

ORDOÑEZITE FROM THE THEODOSO SOTO MINE, SAPIORIS, DURANGO, MEXICO: NEW DATA AND STRUCTURE REFINEMENT

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ABSTRACT

A new occurrence of the rare mineral species ordoñezite has been found at the Theodoso Soto tin mine, near Sapioris, Durango, Mexico. The average composition of the samples is $(\text{Zn}_{0.98}\text{Fe}_{0.02})_{\Sigma 1.00}\text{Sb}_{2.00}\text{O}_6$; the core of the crystals is slightly richer in Fe than the rim. The mineral is uniaxial (+), with all n greater than 2.30 (n_{calc} is 2.38 at 589 nm); D_{obs} 6.66 g/cm³, D_{calc} 6.67 g/cm³. It is isostructural with ferrotapiolite, with a 4.668(2), c 9.269(6) Å (from powder-diffraction data), space group $P4_2/mnm$, and is twinned on {103}. Its crystal structure, refined to $R = 4.1$, $wR = 4.3\%$ using 163 observed reflections, is fully cation-ordered.

Keywords: ordoñezite, ferrotapiolite group, crystal structure, new data, Theodoso Soto mine, Durango, Mexico.

SOMMAIRE

Nous décrivons les propriétés d'un nouvel exemple d'ordoñezite, espèce rarissime, à la mine d'étain Theodoso Soto, près de Sapioris, Durango, au Mexique. La composition moyenne des échantillons est $(\text{Zn}_{0.98}\text{Fe}_{0.02})_{\Sigma 1.00}\text{Sb}_{2.00}\text{O}_6$; le centre des cristaux est légèrement plus enrichi en fer que la bordure. Il s'agit d'un minéral uniaxe positif dont tous les indices de réfraction dépassent 2.30 (n_{calc} est 2.38 à 589 nm); D_{obs} 6.66 g/cm³, D_{calc} 6.67 g/cm³. L'ordoñezite possède la même structure que la ferrotapiolite, avec a 4.668(2), c 9.269(6) Å (par affinement des données de diffraction X sur poudre), groupe spatial $P4_2/mnm$; elle est maclée sur {103}. Sa structure cristalline, affinée jusqu'à $R = 4.1$, $wR = 4.3\%$ en utilisant 163 réflexions observées, montre que les cations sont complètement ordonnés.

(Traduit par la Rédaction)

Mots-clés: ordoñezite, groupe de la ferrotapiolite, structure cristalline, données nouvelles, mine Theodoso Soto, Durango, Mexique.

INTRODUCTION

Ordoñezite is an extremely rare mineral species. It was first encountered by Switzer & Foshag (1955) from the Santín mine, Guanajuato, Mexico. It is also apparently found at El Antimonio, Agua Prieta area, Sonora, Mexico (holdings of Peabody Museum, Yale University, no publication), and in man-made slags from anti-

mony deposits in the Little Carpathian Mountains along the Czech – Slovak border (Mederer & Wippermann 1994). The crystal structure of synthetic ordoñezite (ZnSb_2O_6) was determined by Byström *et al.* (1942), but has not been refined. The subject of the current study is a new occurrence of ordoñezite, from a hydrothermal tin deposit genetically similar to that at the type locality. Samples from the new occurrence are of sufficient

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quality to allow us to deal with some of the deficiencies in the type description.

The Theodoso Soto mine is located 0.5 km east of El Pinto and 4 km northeast of Saporis, Durango, Mexico. The mine is on an east-trending system of tin-bearing veins in the northeastern part of a large rhyolite flow-dome complex, in a halo of argillic alteration surrounding a large central core subjected to intense vapor-phase alteration. The vein system, in a zone 1–2 m wide, is composed of anastomosing veinlets and short vein segments containing lenses of cassiterite-hematite ore. Numerous joint and fracture surfaces in and adjacent to the vein system are lined with sparse to abundant tiny euhedral crystals of red cassiterite and locally of greenish brown to tan or brown ordoñezite attached to a joint or fracture face.

CHEMICAL COMPOSITION

Crystals of ordoñezite from Durango were analyzed with a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. The operating potential was 15 kV; a 25 nA beam current was used. The beam diameter was set at 20 μm as a safeguard against potential decay of the KSb_2PO_8 standard during electron bombardment. Data for standards were collected for 50 s or 0.25% precision per element, whichever was attained first; for samples, the pertinent numbers were 50 s or 0.5% precision. Willemite ($\text{ZnL}\alpha$), magnetite ($\text{FeK}\alpha$) and KSb_2PO_8 ($\text{SbL}\alpha$) were used as standards; no other element with $Z > 11$ was found in a 300-s energy-dispersion spectrum collected on the analyzed crystal. Data reduction was done with a conventional ZAF routine in the Tracor Northern TASK series of programs. The crystals contain 19.8% ZnO, 0.3% FeO, 80.5% Sb_2O_5 , total 100.6 wt.%, giving the formula $(\text{Zn}_{0.98}\text{Fe}_{0.02})_{\Sigma 1.00}\text{Sb}_{2.00}\text{O}_6$ on a basis of six atoms of oxygen. The crystals exhibit slight Fe–Zn zoning, from a Fe-rich core (0.7 wt.% FeO) to a Fe-depleted rim (0.25 wt.% FeO).

SELECTED OPTICAL AND PHYSICAL PROPERTIES

Ordoñezite is uniaxial positive. Its indices of refraction are above 2.30, as determined by use of S–Se melts. Reflectivities at the four standard wavelengths were determined using a Zeiss microscope with attached microphotometer (16 \times objective, 0.15 photometer field stop) and SiC as a standard. Results are: 470 (19.9, 18.6), 546 (16.8, 16.3), 589 (17.0, 16.5), and 650 nm (R_g 16.9%, R_p 16.3%). The calculated mean index of refraction at 589 nm is 2.38 [using $R = (n - 1)^2 / (n + 1)^2$]. The compatibility index [$1 - (K_p / K_C)$] is -0.017 , which is in the “superior” category of Mandarino (1981). The k value of 0.222 for Sb_2O_5 from Larsen (1921) was used instead of the extrapolated value of 0.153 given by Mandarino (1981). $D_{\text{obs.}}$ is 6.66 g/cm^3 as determined on a Berman microbalance, and $D_{\text{calc.}}$ is 6.67

g/cm^3 using the molecular weight and volume determined.

X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction data were collected using a Guinier–Hägg parafocusing camera with $\text{CuK}\alpha$ radiation. NBS SRM 640a silicon was used as an internal standard, and ordoñezite lines were corrected to a linear fit of the standard lines. The unit cell was refined on the basis of 30 diffraction lines, four of which were constrained. Extinction conditions commensurate with space group $P4_2/mmm$ were used. The refinement converged in seven cycles with a maximum observed standard error of $0.01^\circ 2\theta$. Intensities were measured from the film using a Siemens Type Z recording photometer. Indexed diffraction-maxima, observed intensities, and refined unit-cell data are given in Table 1.

STRUCTURE REFINEMENT

Ordoñezite has the tapiolite, or “trirutile” structure, a cation-ordered derivative of the rutile structure (Byström *et al.* 1942). As in the rutile structure, the tapiolite structure consists of a hexagonal closest-packing of oxygen atoms with cations occupying one-half of the octahedral interstices, producing straight chains of edge-sharing octahedra, linked to adjacent chains by corner-sharing. Unlike the rutile structure, cations in the tapiolite structure order at two distinct sites, resulting in the intra-chain ordering sequence $\dots -M^{2+} - M^{5+} - M^{5+} \dots$ along the Z axis, which triples the c cell edge. Although crystal-structure refinements exist for tantalum-dominant members of the tapiolite group (*e.g.*, Weitzel & Klein 1974), and for some synthetic analogues that have no natural equivalent (*e.g.*, Reimers *et al.* 1989), the structure of a natural antimony-dominant member of the group has never been refined; hence, we decided to refine the crystal structure of ordoñezite.

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

hkl	$d_{\text{obs.}}$ (Å)	$I_{\text{obs.}}$	$d_{\text{calc.}}$ (Å)	hkl	$d_{\text{obs.}}$ (Å)	$I_{\text{obs.}}$	$d_{\text{calc.}}$ (Å)
002*	4.631	26	4.635	301	1.534	< 1	1.534
101*	4.170	37	4.169	310	1.476	50	1.476
110*	3.303	93	3.301	312	1.407	26	1.406
112*	2.688	27	2.689	116	1.399	64	1.399
103	2.578	97	2.576	303	1.390	60	1.390
200	2.334	51	2.334	224	1.344	< 1	1.344
113	2.256	28	2.256	313	1.333	< 1	1.332
210	2.086	24	2.088	206	1.288	37	1.288
211	2.036	25	2.037	321	1.282	20	1.282
114	1.897	20	1.897	323	1.194	51	1.194
213	1.730	100	1.730	400	1.167	25	1.167
105	1.723	< 1	1.723	226	1.128	38	1.128
220	1.651	52	1.650	411	1.124	20	1.124
204	1.644	7	1.644	217	1.118	10	1.118
222	1.555	22	1.555	330	1.100	27	1.100
006	1.545	35	1.545	118	1.094	20	1.093

Data collection was done using a Nicolet *R3m* automated four-circle diffractometer according to the experimental method of Ercit *et al.* (1986). A hand-smoothed fragment with a mean diameter of 0.12 mm was used for the study. Twenty-five intense reflections were centered using graphite-monochromated MoK α radiation. Least-squares refinement of the setting angles gave the unit-cell parameters listed in Table 2 and the orientation matrix used for data collection. Intensity data were collected over four asymmetric units to a maximum $\sin \theta/\lambda$ of 0.7035. An empirical absorption-correction (ϕ -scan), and L - p and background corrections were made. At this stage, equivalent reflections were merged, resulting in 182 unique data and a merging R of 6.9%. Although high, this initial result was considered acceptable given the value of μ (194 cm $^{-1}$). However, for certain reflections, the standard deviations of their structure factors were unacceptably higher than the norm; large systematic errors associated with the absorption correction, or a polycrystalline sample, could explain these findings. Examination of the ϕ -scan dataset cast doubt on the first possibility; consequently, long-exposure precession photographs of the crystal were taken to investigate the second possibility. Precession photographs showed the crystal to be twinned on {103}, the most common twin found in members of the tapiolite group. Reflections from the volumetrically more significant member of the twin that were overlapped by reflections from the subordinate member were removed from the original unmerged dataset of intensities. The data were remerged ($R = 5.1\%$) to give the same number of unique data as mentioned above, owing to the multiple number of asymmetric units collected. Of these 182 unique data, 163 were considered observed [$I > 3\sigma(I)$].

The arrangement of atoms was refined to an R of 4.1% (wR 4.3%) using the program RFINE (Finger

1969). Final positional parameters are given in Table 3. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

Bond lengths and angles for ordoñezite are given in Table 4; the labeling of the anions follows Figure 1. Because of the low degree of polyhedron distortion in terms of M -O bond lengths, the mean bond-lengths compare well with predicted values from Shannon (1976): $\langle \text{Zn-O} \rangle_{\text{obs,calc}} = 2.07, 2.10 \text{ \AA}$; $\langle \text{Sb-O} \rangle_{\text{obs,calc}} = 1.98, 1.96 \text{ \AA}$. Bond lengths and angles for ordoñezite are similar to those for ferrotapiolite (Weitzel & Klein 1974) owing to the similarity in ionic radius between Zn versus Fe $^{2+}$ and Sb $^{3+}$ versus Ta. Similarly, bond lengths and angles for the SbO $_6$ polyhedron of ordoñezite compare well to those of the SbO $_6$ polyhedron for the room-temperature structure of CoSb $_2$ O $_6$ (powder neutron diffraction; Reimers *et al.* 1989), as one might expect for the most strongly bonded polyhedron of these isostructural compounds. However, note that the bond-valence sums for the ferrotapiolite structure determined by Weitzel & Klein (1974) deviate significantly from ideality, indicative of either (1) partial disorder of Fe $^{2+}$ and Ta $^{5+}$ over the two cation sites, or (2) oxidation of some of the iron to Fe $^{3+}$, and its subsequent disorder over the two cation sites.

Empirical bond-valences for ordoñezite, calculated from the curves of Brown (1981), are given in Table 5. The sums to the anion sites and the Sb site are within 2σ of their expected values of 2 and 5 valence units, respectively. The sum to the Zn site is 7% higher than expected; this amount is only marginally larger, however, than the root-mean-square error of 5% accorded to bond-valence calculations (Brown 1981). Clark & Fejer (1978) showed that some samples of ferrotapiolite

TABLE 2. SINGLE-CRYSTAL DATA FOR ORDOÑEZITE

a	4.6638(4) Å	Crystal size (mm)	0.12 x 0.12 x 0.13
c	9.263(1)	Rad / Mono	MoK α / graphite
V	201.48(4) Å 3	Total $ F_o , F_c > 3\sigma(I)$	182, 163
Space group	$P4_2/mnm$	Final R, wR (%)	4.1, 4.3
Composition	ZnSb $_2$ O $_6$	μ (cm $^{-1}$)	194
$R = \Sigma (F_o - F_c) / \Sigma F_c $		$wR = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}, w = 1$	

TABLE 3. POSITIONAL PARAMETERS FOR ORDOÑEZITE

Site	x	y	z	B_{eq} (Å 2)
Zn	0	0	0	0.59(6)
Sb	0	0	0.3322(1)	0.30(5)
O1	0.315(3)	0.315(3)	0	0.4(2)
O2	0.304(2)	0.304(2)	0.325(1)	0.5(2)

Anisotropic Displacement Parameters (Å 2)

Site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0059(11)	0.0059(11)	0.0020(3)	-0.0002(2)	0	0
Sb	0.0029(6)	0.0029(6)	0.0011(2)	-0.0001(6)	0	0

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR ORDOÑEZITE

ZnO $_6$ Polyhedron		SbO $_6$ Polyhedron	
Zn-O1a,b	2.08(2) x2	Sb-O1c,d	1.98(1) x2
-O2	2.07(1) x4	-O2e,d	1.95(1) x2
$\langle \text{Zn-O} \rangle$	2.07	-O2e,f	2.00(1) x2
		$\langle \text{Sb-O} \rangle$	1.98
O1a,b-O2a,b,c,d	2.94(2), 90.0(0) x8	O1c -O1d	2.44(4), 76.2(9)
O2a,c-O2b,d	2.59(2), 77.4(6) x2	O1c,d-O1e,f	2.85(1), 91.4(3) x4
O2a,b-O2c,d	3.24(2), 102.6(6) x2	-O2c,d	3.01(1), 100.2(5) x2
$\langle \text{O-O} \rangle$	2.93	O2e -O2d	2.59(2), 83.2(7)
$\langle \text{O-Zn-O} \rangle$	90.0	O2c,d-O2e,f	2.76(1), 88.6(2) x4
		$\langle \text{O-O} \rangle$	2.79
		$\langle \text{O-Sb-O} \rangle$	90.0

TABLE 5. EMPIRICAL BOND-VALENCES (v.u.) FOR ORDOÑEZITE

	Zn	Sb	Σ
O1	0.35 x2 ↓	0.81 x2	1.97
O2	0.36 x4 ↓	0.76, 0.89 x2 ↓	2.01
Σ	2.14	4.92	

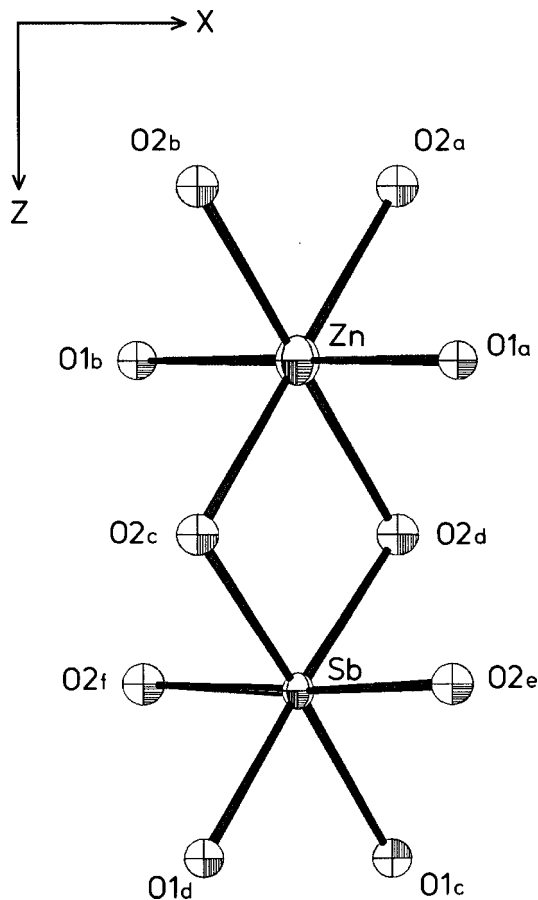


FIG. 1. An asymmetric unit of coordination polyhedra in ordoñezite. Atom labels are as in Table 4.

contain incomplete order of cations. The possibility that the slight deviation in the bond-valence sum to the Zn site might be due to disorder was tested; however, the occupancies of the cation sites refined to values indicative of full order.

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