

# Jeanbandyite

## a new member of the stottite group from Llallagua, Bolivia

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### INTRODUCTION

In 1977 the extensive mineral collection assembled by Dr. Mark Chance Bandy (Jones, 1973; Bandy, 1978) was donated to the Natural History Museum of Los Angeles County by his widow, Jean. The collection includes many fine specimens from worldwide sources, but it is most noteworthy for its remarkable representation of Bolivian minerals.

Between 1936 and 1944, Dr. Bandy was employed by the Patino Company at Huanuni and Llallagua, Bolivia. During this period, he wrote *Mineralogy of Llallagua* for the Patino Company, published in 1944 and reprinted by the Tucson Gem and Mineral Society in 1976 (now available through the LACMNH). His instincts as a mineralogist and mineral collector led him to preserve many specimens of mineralogical interest. Among these were the beautiful colorless, transparent apatite crystals from Llallagua in which he took special delight. It is on these specimens that the new mineral described herein is found. One such specimen bears the label "what-zit," a term which Bandy coined to designate minerals which he could not identify and which he felt required further study.

In light of its occurrence on Mark Bandy's "favorite" specimens, it seems particularly appropriate to name the new mineral, jeanbandyite, in honor of Mrs. Jean Bandy of Wickenburg, Arizona, a charming and gracious lady who was Mark's wife, companion and confidant for 34 years. She joined him in his worldwide travels and was clearly a source of great comfort to him. After Mark's death in 1963, Jean carefully preserved their collection until her decision to donate it to the Los Angeles County Museum in 1977. (Ed. note: *Bandyite*, a hydrated borate-chloride of copper from Chile, was named for Mark C. Bandy in 1938 by Palache and Foshag.)

The name and description have been approved by the Commission on New Minerals and Mineral Names, I.M.A. Type specimens have been deposited at the Smithsonian Institution (NMNH 149348), Harvard Mineralogical Museum (HMM 119125) and the Los Angeles County Museum of Natural History (LACMNH 18309).

### OCCURRENCE

Jeanbandyite has been identified on about three dozen specimens from Llallagua, Bolivia, in the Los Angeles County Museum's "Bandy Collection." On most of these specimens the most prominent mineral is fluorapatite as colorless, tabular to blocky crystals to 5 cm. The matrix is massive stannite, with well-formed crystals to 2 mm lining pockets. Other pocket minerals include pyrite, jamezonite, cassiterite, quartz and crandallite. These specimens were collected from large vugs on and above level 295 of the Contacto vein (Bandy, 1944). Jeanbandyite has been confirmed on similar apatite specimens from Llallagua, Bolivia, in other collections. Most such specimens were probably originally collected by Bandy and others from this same area in the mine.

A few specimens from elsewhere in the mine have also yielded jeanbandyite. On level 250 of the Contacto vein and level 295 of the Contacto-Dolores vein it occurs with fluorapatite, stannite and cassiterite. Twelve meters above level 411 of the Bismark vein it occurs with wolframite, bismuthinite, stannite and pyrite. Twenty meters above level 160 of the Plata vein it occurs with franckeite, stannite and pyrite.

In every case jeanbandyite appears as a late phase in pockets, either growing on or in close proximity to stannite.

### MORPHOLOGY

Jeanbandyite occurs in crudely pseudo-octahedral aggregates generally not exceeding 0.2 mm in maximum dimension. Close examination shows these aggregates to consist of pyramidal tetragonal (pseudo-cuboctahedral) crystals of jeanbandyite in epitactic growth upon the vertices of octahedral crystals of wickmanite with which it is isotypic.

In most cases, jeanbandyite crystals were observed to completely envelope their wickmanite hosts, giving the appearance of crystals twinned about [111] (Fig. 1). The epitactic relationship is clearly indicated, however, by clusters in which the wickmanite is still visible and the individual jeanbandyite crystals are seen perched upon its vertices (Fig. 2).

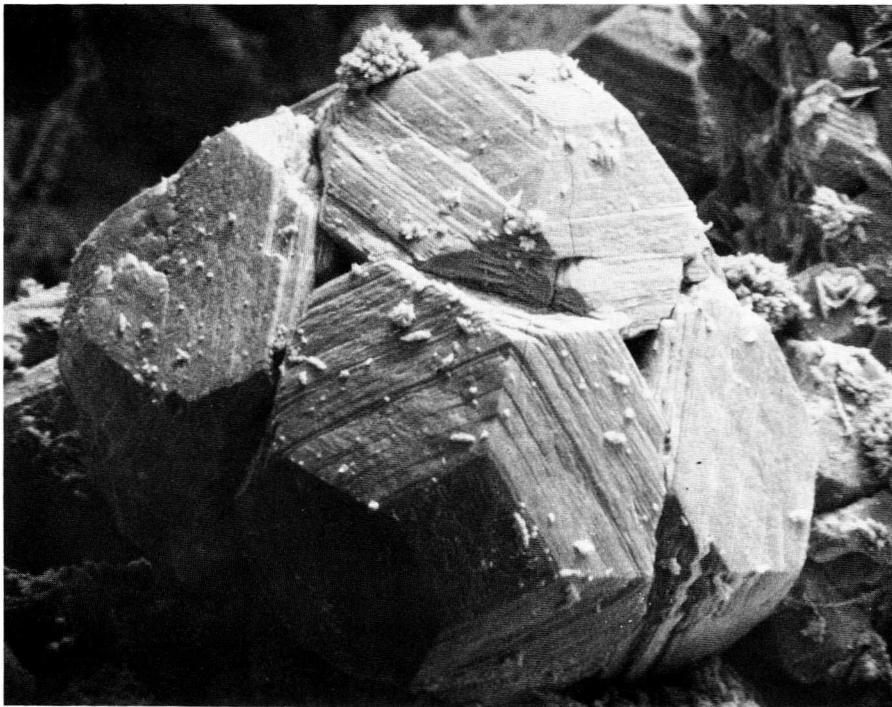
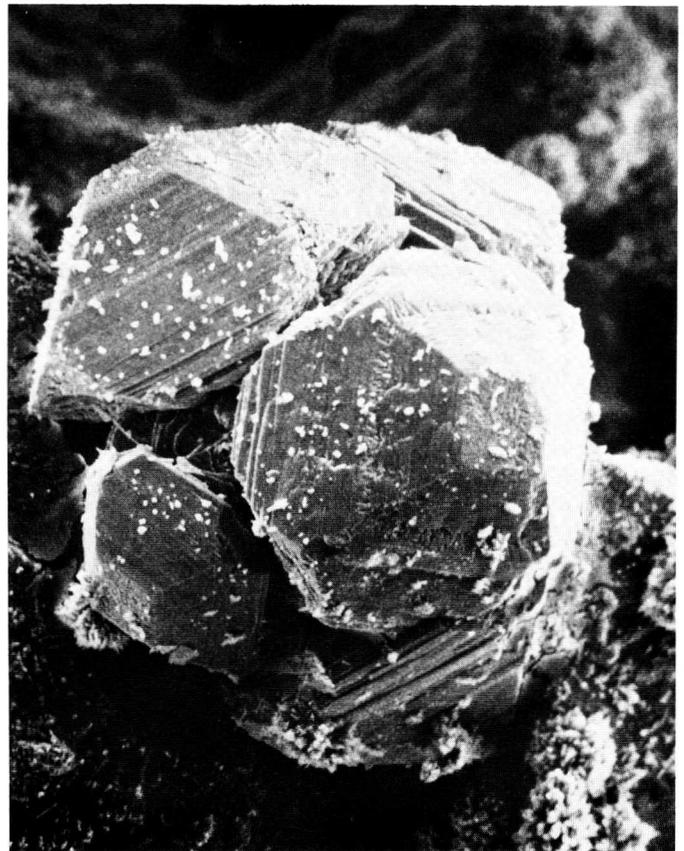


Figure 1. Typical pseudo-octahedral aggregate of jeanbandyite crystals (SEM photomicrograph at 350x).

Figure 2. Unequally developed jeanbandyite crystals with underlying wickmanite octahedron partially visible (SEM photomicrograph at 350x).



The optical orientation of the jeanbandyite crystals in the clusters (Fig. 3) indicates that their *c*-axes radiate from the centers of the clusters. Optical examination gave no indication of twinning in the individual crystals.

The only forms observed on jeanbandyite crystals are the pyramid {111}, pinacoid {001} and prism {100}. The pinacoid and especially the prism faces generally appear rough. The pyramid faces are invariably striated parallel to [100], notably consistent with tetragonal rather than cubic symmetry.

#### PHYSICAL PROPERTIES

Jeanbandyite is brown-orange in color with a pale brown-yellow (buff) streak. Its luster is vitreous to subadamantine. The estimated Mohs' hardness is 3½. Fair cleavage was detected parallel to the pinacoid {001} and prism {100} faces. The mineral is slowly soluble in cold 1:1 HCl.

Individual jeanbandyite fragments were carefully split from their wickmanite hosts for specific gravity determination by sink-float in Clerici solution. This method yielded a specific gravity of 3.81(5).

#### OPTICAL PROPERTIES

Jeanbandyite is light orange-brown in transmitted light and exhibits no discernible pleochroism. It is optically uniaxial negative, but yields an indistinct optic-axis interference figure. Indices of refraction for all measured crystals from Llallagua fell in the range

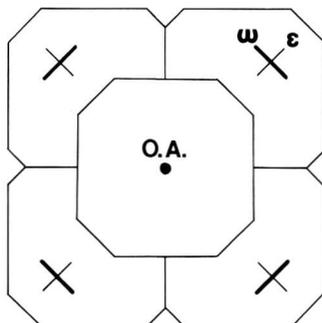


Figure 3. Diagram showing the optical orientation of jeanbandyite crystals in the clusters.

1.82–1.85. All exhibited a very low birefringence of approximately 0.004. A representative sample, from level 295 of the Contacto vein, yielded  $\epsilon = 1.833(5)$  and  $\omega = 1.837(5)$ . No regular variation in index of refraction with chemistry was noted. Within crystals, indices of refraction remained constant or increased slightly toward the crystal peripheries.

The host wickmanite crystals are very pale yellow in transmitted light. They are isotropic and possess an index of refraction of 1.69–1.70.

Mandarino (1979) described the use of the Gladstone-Dale relationship to measure the compatibility of the index of refraction,

density (specific gravity) and chemical composition by comparing the specific refractive energy calculated from the mean refractive index and density ( $K_p$ ) with that calculated from the chemical composition ( $K_c$ ). The quantity  $1 - (K_p/K_c)$  calculated for jeanbandyite (mean refractive index = 1.835) is 0.035 which falls in the range defined by Mandarino as indicating excellent compatibility.

### X-RAY CRYSTALLOGRAPHY

The X-ray powder diffraction pattern of jeanbandyite is entirely consistent with cubic symmetry. No splittings of lines typical of pseudocubic tetragonal symmetry were detected. Nevertheless, the evidence for tetragonal symmetry provided by morphology and optics is regarded as conclusive, and jeanbandyite must be considered pseudocubic. The powder diffraction data are listed in Table 1. Least squared refinement yielded  $a = c = 7.648(7) \text{ \AA}$ .

Table 1. X-ray powder diffraction data for jeanbandyite.

$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{cal}}$	hkl	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{cal}}$	hkl
20	4.41	4.42	111	<<5	1.471	1.47	511
100	3.83	3.82	200	5	1.352	1.352	440
70	2.71	2.70	220	<<5	1.292	1.293	531
5	2.422	2.419	310	15	1.275	1.275	600
10	2.308	2.306	311	10	1.210	1.209	620
15	2.205	2.208	222	10	1.154	1.153	622
<<5	2.039	2.044	321	<<5	1.060	1.061	640
20	1.912	1.912	400	15	1.021	1.022	642
5	1.752	1.755	331	<<5	0.9948	0.9957	553
60	1.710	1.710	420	15	0.9276	0.9275	644
35	1.562	1.561	422	15	0.9016	0.9013	660

114.6 mm Gandolfi camera,  $\text{CuK}\alpha$  radiation, visually estimated intensities.

No significant difference in cell constants was detected on single-crystal precession photographs. Systematic extinctions were consistent with the cubic space groups,  $Pn\bar{3}$  and  $Pn\bar{3}m$ , and the tetragonal space group,  $P4_2/n$ . The latter, naturally, was chosen.

In the light of the chemical data given below, unit-cell size and space group, jeanbandyite should be regarded as a tetragonal member of the stottite group.

If care is not exercised in the preparation of the jeanbandyite powder mount, contamination by the wickmanite core is likely, resulting in additional powder lines corresponding to wickmanite. The wickmanite pattern is generally much weaker and yields an approximate  $a$  cell constant of  $7.81 \text{ \AA}$ .

### CHEMISTRY

Jeanbandyite and wickmanite from the Contacto vein were analyzed by electron microprobe. Analyses of eight points over six jeanbandyite crystals and five points over four wickmanite crystals gave the averages and ranges listed in Table 2. Microchemical tests utilizing potassium ferrocyanide and potassium ferricyanide indicate virtually all iron in jeanbandyite to be in the ferric state. It is, therefore, calculated as  $\text{Fe}_2\text{O}_3$  in the jeanbandyite analyses. Water was calculated by difference.

Chemistry was observed to change abruptly at jeanbandyite-wickmanite interfaces. No regions of intermediate Fe-Mn content were found. Within individual crystals variations of as much as a few percent in  $\text{Fe}_2\text{O}_3$  and MnO were found, but no consistent spacial trends were noted. Variations in chemistry from crystal to crystal were no greater than variations within crystals. Qualitative analyses by energy dispersive X-ray were conducted on samples from elsewhere in the mine, but no significant differences in chemistry were indicated.

Based upon 6 OH, the empirical formulas of jeanbandyite and wickmanite can be expressed as  $(\text{Fe}_{0.71}^{+3}\text{Mn}_{0.21}^{+2}\text{Mg}_{0.04}^{+2})(\text{Sn}_{0.84}^{+4}\text{Si}_{0.03}^{+4})(\text{OH})_6$  and  $(\text{Mn}_{0.68}^{+2}\text{Mg}_{0.24}^{+2}\text{Fe}_{0.08}^{+2})(\text{Sn}_{0.96}^{+4}\text{Si}_{0.04}^{+4})(\text{OH})_6$ , respectively. The formula for jeanbandyite has a positive charge excess of 0.11 suggesting that a small portion of the iron may be ferrous. All iron in wickmanite is considered ferrous for charge balance.

The above formula for jeanbandyite requiring cation vacancies is preferred to one in which the charge balance would be maintained by substitution of  $\text{O}^{2-}$  for OH (i.e.,  $(\text{Fe}_{0.77}^{+3}\text{Mn}_{0.23}^{+2})(\text{Sn}_{0.92}^{+4}\text{Mg}_{0.04}^{+2}\text{Si}_{0.04}^{+4})(\text{OH}_{5.32}\text{O}_{0.68})$ ) because it is much more compatible with the amount of  $\text{H}_2\text{O}$  calculated by difference and because it provides a calculated density of  $3.81 \text{ gcm}^{-3}$ , in exact agreement with the measured specific gravity. The formula based upon  $\text{O}^{2-}$  substitution provides a calculated density of  $3.98 \text{ gcm}^{-3}$ . The ideal formula for jeanbandyite, therefore, takes the somewhat unusual form:  $\text{Fe}_{1-x}^{+3}\text{Sn}_{1-y}^{+4}(\text{OH})_6$  or  $(\text{Fe}_{1-x}^{+3}\square_x)(\text{Sn}_{1-y}^{+4}\square_y)(\text{OH})_6$ , where  $3x + 4y = 1$  and  $\square$  designates a vacancy.

Si was detected in small but significant amounts in all jeanbandyite and wickmanite samples tested. It has been tentatively assigned to the octahedral  $\text{Sn}^{+4}$  site, as was done by White and Nelen in tetrawickmanite.  $\text{Si}^{+4}$  in octahedral coordination is recognized as highly unusual and the amounts determined may in fact be due to sub-micron impurities. If the latter is the case, the conclusions drawn here would not be appreciably affected. (The calculated density would be less than one percent smaller.)

### RELATED MINERALS

White and Nelen (1973) provided a survey of natural and synthetic members of the stottite group and included data on a mineral from Llallagua which probably corresponds to jeanbandyite. The "tiny brownish orange crude spherules (up to 0.1 mm)" gave powder data identical to that reported here and led them to the assumption that the mineral was cubic. Inexplicably, their "rough" microprobe analysis (converted to oxides),  $\text{SnO}_2$  41.3,  $\text{Fe}_2\text{O}_3$  29.2, MnO 1.8, CaO 14.1, MgO 0.8, differs significantly from that reported here. They did not report optics, but likened the material to unidentified crystals reported by Gordon (1944) from Llallagua.

Gordon described clusters with isotropic octahedral cores, slightly greenish-brown under the petrographic microscope and with an index of refraction of 1.745. Upon each of the octahedral edges, he observed epitactic overgrowths of anisotropic prismatic crystals with about the same index of refraction. The octahedral cores correspond most closely to natanite (see below). However, the overgrowths remain a mystery. They clearly differ from jeanbandyite in both morphology and refractive index.

Marshukova, Pavlovskiy and Sidorenko (1969) described cubic  $\text{FeSn}(\text{OH})_6$  from tin deposits in Middle Asia (Tian-Shan). This mineral has recently been approved by the Commission on New Minerals and Mineral Names under the name of natanite (Marshukova, Parlovskiy, Sidorenko and Chistjakova, 1980). It yields

Table 2. Microprobe analyses of jeanbandyite and wickmanite.\*

	JEANBANDYITE <sup>1</sup>	WICKMANITE <sup>2</sup>
MgO	0.61 ( 0.24– 1.27)	3.91 ( 3.68– 4.26)
$\text{SiO}_2$	0.79 ( 0.55– 0.94)	0.96 ( 0.74– 1.12)
MnO	5.82 ( 4.04– 7.54)	19.02 (18.29–20.20)
$\text{Fe}_2\text{O}_3$ <sup>3</sup>	22.07 (19.22–24.71)	2.35 ( 1.78– 3.25)
$\text{SnO}_2$	49.61 (48.30–51.59)	53.50 (52.85–54.35)
$\text{H}_2\text{O}$ <sup>4</sup>	21.10 (18.14–22.44)	20.26 (19.19–21.15)

<sup>1</sup> Average and range of eight analyses.

<sup>2</sup> Average and range of five analyses.

<sup>3</sup> Calculated as FeO for wickmanite.

<sup>4</sup> By difference.

\*in weight percent

powder data nearly identical to jeanbandyite except  $a = 7.69 \text{ \AA}$ . Its color is greenish-brown, nearly colorless in thin-section, and it is isotropic with  $n = 1.755$ . The results of microprobe analyses were consistent with all iron being ferrous. The cell constant reported by Strunz and Contag (1960) for synthetic cubic  $\text{FeSn}(\text{OH})_6$  is  $7.79 \text{ \AA}$ . The smaller cell determined for natanite is probably due to significant substitution of  $\text{Cu}^{+2}$  and  $\text{Zn}^{+2}$  for  $\text{Fe}^{+2}$ .

Natural  $\text{FeSn}(\text{OH})_6$  has also been reported to occur at Tsumeb, Namibia, by Geier and Ottemann (1970) and at a Malayan tin deposit by Grubb and Hannaford (1966). However, data reported in both works is sketchy and does not state whether the minerals are cubic or tetragonal or whether the iron is ferrous or ferric.

A single micromount specimen from Santa Eulalia, Chihuahua, Mexico, submitted by Richard Thomssen of Carson City, Nevada, exhibits red-brown octahedral crystals to 0.5 mm in association with pyrrhotite, quartz and siderite. Qualitative analysis by energy dispersive X-ray methods showed substantial tin and iron and minor manganese. The powder pattern suggested tetragonal symmetry; however, precession photographs indicated cubic symmetry. Observation of fragments in grain mounts under the polarizing microscope explained this ambiguity. Crystals were seen to consist of a nearly colorless, isotropic octahedron with  $n = 1.728$  covered by an approximately 0.01 mm thick brownish-orange, weakly anisotropic coating with  $n = 1.845$ .

The powder pattern is, therefore, interpreted as a composite of two patterns, one cubic and one pseudocubic. The lower angle pattern is considerably more intense and clearly is produced by the central octahedron. It yields a cell constant  $a = 7.79 \text{ \AA}$ . The weaker pattern produced by the coating yields  $a = 7.64 \text{ \AA}$ . The observations above indicate that the crystals from Santa Eulalia are natanite coated by jeanbandyite.

Wickmanite has been reported previously from four localities: Långban, Sweden (Moore and Smith, 1967), Tvedalen, Norway (Åmli and Griffin, 1972), Pitkäranta, Karelia, USSR (Nefedov, Griffin and Kristiansen, 1977), and El Hamman, Central Morocco (Sonnet, 1981). Complete chemical and crystallographic data have been published for all but the El Hamman wickmanite. Llallagua wickmanite contains somewhat more MgO than Pitkäranta wickmanite (3.91 vs. 2.4 percent) and much more than Långban (0.5 percent) or Tvedalen (not detected) wickmanite. Of the four (excluding El Hamman) only Llallagua wickmanite has been found to contain  $\text{SiO}_2$  (0.96 percent). The cell constant  $a$  of Llallagua wickmanite ( $7.81 \text{ \AA}$ ) is significantly smaller than those of the other reported wickmanites and also smaller than that predicted by Nefedov, *et al.*, for a wickmanite with its Mn-Mg-Fe content ( $7.85 \text{ \AA}$ ). This may be due, at least in part, to  $\text{Si}^{+4}$  substituting for  $\text{Sn}^{+4}$ .

## DISCUSSION

A discrepancy between cell geometry and optics similar to that observed in jeanbandyite has been noted by Sonnet (1981) in the newly described stottite group mineral burtite,  $\text{CaSn}(\text{OH})_6$ . X-ray single crystal study showed no deviation from cubic symmetry, while optics and morphology indicated trigonal symmetry. Sonnet attributed the optics to a simple trigonal distortion of the cubic cell and suggested that the apparent cubic symmetry observed in the X-ray study might be due to twinning. The same explanation does not seem applicable to the cubic-tetragonal inconsistency in jeanbandyite since twinning has not been detected in individual jeanbandyite crystals.

It is tempting to try to correlate the discrepancy between cell geometry and optics (and morphology) in jeanbandyite with the presence of ferric iron since both characteristics set this mineral apart from natanite as well as from the rest of the stottite group. The key to such a correlation may be the inferred presence of cation vacancies.

The vacancies could have resulted from growth under oxidizing conditions from solutions particularly rich in  $\text{Fe}^{+3}$  and  $\text{Sn}^{+4}$ . The initiation of growth upon the surfaces of wickmanite or natanite crystals could have induced tetragonal ordering of the vacancies and in so doing stabilized the jeanbandyite structure. Tetragonal ordering of vacancies could produce tetragonal optics and morphology without yielding a significant deviation from cubic cell geometry.

A detailed crystal structure analysis of jeanbandyite will be necessary to prove the existence of cation vacancies and to determine whether ordering is present. Previous structure studies on stottite (tetragonal) by Strunz and Giglio (1961) and on various synthetic cubic stottite group compounds by Strunz and Contag (1960) and Cohen-Addad (1968) utilized only powder data and are consequently in need of modern refinements before they will be useful in helping to decipher the jeanbandyite problem.

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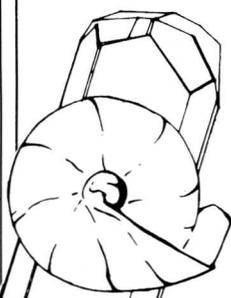
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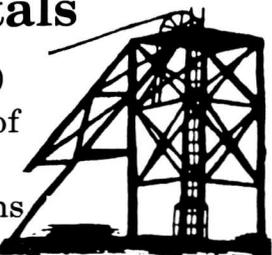
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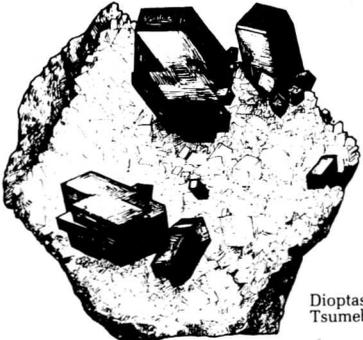
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