.

Six chemical analyses were obtained from the synthetic material (Table 4). The averages (standard deviations) expressed in wt.% are: S 30.73 (0.18), Cu 28.05 (0.22), Ga 15.99 (0.13), In 11.86 (0.08), Zn 7.37 (0.12), and Fe 6.13 (0.15). The empirical formula of the synthetic analogue is (Cu<sub>0.45</sub>Ga<sub>0.24</sub>Fe<sub>0.11</sub>In<sub>0.11</sub>Zn<sub>0.11</sub>) $\Sigma$ 1.02S<sub>0.98</sub>.

#### RELATION TO OTHER SPECIES

Ishiharaite is isostructural with sphalerite and therefore should be placed in the Strunz group 2.CB.05a.

No mineral (approved by IMA or not; Smith & Nickel 2007) with the composition of ishiharaite was found in the literature, and it is the first mineral species with indium and gallium together in its structure. A mineral previously mentioned by Kissin & Owens (1986) is similar to ishiharaite, although it was never fully described or presented to the IMA for approval. It is a sakuraiite-like mineral, found in the metatype material studied by Kato (1965) from the Kanagase vein, Ikuno mine, Hyogo Prefecture, Japan, that was sent to the Mineralogy Section of CANMET. This mineral might be the Ga-analogue of sakuraiite, though there are significant differences between the two minerals (Table 5).

#### DISCUSSION

Ishiharaite formed at ~245 °C, according to the temperature obtained from fluid inclusion assemblages hosted in quartz from stage III (Márquez-Zavalía 1999), during a relatively late stage of mineralization (Fig. 2). It was possibly formed during decreasing



TABLE 4. CHEMICAL COMPOSITION OF SYNTHETIC ANALOGUE (SA) OF ISHIHARAITE

No.	1	2	3	4	5	6	Avr.	Max.	Min.	St.Dev.
wt. %										
S	30.64	30.89	30.44	30.86	30.64	30.90	30.73	30.90	30.44	0.18
Cu	28.46	27.97	28.02	27.87	28.09	27.90	28.05	28.46	27.87	0.22
In	11.94	11.97	11.82	11.78	11.84	11.80	11.86	11.97	11.78	0.08
Ga	15.82	16.03	16.09	16.17	15.86	15.95	15.99	16.17	15.82	0.13
Fe	6.20	5.99	5.92	6.08	6.30	6.27	6.13	6.30	5.92	0.15
Zn	7.35	7.48	7.22	7.50	7.24	7.42	7.37	7.50	7.22	0.12
Total	100.41	100.33	99.50	100.25	99.97	100.23	100.13			
apfu										
S	1	1	1	1	1	1	Avr.	Max.	Min.	St.Dev.
Cu	0.47	0.46	0.46	0.46	0.46	0.46	0.46	0.47	0.46	0.01
In	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.00
Ga	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.00
Fe	0.12	0.11	0.11	0.11	0.12	0.12	0.11	0.12	0.11	0.00
Zn	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.00
Total	2.05	2.03	2.04	2.03	2.04	2.04	2.04			

temperatures by exsolution of the In and Ga contents carried in tennantite; this is in agreement with a Schwarz-Schampera & Herzig (2002) statement that decreasing temperatures deplete indium solubility.

The presence of indium and tin together in the vein could imply, as stated by Schwarz-Schampera & Herzig (2002), strong evidence for metallogenic processes within the continental crust. These authors also point

out that the close association of deposits with back-arc settings during geotectonically active periods (*e.g.*, during the Tertiary) suggests the mobilization of metals such as In, Sn, Cu, Zn, Ag, Pb, and As from the subducting slab and later introduction into the overlying mantle wedge, followed by magmatic (hydrothermal) recycling. These facts match the geological setting of the Nueva Esperanza vein and its paragenesis.

TABLE 5. DIFFERENCES BETWEEN ISHIHARAITE AND SAKURAIITE

	Ishiharaite <sup>1</sup>	Sakuraiite
Color under reflected light	Burgundy brown with a faint violet hue (air) Violet-burgundy (oil)	Purplish olive gray without pleochroism <sup>2</sup>
Reflectance values (R <sub>air</sub> )	18.27(470), 20.10(546), 21.74(589), 23.94(650)	Pure gray without any significant tint <sup>3</sup> 22.6(470), 22.7(540), 22.5(580), 22.6(640)
X-ray powder-diffraction lines	3.096(100), 1.897(60), 1.620(40), 2.684(20)	3.15(100), 1.932(60), 1.647(40), 2.74(30) <sup>2,3</sup>
Structure	<i>F</i> 43 <i>m</i>	<i>I</i> 42 <i>m</i> or <i>I</i> 4 <sup>2</sup> <i>P</i> 432, <i>P</i> 43 <i>m</i> , and <i>Pm</i> 3 <i>m</i> <sup>3</sup>
Chemistry	Sn and Ag < d. l. Ga average (n = 22) = 13.31 wt. % Cu > Fe ≥ Zn, Sn < d. l.; In:Sn is 100:0	Sn + Ag = 7.5 <sup>3</sup> , 12 <sup>4</sup> , and 13 <sup>2</sup> wt. % < d. l. Cu > Zn > Fe / Zn > Cu > Fe, In > Sn; In:Sn ≤ 89:11
Element ratios		
Formula accepted by IMA	(Cu,Ga,Fe,In,Zn)S	(Cu,Zn,Fe,In,Sn)S

<sup>1</sup>This paper<sup>2</sup>Kato (1965)<sup>3</sup>Kissin & Owens (1986)<sup>4</sup>Shimizu *et al.* (1986)

X-ray powder-diffraction lines [d in Å (l)]

&lt; d. l. : below detection limits

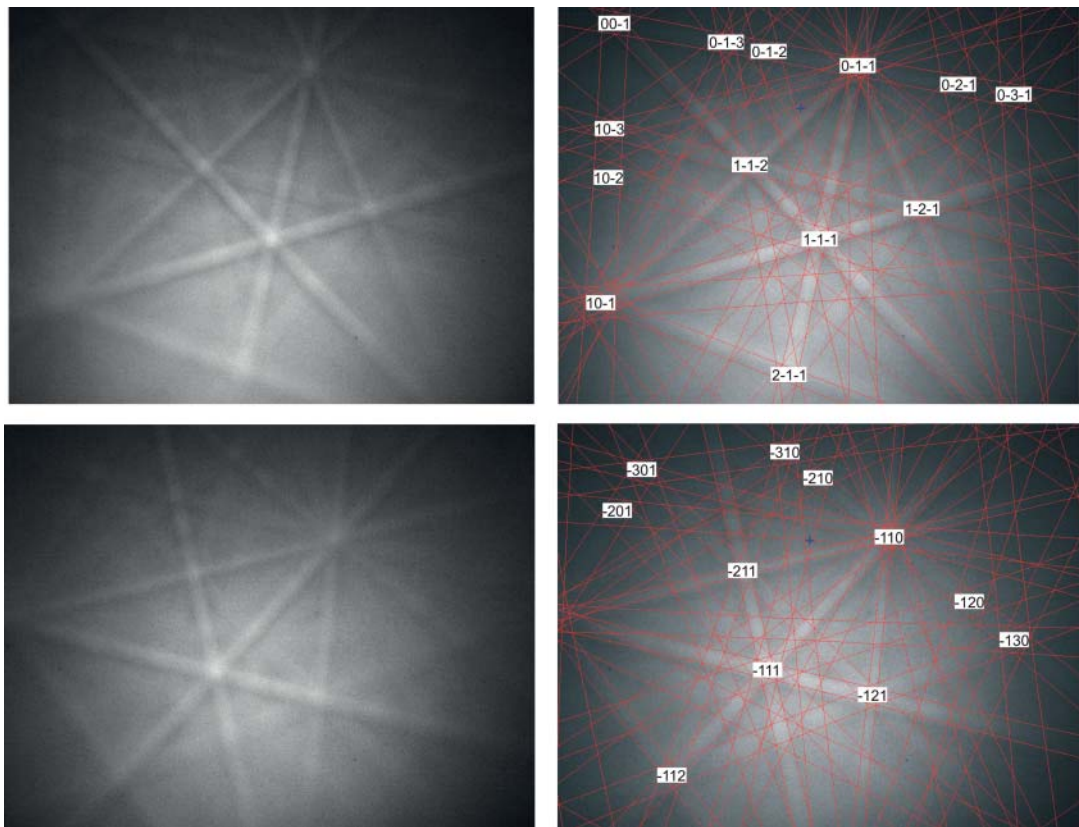


FIG. 5. EBSD image of natural ishiharaite; in the right panes, the Kikuchi bands are indexed.

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#### REFERENCES

- HOLLAND, T.J.B. & REDFERN, S.A.T. (1997) Unit cell refinement from powder diffraction data; the use of regression diagnostics. *Mineralogical Magazine* **61**, 65–77.
- ISAAKS, B., JORDAN, T., ALMENDINGER, R., & RAMOS, V.A. (1982) La segmentación tectónica de los Andes Centrales y su relación con la placa de Nazca subductada. *V Congreso Latinoamericano de Geología, Actas III*, 587–606.
- JICA (JAPAN INTERNATIONAL COOPERATION AGENCY) (1978–81) Informe de estudios básicos sobre la explotación de recursos minerales en la zona norte de la República Argentina. Cuatro etapas: Dirección General de Fabricaciones Militares, Informe inédito, Buenos Aires, Argentina (in Spanish).
- JORDAN, T.E., BRYAN, L.I., ALLMENDINGER, R.W., BREWER, J.A., RAMOS, V.A., & ANDO, C.J. (1983) Andean tectonics related to geometry of subducted Nasca plate. *Geological Society of America Bulletin* **94**, 341–361.
- KATO, A. (1965) Sakuraiite, a new mineral. *Chigakw Kenkyu (Earth Science Studies)*, Sakurai Volume, 1–5 (in Japanese).
- KISSIN, S.A. & OWENS, R.D. (1986) The crystallography of sakuraiite. *Canadian Mineralogist* **27**, 679–683.
- MÁRQUEZ-ZAVALÍA, M.F. (1999) El Yacimiento Capillitas, Catamarca. In *Recursos Minerales de la República Argentina* (E.O. Zappettini, ed.). SEGEMAR, Buenos Aires, Argentina, **35**, 1643–1652 (in Spanish).

- MÁRQUEZ-ZAVALÍA, M.F. (2006) El extremo rico en As de la serie Jordanita-Geocronita de Capillitas, Catamarca, Argentina. *Revista de la Asociación Geológica Argentina* **61**, 231–235 (in Spanish).
- MÁRQUEZ-ZAVALÍA, M.F. & CRAIG, J.R. (2004) Telluride and precious metal mineralization at Mina Capillitas, North-western Argentina. *Neues Jahrbuch für Mineralogie - Monatshefte* **2004(4)**, 176–192.
- MÁRQUEZ-ZAVALÍA, M.F., CRAIG, J.R., & SOLBERG, T.N. (1999) Duranusite, product of realgar alteration, Mina Capillitas, Argentina. *Canadian Mineralogist* **37**, 1255–1259.
- PAAR, W.H., ROBERTS, A.C., BERLEPSCH, P., AMBRUSTER, T., TOPA, D., & ZAGLER, G. (2004) Putzite,  $(\text{Cu}_{4.7}\text{Ag}_{3.3})_{28}\text{GeS}_6$ , a new mineral species from Capillitas, Catamarca, Argentina: Description and crystal structure. *Canadian Mineralogist* **42**, 1757–1769.
- POUCHOU, J.L. & PICHOR, F. (1985) “PAP” ( $\phi\rho Z$ ) correction procedure for improved quantitative microanalysis. In *Microbeam Analysis* (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California, United States (104–106).
- PUTZ, H., PAAR, W.H., TOPA, D., MAKOVICKY, E., & ROBERTS, A.C. (2006) Catamarcaite,  $\text{Cu}_6\text{GeWS}_8$ , a new germanium sulfide mineral species from Capillitas, Catamarca, Argentina: Description, paragenesis and crystal structure. *Canadian Mineralogist* **44**, 1481–1497.
- PUTZ, H., PAAR, W.H., & TOPA, D. (2009) Aportes al conocimiento de la mineralización de mina Capillitas, Catamarca. *Revista de la Asociación Geológica Argentina* **64**, 514–524.
- SCHMIDT, N.H., BILDESORENSEN, J.B., & JENSEN, D.J. (1991) Band positions used for online crystallographic orientation determination from electron back scattering patterns. *Scanning Microscopy* **5**, 637–643.
- SCHWARZ-SCHAMPERA, U. & HERZIG, P.M. (2002) *Indium: geology, mineralogy and economics*. Springer-Verlag, Heidelberg, Germany.
- SHIMIZU, M., KATO, A., & SHIOZAWA, T. (1986) Sakuraiite: Chemical composition and extent of (Zn-Fe)In for Cu-Sn substitution. *Canadian Mineralogist* **24**, 405–409.
- SILLITOE, R.H. (1976) Andean mineralization: A model for the metallogeny of convergent plate margins. Geological Association of Canada, Special Paper **14**, 59–100.
- SMITH, D.G.W. & NICKEL, E.H. (2007) A system of codification for unnamed minerals: Report of the Subcommittee for Unnamed Minerals of the IMA Commission on New Minerals, Nomenclature and Classification. *Canadian Mineralogist* **45**, 983–1055.
- VIRAMONTE, J.G., GALLISKI, M.A., ARAÑA SAAVEDRA, V., APARICIO, A., GARCÍA CACHO, L., & MARTÍN ESCORZA, C. (1984) El finivulcanismo básico de la depresión de Arizaro, provincia de Salta. *IX Congreso Geológico Argentino, Actas, III*, 234–251.
- WHITNEY, D.L. & EVANS, B.W. (2010) Abbreviations for names of rock-forming minerals. *American Mineralogist* **95**, 185–187.

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