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HUANZALAITE, $MgWO_4$, A NEW MINERAL SPECIES FROM THE HUANZALA MINE, PERU

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Abstract

Huanzalaite, ideally $MgWO_4$, occurs as inclusions in scheelite in the Huanzala mine, Peru. It forms orange to reddish brown aggregates composed of minute (<10 μm) crystals. The average size of the aggregates is approximately 0.1 mm across. It is monoclinic, *P*2/*c*, with cell parameters *a* 4.7027(15), *b* 5.6894(11), *c* 4.9413(9) Å, β 90.70(2)°, *V* 132.20(5) Å^3 and *Z* = 2. The strongest seven lines in the powder XRD pattern [*d* in (Å)(I/I_0)(*hkl*)] are: 3.73(100)(011), 2.91(94)(111), 2.93(83)(11$\bar{1}$), 4.70(74)(100), 3.63(39)(110), 2.47(39)(002) and 2.18(32)(121). The mean composition derived from ten electron-microprobe analyses contains (wt.%); WO_3 84.81, MgO 12.49, MnO 1.78, FeO 1.39, with trace amounts of Ca, and lead to the empirical formula $(Mg_{0.85}Mn_{0.07}Fe_{0.05})_{\Sigma 0.97}W_{1.01}O_4$. Huanzalaite is a member of the wolframite group (class 4.DB of Strunz & Nickel), and is the Mg-dominant analogue of hübnerite, $MnWO_4$, ferberite, $FeWO_4$, and sanmartinite, $ZnWO_4$. The calculated density of huanzalaite is 6.953 g/cm^3. Huanzalaite shows bluish fluorescence under UV light. The mineral formed during the metasomatic emplacement of the copper orebody. The source of Mg in this mineral, as well as in the associated sellaite, talc and tremolite, may be dolomite in limestone, which is the host rock of the orebody.

Keywords: huanzalaite, new mineral species, magnesium, tungstate, wolframite-group mineral, Huanzala mine, Peru.

Sommaire

La huanzalaïte, de composition idéale $MgWO_4$, se présente en inclusions dans la scheelite de la mine Huanzala, au Pérou. Elle se présente en agrégats de petits cristaux (<10 μm) oranges à brun rougeâtre. Ces agrégats ont un diamètre d'environ 0.1 mm. Le minéral est monoclinique, *P*2/*c*, avec paramètres réticulaires *a* 4.7027(15), *b* 5.6894(11), *c* 4.9413(9) Å, β 90.70(2)°, *V* 132.20(5) Å^3 et *Z* = 2. Les sept raies les plus intenses du spectre de diffraction, méthode des poudres [*d* en Å(I/I_0)(*hkl*)] sont: 3.73(100)(011), 2.91(94)(111), 2.93(83)(11$\bar{1}$), 4.70(74)(100), 3.63(39)(110), 2.47(39)(002) et 2.18(32)(121). Les dix analyses effectuées avec une microsonde électronique ont donné la composition moyenne (%, poids): WO_3 84.81, MgO 12.49, MnO 1.78, FeO 1.39, avec des traces de Ca, et mènent à la formule empirique $(Mg_{0.85}Mn_{0.07}Fe_{0.05})_{\Sigma 0.97}W_{1.01}O_4$. La huanzalaïte appartient au groupe de la wolframite (classe 4.DB de Strunz et Nickel), et serait le membre à dominance de Mg, analogue de la hübnerite, $MnWO_4$, ferberite, $FeWO_4$, et sanmartinite, $ZnWO_4$. Sa densité calculée est 6.953 g/cm^3. La huanzalaïte fait preuve d'une fluorescence bleuâtre en lumière ultraviolette. Elle s'est formée au cours de la formation métasomatique du gisement de cuivre. La source du Mg dans ce minéral, de même que dans la sellaïte, le talc et la trémolite associés, pourrait bien être la dolomite dans le calcaire, qui constitue la roche hôte du gisement.

(Traduit par la Rédaction)

Mots-clés: huanzalaïte, nouvelle espèce minérale, magnésium, tungstate, minéral du groupe de la wolframite, mine Huanzala, Pérou.

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Introduction

Huanzalaite was first encountered as a single small grain in a concentrate of heavy minerals in the tailings at the Huanzala mine in Peru by one of the authors, H.F., in September, 2008. It was discovered again in a specimen of copper ore consisting of enargite and chalcopyrite from the F–740 V–2T pit during an investigation of the ore-forming minerals in November, 2008. The mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification, IMA, in July 2009 (IMA 2009–018). The mineral is named after the type locality, the Huanzala mine, Peru. The type material is housed in the mineralogical collections of the National Museum of Nature and Science, Tokyo, Japan, under the registered number NSM–MF15366.

Geological Background and Occurrence

Huanzalaite occurs as an inclusion in scheelite from the copper ore beds in the F–740 V–2T pit of the Huanzala mine, Huallanca district, Bolognesi Province, Ancash Department, Peru (77°00’W, 9°51’S) (Fig. 1a). The position of the type locality of huanzalaite in the F–740 V–2T pit is indicated in the geological sketch-map (Fig. 1b) and the longitudinal section of the V–2T orebody (Fig. 1c). Associated minerals are scheelite, enargite, chalcopyrite, pyrite, calcite, fluorite, quartz and muscovite.

The deposit results from the replacement of Lower Cretaceous limestone and intercalations of shale and sandstone; the orebodies are related to the intrusion of a Miocene or Pliocene granodiorite porphyry stock, and sheets and dikes of quartz porphyry. The orebodies are

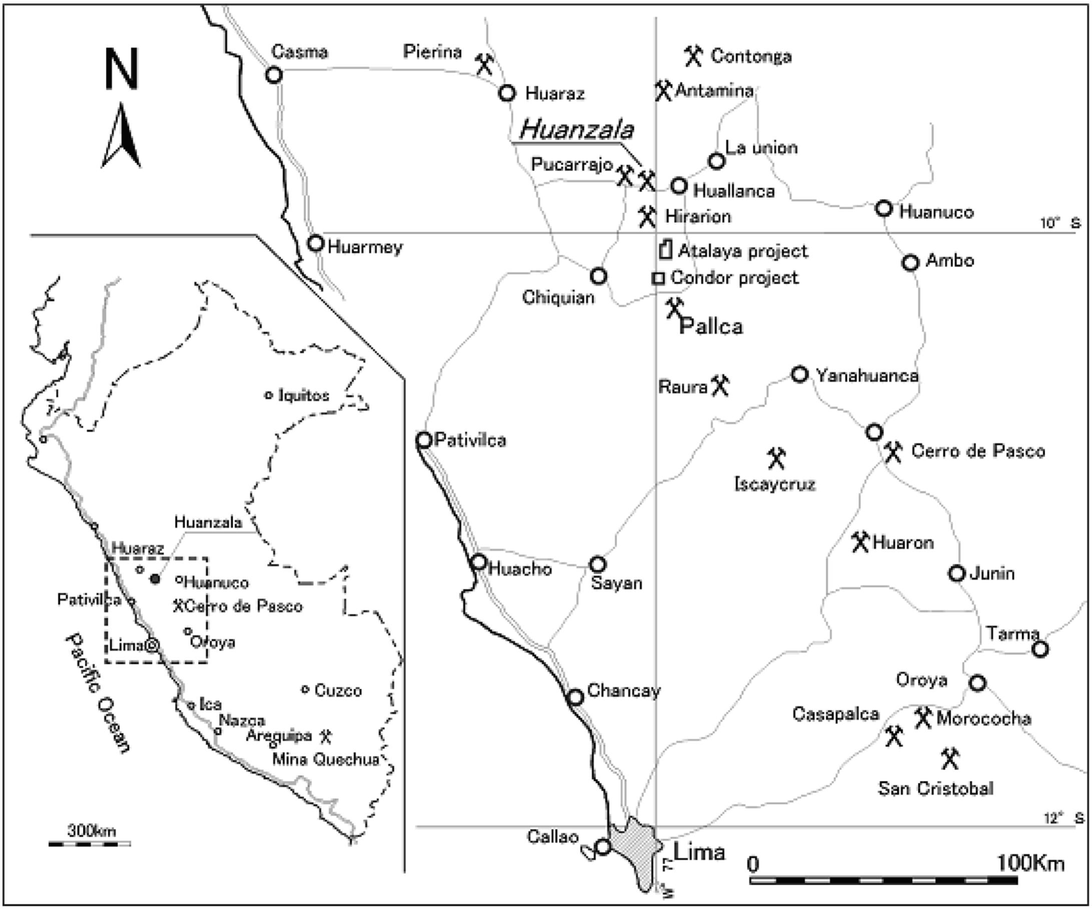

Fig. 1a. A location map of the Huanzala mine in Peru.

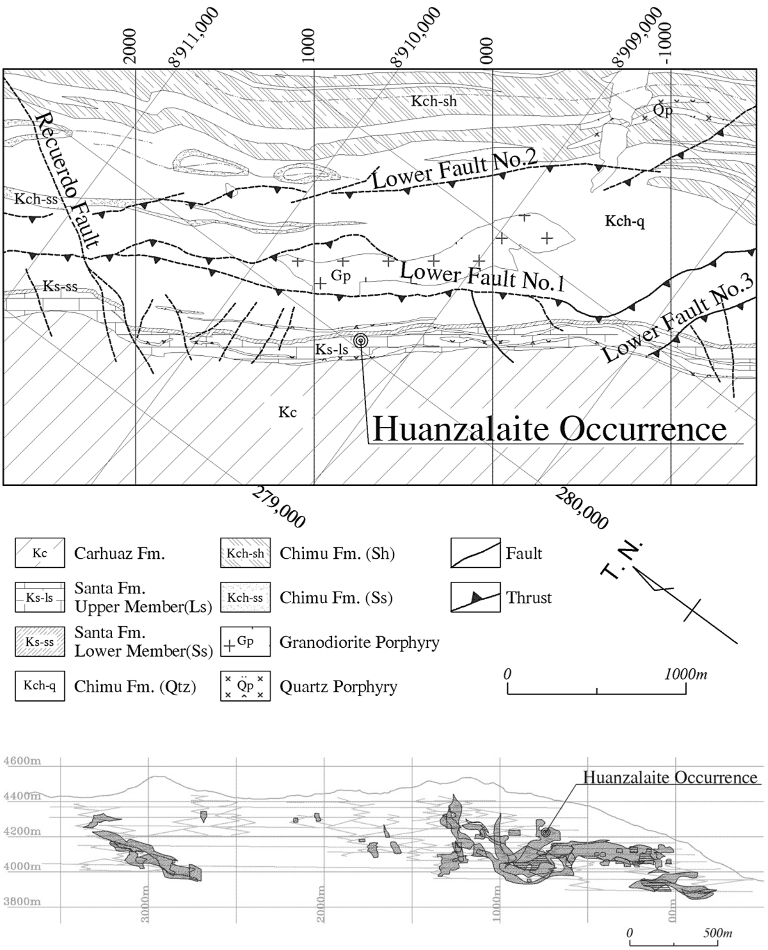

FIG. 1b, c. Regional geological sketch-maps of the Huanzala mine, with the indication of the position of the type locality of huanzalaite. (b) A geological sketch-map (after Murakami *et al*. 2009), and (c) a longitudinal section of the V–2T orebody.

composed of pyrite, sphalerite and galena, including sporadic skarn minerals, and copper minerals accompanied by silver–tin–tungsten-bearing assemblages (Imai *et al*. 1985, Imai 1986, 1999). The mineral assemblage of copper ore of the F–740 V–2T pit, enargite, pyrite, sphalerite, scheelite, quartz, calcite and "sericite", is the acidic-sulfate type of ore (B) referred to by Imai (1999), which follows the lead–zinc ore, namely the "adularia–sericite" type of ore (A). The acidic-sulfate type of ore (B) may have originated from an ore fluid rich in magnesium because of the existence of dolomitic limestone in the wallrock; chlorite, dolomite, sellaite, talc, and phlogopite are typical gangue minerals.

APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Huanzalaite forms orange to reddish brown aggregates composed of minute (< 10 μm) crystals (Fig. 2). The average size of the aggregates is approximately 0.1 mm across, but the maximum diameter exceeds 0.4 mm in the type specimen. It is transparent, and shows a white streak and vitreous to adamantine luster. Although the fluorescence of scheelite affects the observations, a more bluish fluorescence can be observed than that from the neighboring scheelite under short- (254 nm) and long-wavelength (365 nm) ultraviolet (UV) radiation. The same fluorescence can be observed in the highpurity reagent $MgWO_4$ under short- and long-wave UV light. The pale blue fluorescence is less bright under the long-wavelength UV. The weak pale blue fluorescence allows one to distinguish huanzalaite from scheelite, which does not fluoresce under the long-wavelength UV. As huanzalaite occurs as fine crystals, hardness, tenacity, cleavage, fracture, density and optical properties could not be measured. The density calculated on the basis of the empirical formula and unit cell is 6.953 g cm^{-3}. The calculated mean index of refraction based on the Gladstone–Dale relationship is 2.20. The crystal fragments of huanzalaite in a crystal of scheelite show simultaneous oblique extinction. The difference in the extinction angle is approximately 20° from the straight extinction of the host crystal of scheelite. This statement indicates a preferred orientation of the crystals of huanzalaite with respect to the host. Synthetic crystals of $MgWO_4$ grown in KCl flux show a short prismatic habit [001] with {102} usually dominant (Endo *et al.* 1986).

Chemical Composition

Chemical analyses (10) were carried out by means of a JEOL JXA–8800M electron microprobe (WDS mode, 15 kV, 20 nA, 2 μm beam diameter). Standard materials for the analysis were as follows: synthetic $MgWO_4$ for Mg$K\alpha$ and W$L\alpha$, rhodonite for Mn$K\alpha$, synthetic Fe_2SiO_4 for Fe$K\alpha$ and synthetic $CaWO_4$ for Ca$K\alpha$. No other element with atomic number greater than ten was detected. Analytical results are given in Table 1. The empirical formula (based on O = 4) is $(Mg_{0.85}Mn_{0.07}Fe_{0.05})_{\Sigma 0.97}W_{1.01}O_4$. The simplified formula is $MgWO_4$, which requires MgO 14.81, WO_3 85.19, total 100.00 wt.%.

Huanzalaite contains small amounts of Mn and Fe in solid solution toward hübnerite, $MnWO_4$, and ferberite, $FeWO_4$. The orange to reddish brown color of huanzalaite may come from these transition metals. The concentration of Ca in huanzalaite is negligible. The electron-microprobe analyses reveal that the

TABLE 1. ANALYTICAL RESULTS FOR HUANZALAITE AND MAGNESIAN FERBERITE

	Present study												Ferenc & Uher (2007)			Barkov *et al.* (2008)		
	1	2	3	4	5	6	7	8	9	10	mean	s.d.	MgW ROW33	MgW 65945	MgW 65992	5	1	4
WO_3	85.19	83.94	84.06	86.17	85.61	85.28	84.69	85.56	84.06	83.55	84.81	0.83	79.34	79.22	79.67	77.01	76.71	76.80
Nb_2O_5													0.00	0.00	0.05	0	0.02	0
TiO_2													0.00	0.00	0.00	0.03	0.10	0.06
V_2O_3																0.02	0.01	0
MoO_3																0.05	0.07	0.02
SnO													0.00	0.00	0.08			
MgO	13.14	12.68	12.59	12.56	12.55	12.54	12.46	12.26	12.22	11.85	12.49	0.32	7.75	6.68	6.34	1.65	1.38	1.35
MnO	0.83	1.06	1.08	3.15	2.35	0.97	1.19	1.26	2.03	3.92	1.78	1.00	1.64	3.05	3.24	1.55	1.53	1.69
FeO	1.52	1.89	1.89	0.22	0.90	1.85	2.05	1.98	0.96	0.63	1.39	0.62	8.45	9.46	9.83	19.77	20.24	20.03
CaO	0.00	0.07	0.02	0.00	0.01	0.01	0.01	0.02	0.00	0.01	0.02	0.02	0.03	0.00	0.00	0.01	0	0.02
NiO																0.02	0	0.03
ZnO													0.00	0.00	0.00	0.05	0.06	0.03
CoO																0	0.01	0.01
Cr_2O_3																0.04	0	0
UO_2													0.04	0.00	0.00			
Total	100.67	99.64	99.65	102.09	101.42	100.65	100.41	101.08	99.26	99.97	100.47		97.25	98.41	99.21	100.19	100.13	100.03
W *apfu*	1.006	1.004	1.006	1.009	1.008	1.012	1.007	1.013	1.012	1.001	1.008		1.006	1.001	1.001	0.99	0.99	0.99
Nb													0.000	0.000	0.001	0	0.001	0
Ti													0.000	0.000	0.000	0.001	0.004	0.002
Mo																0.001	0.001	0
Sn													0.000	0.000	0.002			
Mg	0.893	0.872	0.867	0.846	0.850	0.856	0.853	0.835	0.846	0.817	0.854		0.565	0.486	0.458	0.12	0.10	0.10
Mn	0.032	0.041	0.042	0.121	0.090	0.038	0.046	0.049	0.080	0.154	0.069		0.068	0.126	0.133	0.07	0.06	0.07
Fe	0.058	0.073	0.073	0.008	0.034	0.071	0.079	0.076	0.037	0.024	0.053		0.346	0.386	0.399	0.82	0.84	0.84
Ca	0.000	0.003	0.001	0.000	0.001	0.000	0.001	0.001	0.000	0.001	0.000		0.002	0.000	0.000			
Ni																0.001	0	0.001
Zn													0.000	0.000	0.000	0.002	0.002	0.001
U													0.000	0.000	0.000			

Compositions are first presented in wt% oxides, then converted on the basis of four atoms of oxygen per formula unit (*apfu*).

TABLE 2. POWDER X-RAY-DIFFRACTION DATA FOR HUANZALAITE

Huanzalaite Present study						Synthetic $MgWO_4$ (PDF #27-0789)		Calc.*	
I/I_0	d_{meas}	d_{calc}	h	k	l	I	d	I_{calc}	d_{calc}
28	5.69	5.69	0	1	0	20	5.67	24	5.66
74	**4.70**	**4.70**	**1**	**0**	**0**	**95**	**4.68**	**98**	**4.68**
100	**3.73**	**3.73**	**0**	**1**	**1**	**100**	**3.719**	**100**	**3.71**
39	**3.63**	**3.62**	**1**	**1**	**0**	**45**	**3.61**	**40**	**3.61**
83	**2.93**	**2.94**	**1**	**1**	**$\bar{1}$**	**100**	**2.929**	**81**	**2.92**
94	**2.91**	**2.91**	**1**	**1**	**1**	**95**	**2.901**	**80**	**2.90**
18	2.85	2.84	0	2	0	25	2.836	15	2.83
39	**2.47**	**2.47**	**0**	**0**	**2**	**40**	**2.463**	**24**	**2.46**
		2.47	0	2	1	40	2.459	24	2.45
14	2.44	2.43	1	2	0	18	2.427	16	2.42
3	2.36	2.35	2	0	0	20	2.343	14	2.34
3	2.27	2.27	0	1	2	3	2.261	3	2.26
19	2.20	2.20	1	0	$\bar{2}$	25	2.191	22	2.18
32	**2.18**	**2.18**	**1**	**2**	**1**	**40**	**2.172**	**27**	**2.17**
6	2.05	2.05	1	1	$\bar{2}$	6	2.044	6	2.04
5	2.03	2.03	1	1	2	11	2.027	7	2.03
4	1.998	1.997	2	1	$\bar{1}$	13	1.9919	13	1.984
12	1.981	1.981	2	1	1	18	1.9751	17	1.976
4	1.896	1.896	0	3	0	8	1.8913	7	1.887
10	1.865	1.865	0	2	2	13	1.86	11	1.857
9	1.813	1.812	2	2	0	12	1.8068	11	1.803
19	1.759	1.759	1	3	0	25	1.754	21	1.750
5	1.739	1.739	1	2	$\bar{2}$	6	1.7346	5	1.728
5	1.728	1.728	1	2	2	7	1.7243	7	1.723
		1.714	2	0	$\bar{2}$	15	1.7087	12	1.700
12	1.708	1.707	2	2	$\bar{1}$	17	1.702	15	1.696
24	1.695	1.696	2	2	1	20	1.6909	16	1.691
		1.693	2	0	2	25	1.6881	11	1.691
2	1.658	1.659	1	3	$\bar{1}$	2	1.6552	1	1.650
		1.655	1	3	1	2	1.6508	1	1.648
2	1.623	1.623	2	1	2	2	1.618	1	1.620
6	1.582	1.582	0	1	3	7	1.5782	7	1.575
		1.505	1	1	$\bar{3}$	18	1.5011	12	1.495
17	1.504	1.504	0	3	2			6	1.497
7	1.494	1.494	1	1	3	10	1.4904	9	1.490
6	1.475	1.476	2	3	0	7	1.472	7	1.469
5	1.453	1.455	2	2	2	6	1.4508	4	1.451
		1.450	3	1	$\bar{1}$	11	1.4458	9	1.440
		1.440	3	1	1	14	1.436	9	1.436
11	1.436	1.436	1	3	$\bar{2}$	17	1.4327	9	1.427
		1.430	1	3	2	12	1.4264	10	1.424
12	1.426	1.425	0	2	3	15	1.4222	10	1.419
		1.368	1	2	$\bar{3}$	13	1.3641	3	1.360
9	1.367	1.367	0	4	1			9	1.360
7	1.314	1.314	1	4	$\bar{1}$	8	1.3102	6	1.306
2	1.281	1.282	3	1	2	2	1.2786	1	1.280
3	1.271	1.271	2	3	$\bar{2}$	4	1.2681	4	1.263
2	1.262	1.263	2	3	2			3	1.259
2	1.234	1.235	0	0	4			2	1.230
2	1.225	1.225	2	2	$\bar{3}$			2	1.216
4	1.208	1.208	3	3	0			5	1.202
2	1.191	1.191	1	0	4			2	1.188
5	1.181	1.183	2	4	$\bar{1}$			4	1.177
		1.180	2	4	1			4	1.175
1	1.166	1.166	1	1	4			1	1.163
2	1.132	1.133	0	2	4			2	1.128
6	1.108	1.109	0	5	1			1	1.103
		1.107	3	1	3			3	1.105
6	1.106	1.106	1	5	0			2	1.100
		1.099	2	0	$\bar{4}$			2	1.091
3	1.099	1.099	1	2	4			1	1.095
3	1.099	1.099	1	2	4			1	1.095

The strongest seven lines are given in bold face. Values of d are quoted in Å. * Calculated after Kravchenko (1969).

surrounding scheelite is almost free of Mg, Fe and Mn (less than 0.05 wt.% as oxides). Huanzalaite and the adjacent scheelite show a perfect partitioning involving larger Ca^{2+} ions and smaller $(Mg,Fe,Mn)^{2+}$ ions.

Crystallography

Powder X-ray-diffraction data were obtained using a 114.6 mm diameter Gandolfi camera with Ni-filtered Cu$K\alpha$ radiation. A fragment of huanzalaite was hand-picked under a binocular microscope from the thin section used for the chemical analysis. The data were recorded on an imaging plate (IP) and processed with a Fuji BAS–2500 bio-image analyzer using a computer program written by Nakamuta (1999). The X-ray powder-diffraction data were indexed by analogy with those of the monoclinic form of synthetic $MgWO_4$ (PDF# 27–0789) and a simulated pattern based on the single-crystal structure reported by Kravchenko (1969). The unit-cell parameters were refined from the diffraction data calibrated with quartz as an internal standard (reference material NIST SRM #1878a), using the computer program of Toraya (1993). The powder-diffraction data for huanzalaite are given in Table 2, along with those of the synthetic $MgWO_4$ and the simulated pattern based on the crystal structure of $MgWO_4$ (Kravchenko 1969), for comparison. Huanzalaite is monoclinic, space group $P2/c$. The unit-cell parameters were refined from the diffraction data as follows, a 4.7027(15), b 5.6894(11), c 4.9413(9) Å, β 90.70(2)°, V 132.20(5) Å^3, $Z = 2$. The unit cell of huanzalaite is smaller than those of hübnerite, ferberite, sanmartinite and their synthetic equivalents, whereas it is slightly larger than that of synthetic $MgWO_4$ (Table 3).

Discussion

Huanzalaite formed during the metasomatic emplacement of a copper orebody. The source of Mg needed to form huanzalaite in the ore, as well as sellaite, talc and tremolite, may be dolomite in the limestone, which is the host rock of the orebody (Imai *et al.* 1985).

Huanzalaite is a member of the wolframite group (Strunz & Nickel 2001, class 4.DB), and is the Mg-dominant analogue of hübnerite, $MnWO_4$, ferberite, $FeWO_4$, and sanmartinite, $ZnWO_4$. Barkov *et al.* (2008) reported a series of continuous solid-solutions between hübnerite and ferberite in their sample from Canadian Creek, Yukon (Fig. 3). Ferenc & Uher (2007) pointed out that the Mg content of ferberite and hübnerite is usually negligibly low. However, some Mg-rich compositions were reported for ferberite. A solid solution of 12 mol.% $MgWO_4$ in ferberite has been described (Barkov *et al.* 2008). Considerable replacement of Mg for Fe

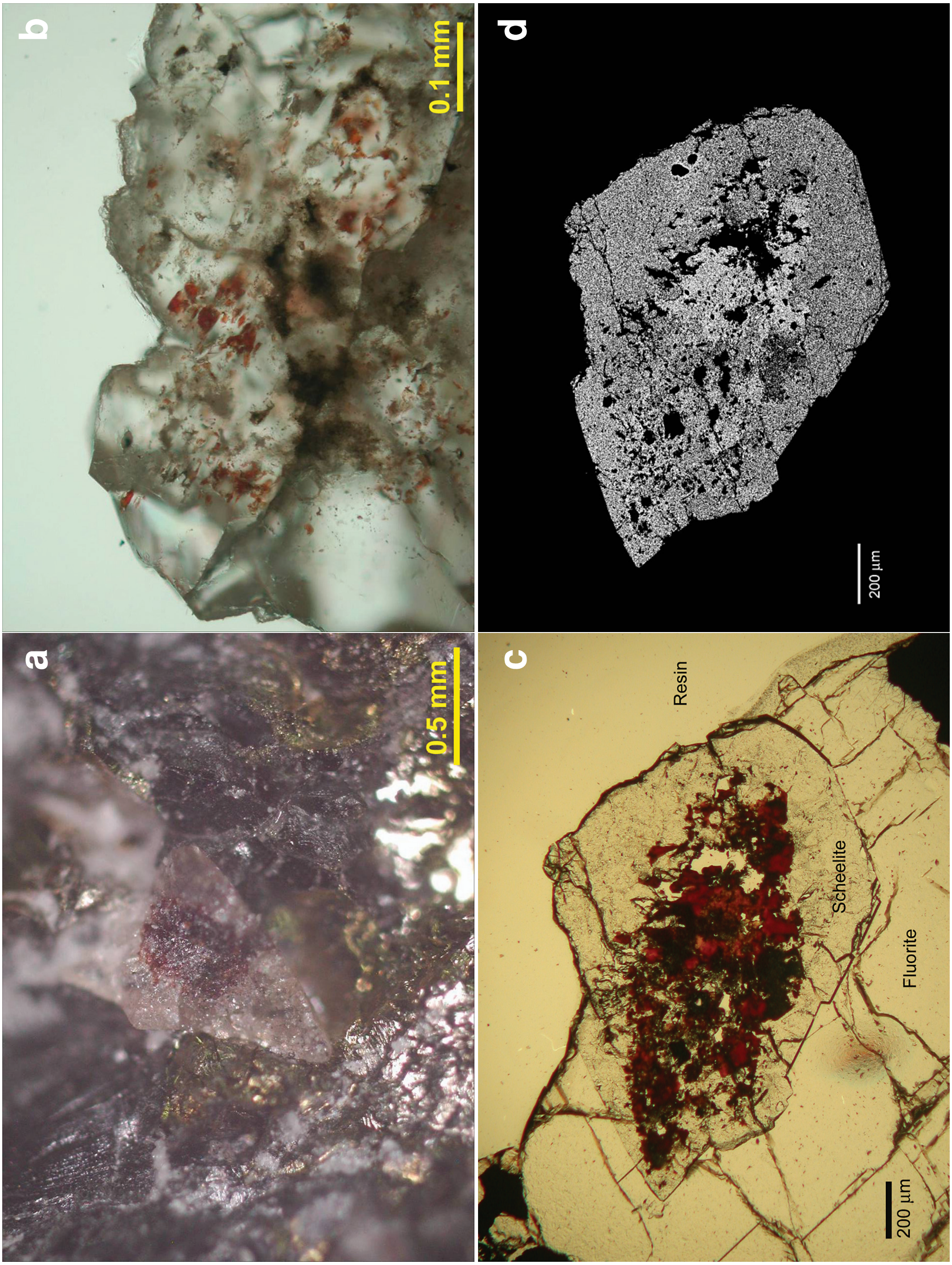

FIG. 2. Photomicrographs of huanzalaite. (a) The center of the figure shows a grain of the reddish huanzalaite embedded in colorless scheelite. (b) Reddish grain of huanzalaite embedded in scheelite in a thin section. (c) Reddish aggregates of the holotype of huanzalaite in a colorless crystal of scheelite. (d) Back-scattered electron image of the holotype of huanzalaite (pale gray) in scheelite (light gray). Fluorite, as well as resin and holes, are blacked out by adjusting the contrast.

and Mn in a wolframite-group mineral was reported by Ferenc & Uher (2007). Several of their electron-microprobe analyses show a Mg-dominant composition. The Mg-dominant member of wolframite-group minerals, which was tentatively named “magnesiowolframite”, can now be classified as huanzalaite. The variable Mg contents in wolframite-group minerals suggest a continuous solid-solution with an isomorphous substitution of Mg for Fe, Mn and Zn in the minerals.

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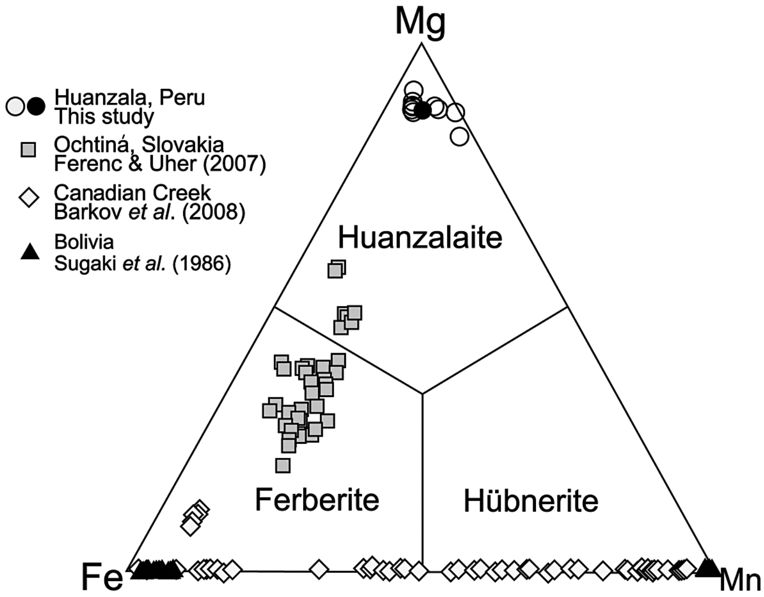

FIG. 3. Plot of compositions of huanzalaite, ferberite and hübnerite (atomic proportions). The open and solid circles indicate the compositions of huanzalaite at individual analytical spots on the type specimen and their mean value, respectively.

TABLE 3. CRYSTAL DATA FOR WOLFRAMITE-GROUP MINERALS AND THEIR SYNTHETIC EQUIVALENTS

	Huanzalaite [1]	Synthetic [2]	Ferberite [3]	Synthetic [4]	Hübnerite [5]	Synthetic [6]	Sanmartinite [7]	Synthetic [8]
Composition	$(Mg,Mn,Fe)WO_4$	$MgWO_4$	$(Fe,Mn)WO_4$	$FeWO_4$	$(Mn,Fe)WO_4$	MnWO	$(Zn,Fe)WO_4$	$ZnWO_4$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2/*c*	*P*2/*c*	*P*2/*c*	*P*2/*c*	*P*2/*c*	*P*2/*c*	*P*2/*c*	*P*2/*c*
a (Å)	4.7027(15)	4.696(2)	4.739(1)	4.730	4.83	4.8238(7)	4.712	4.72
b (Å)	5.6894(11)	5.683(2)	5.718(2)	5.703	5.77	5.7504(10)	5.738	5.70
c (Å)	4.9413(9)	4.945(3)	4.965(1)	4.952	4.98	4.9901(8)	4.958	4.95
β (°)	90.70(2)	90.83(5)	90.12(3)	90	90.88	91.18(1)	90.47	90.08
V ($Å^3$)	132.20(5)	131.96	134.54	133.58	138.77	138.39	134.05	133.17
Z	2	2	2	2	2	2	2	2

References: 1: Present study, 2: Macavei & Schulz (1993), 3: Sugaki *et al.* (1986), 4: Ülkü (1967), 5: Palache *et al.* (1951), 6: Weitzel (1976), 7: Angelelli & Gordon (1948), 8: Filipenko *et al.* (1968).

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