

# The composition and structure of jeanbandyite and natanite

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## ABSTRACT

The rare iron-tin hydroxide minerals natanite and jeanbandyite occur as small pseudo-octahedral crystals in high-temperature Sn-Cu-As veins at Penberthy Croft Mine and Hingston Downs Quarry, Cornwall. The lattice parameters for jeanbandyite and natanite are reported and compared to previously calculated values. The chemical composition of jeanbandyite is discussed and a significant proportion of divalent Fe and Mn is shown to be present.

**KEYWORDS:** Cornwall, jeanbandyite, natanite.

JEANBANDYITE and natanite are closely related iron-tin hydroxide minerals which typically crystallise at a late stage in high-temperature hydrothermal Sn-W-As veins. The chemical formula of jeanbandyite is idealised as  $(\text{Fe}_{1-x}^{3+}\square_x)(\text{Sn}_{1-y}^{4+}\square_y)(\text{OH})_6$  with  $3x + 4y = 1$  and  $\square$  indicating a vacancy (Kampf, 1982). Natanite is chemically similar, the ideal formula being  $\text{Fe}^{2+}\text{Sn}^{4+}(\text{OH})_6$  (Marshukova *et al.*, 1981).

The type locality for jeanbandyite is at Llallagua, Bolivia, and the only other confirmed records are from Santa Eulalia, Chihuahua, Mexico (Kampf, 1982) and the Mount Pleasant mine, New Brunswick, Canada (R. Bideaux, *pers. comm.*). The type locality for natanite is the Trudov (and Mushiston) tin deposit in Tadzhikistan, Central Asia; it also occurs in the Chat-Karagai tin ores (Marshukova *et al.*, 1981), and with jeanbandyite at Santa Eulalia, Chihuahua, Mexico (Kampf, 1982). Natural  $\text{FeSn}(\text{OH})_6$  occurs at Tsumeb, Namibia (Geier and Otteman, 1970), and at a tin deposit in Malaya (Grubb and Hannaford, 1966), but it is not

clear whether this is jeanbandyite, natanite or an intergrowth of the two.

## Experimental

A combination of techniques is required to identify jeanbandyite and natanite. Their structural similarities to other members of the stottite and schoenfliesite groups means that identifications based solely on X-ray powder diffraction data must be treated with caution. Chemically, they differ very slightly in their stoichiometry and in the oxidation state of the iron which is largely present as  $\text{Fe}^{3+}$  in jeanbandyite as compared to  $\text{Fe}^{2+}$  in natanite.

Specimens from Penberthy Croft Mine were identified at the Natural History Museum (London) using a combination of X-ray diffractometry and electron probe microanalysis. The X-ray diffraction pattern was recorded, using a 114.6 mm diameter Debye-Scherrer camera and  $\text{Cu-K}\alpha$  radiation. Chemical analyses were performed on a resin-embedded polished crystal fragment using a

Cameca SX50 wavelength-dispersive microprobe operating at 15 kV and 20 nA. Since the morphology of jeanbandyite and natanite are useful indicators of their identity, two groups of crystals were examined in an ISI ABT55 SEM with an environmental chamber, allowing imaging of uncoated specimens at low pressure.

Specimens from Hingston Downs Quarry were identified at Manchester University using a combination of polarized light microscopy, X-ray diffractometry, electron probe microanalysis, and wet chemistry. Crystal grains were mounted in epoxy resin on a probe slide, and a polished grain mount 100  $\mu\text{m}$  thick produced. The mounted grains were examined by polarized light microscopy to determine their optical properties (since jeanbandyite is tetragonal while natanite is cubic). Quantitative analyses were subsequently performed using a Cameca Camebax electron probe microanalyser operating at 15 kV, 20 nA and fitted with a Link A10/85s X-ray analyser using SPECTRA ED/WD automation software. A Link ZAF4 correction model was applied to the raw data and the compositions calculated as wt.% oxides. Details of the calibration standards used are given in Table 1. The oxidation state of iron in the crystals was determined using microchemical tests. Crystal fragments for powder diffractometry were finely ground and applied in a solvent suspension onto a glass slide; evaporation of the solvent left a thin uniform film of powder on the slide surface. The slide was mounted in a Philips diffractometer and the powder diffraction pattern recorded at  $0.02^\circ$

TABLE 1. Quantitative chemical data for jeanbandyite from Hingston Downs Quarry. The data are based on nine analyses on three separate crystal fragments. Water was calculated by difference. Standards used were: Mg, periclase; Si, wollastonite; Mn, tephroite; Fe, fayalite; Sn tin metal

Oxide	Weight %	(Range)
MgO	0.52	(0.36–0.84)
SiO <sub>2</sub>	1.12	(0.81–1.32)
MnO	3.83	(3.27–4.48)
FeO	19.46	(18.68–20.34)
SnO <sub>2</sub>	52.59	(51.88–53.66)
H <sub>2</sub> O	22.48	(20.72–23.55)
Total	100.0	

intervals in  $2\theta$ . Silicon was used as an internal standard to check the accuracy of the diffractometer where lattice constants were being determined.

## Occurrence

Jeanbandyite and natanite occur at two localities in Cornwall: Penberthy Croft Mine, St Hilary, and Hingston Downs Quarry, Calstock. These are the first reports of the minerals from the British Isles.

### Penberthy Croft Mine

Penberthy Croft Mine [national grid reference SW 555 324] produced copper, tin and lead from a series of east-west lodes emplaced in Devonian metasediments consisting of low-grade greenschist-facies slates known locally as killas. The orebodies exploited by the mine are now inaccessible. However, examination of dump material suggests they contained a number of distinct mineral assemblages including early high-temperature hydrothermal Sn-As-W-Cu veins, later lower-temperature mesothermal to epithermal Pb-Zn mineralisation, and late-stage low-temperature Fe-Mn mineralisation. Supergene oxidation has produced a wide variety of secondary minerals which (in order of approximate abundance) include arsenates, sulphates, arsenate-sulphates and phosphates (e.g. Camm and Merry, 1991).

At Penberthy Croft Mine, jeanbandyite occurs in intimate intergrowth with natanite in lustrous, yellow, transparent to translucent, pseudo-octahedral crystals up to 0.4 mm across. The best developed crystal form is always the pyramid {111} whereas the prism {100} and pinacoid {001} are usually present although minute (Fig. 1). The crystals occur in high-temperature veins containing major quartz and arsenopyrite, minor sphalerite and a chlorite-group mineral and rare galena. Very few specimens were collected despite a thorough search of the mine dumps and it is clear that they are very rare.

### Hingston Downs Quarry

Hingston Downs Quarry [national grid reference SX 409 719] is situated on the Cornish side of the Tamar river valley above the village of Gunnislake. It produces roadstone from an isolated microgranite boss between Dartmoor and Bodmin Moor.

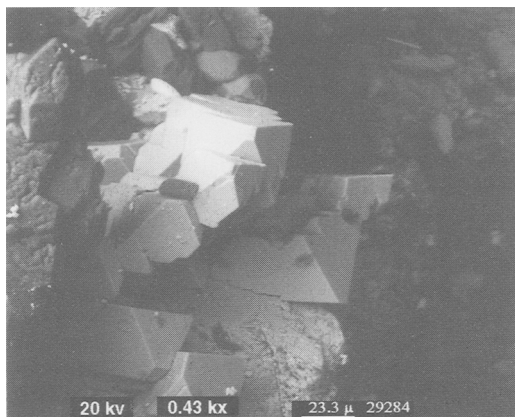


FIG. 1. SEM photo of mixed jeanbandyite-natanite crystals from Penberthy Croft Mine.

Specimens were collected from two nearby areas on an east-west striking vein exposed in the southern face of the quarry in 1994. The first area contained lustrous pseudo-octahedral crystals of jeanbandyite to 1.2 mm. At a second nearby locality, opaque yellow-brown octahedral crystals to 2 mm which proved to be jeanbandyite-natanite intergrowths were relatively common. The major primary minerals present at both points in the vein were quartz, arsenopyrite, ferrokesterite and chalcopyrite with cassiterite as 'sparable tin' as a minor late-stage primary phase.

Jeanbandyite crystallised later than cassiterite in the vein paragenesis, and it is therefore later than all of the major primary minerals. As at Penberthy Croft Mine, its relationship to the minor secondary mineralisation developed in the vein could not be determined, although the presence of a few crystals embedded in arsenopyrite suggests a very late-stage primary origin, from residual tin-rich hydrothermal fluids.

## Discussion

At Llallagua, jeanbandyite occurs as a late-stage primary phase in cavities in high-temperature Sn-W-Cu bearing hydrothermal veins where it forms striated, orange-brown, crudely pseudo-octahedral crystals usually less than 0.2 mm in size. It occurs at Santa Eulalia as an orange-brown overgrowth on natanite crystals up to 0.5 mm. In both cases there is substantial substitution of  $Mn^{2+}$  for iron (Kampf, 1982). Natanite occurs as small greenish-brown crystals in the Sn-bearing veins of the

Trudov and Mushiston deposits where it forms as an alteration product of stannite, and at Chat-Karagai as an alteration product of hocartite.

The high-temperature Sn-Cu-As-bearing assemblages at Penberthy Croft Mine and Hingston Downs Quarry closely resemble those at the previously reported localities for jeanbandyite and natanite. In common with these localities, crystallisation is late in the paragenetic sequence, following the major primary phases. It has not been possible to determine with certainty whether the minerals are late-stage primary or supergene in origin, and although the balance of evidence suggests the former (see also Marshukova *et al.*, 1981, who suggest natanite from central Asia is a late-stage primary phase), we cannot rule out a supergene origin for the Cornish specimens.

Jeanbandyite is assigned to the tetragonal system on the basis of morphology and optics, although X-ray diffraction shows no detectable difference in the *a* and *c* lattice parameters ( $a = c = 7.648 \text{ \AA}$ ) (Kampf, 1982). Natanite is cubic with  $a = 7.83 \text{ \AA}$  in synthetic material and with a range of lower values determined on natural material (e.g.  $a = 7.79 \text{ \AA}$  (Kampf, 1982);  $a = 7.69 \text{ \AA}$  (Roberts *et al.*, 1990);  $a = 7.64 \text{ \AA}$  the lower value quoted on JCPDS: PDF 31-653).

A least squares fit to the X-ray data (based on the six most intense diffraction peaks and using silicon as an internal standard) gives a value for the lattice parameter for jeanbandyite from Hingston Downs Quarry of  $a = c = 7.649(5) \text{ \AA}$ . This is almost identical to the value of  $7.648 \text{ \AA}$  determined on the type material. There is no detectable broadening of the diffraction lines which might indicate slightly differing values of *a* and *c*. The natanite diffraction pattern, gives a lattice parameter of  $a = 7.722(8) \text{ \AA}$  which falls near the centre of the range of values determined for natanite which vary between  $7.83 \text{ \AA}$  in artificial material and  $7.64 \text{ \AA}$  in some natural material.

Three jeanbandyite crystals (not intergrown with natanite) from Hingston Downs Quarry were analysed by electron probe with the results given in Table 1.

In the original analyses, Kampf (1982) arrived at an empirical formula for jeanbandyite based on six (OH) groups of  $(Fe_{0.71}^{3+}, Mn_{0.21}^{2+}, Mg_{0.04}^{2+}) (Sn_{0.84}^{4+}, Si_{0.03}^{4+}) (OH)_6$ . This has a slight positive excess charge which can be explained if some of the iron is ferrous. Using similar assumptions, we obtain a formula  $(Fe_{0.70}^{3+}, Mn_{0.14}^{2+}, Mg_{0.03}^{2+})$

$(\text{Sn}_{0.90}, \text{Si}_{0.05})\text{(OH)}_6$  for jeanbandyite from Hingston Downs Quarry. Once again there is a slight positive charge imbalance (of 0.24), which might be explained if some of the iron is present as  $\text{Fe}^{2+}$ , or alternatively if silicon was not assigned to the  $\text{Si}^{4+}$  state. The former assumption produces a formula  $(\text{Fe}_{0.46}^{3+}, \text{Fe}_{0.24}^{2+}, \text{Mn}_{0.14}^{2+}, \text{Mg}_{0.03}^{2+})\text{(Sn}_{0.90}, \text{Si}_{0.05})\text{(OH)}_6$ . This differs slightly from the ideal stottite group formula,  $A^{2+}B^{4+}\text{(OH)}_6$ , in that the presence of trivalent iron must be balanced by vacancies in the crystal structure. However, since microchemical tests on jeanbandyite from Hingston Downs Quarry give a strong positive

reaction for  $\text{Fe}^{3+}$  and also a definite reaction for  $\text{Fe}^{2+}$ , it seems likely that the formula is of this type.

Specimens from Hingston Downs Quarry exhibit small compositional differences when compared to the type material. In particular the amount of Sn is higher in Hingston Downs specimens whereas the Mn is generally lower and it seems likely therefore that the distribution of lattice vacancies is different. The presence of significant  $\text{Mn}^{2+}$  (and  $\text{Fe}^{2+}$ ) in the jeanbandyite analysed here, as well as in the specimens from the type locality suggests an essential role for

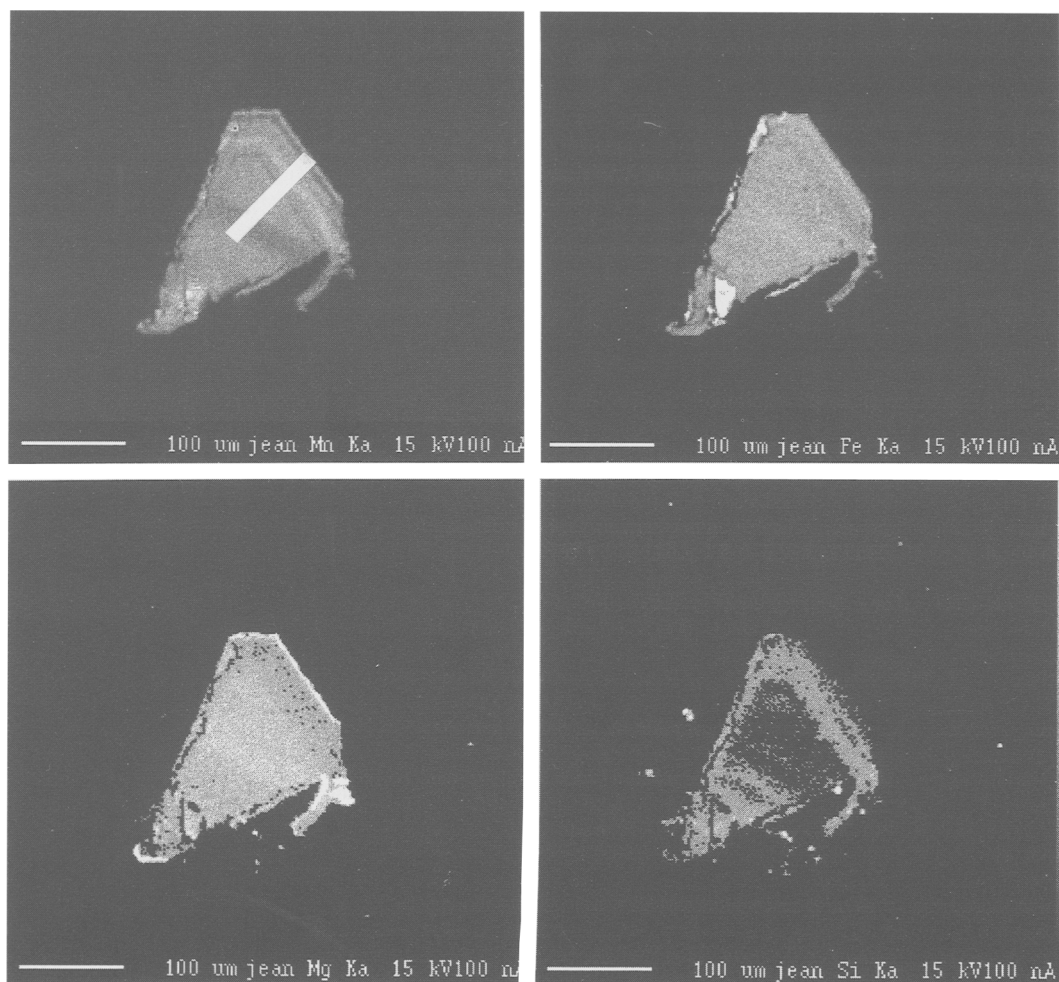


FIG. 2. Element maps for Mn, Fe, Mg, and Si, in a single jeanbandyite crystal fragment from Penberthy Croft Mine. The line on the Mn map indicates the traverse along which the spot analyses of Fig. 3 were measured.

# JEANBANDYITE AND NATANITE

## Variation of Si, Fe, Mg, and Mn

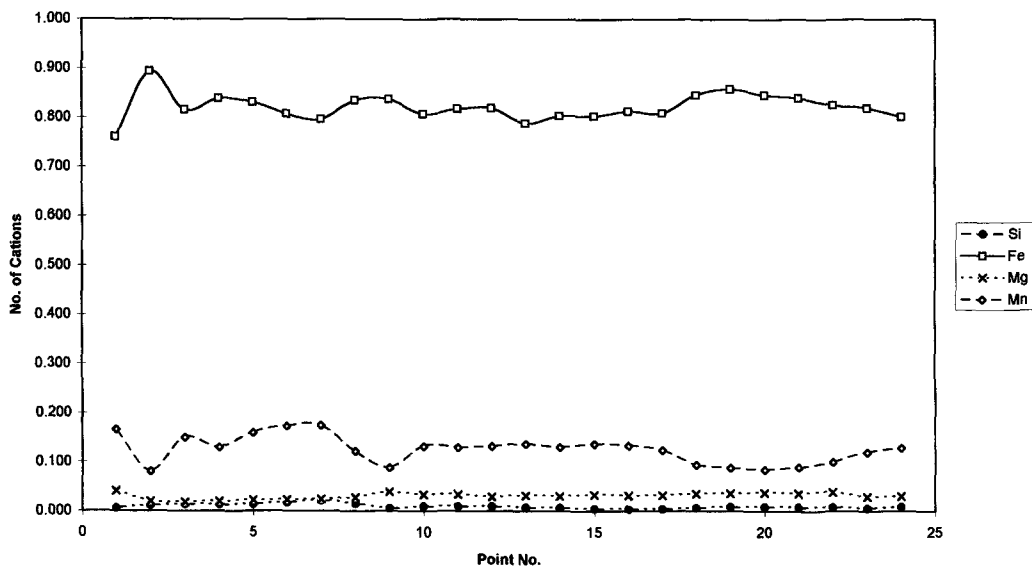


FIG. 3. Graph showing the variations in Mn, Fe, Mg, and Si, along the traverse of Fig. 2.

divalent metal ions in the jeanbandyite structure, perhaps to maintain charge balance. Indeed, the formula which is normally quoted,  $(\text{Fe}_{1-x}^{3+}\square_x)(\text{Sn}_{1-y}^{4+}\square_y)(\text{OH})_6$ , appears to be an oversimplification, in that no account is taken of the presence of divalent metals. A study of the jeanbandyite structure using single crystal X-ray techniques was initiated to further investigate this, but unfortunately none of the crystal fragments examined thus far have proved suitable.

During electron-probe microanalysis of the mixed jeanbandyite-natanite crystal fragment from Penberthy Croft Mine, distinct chemical zonation was noted, which it was hoped might delineate the two species. The complete crystal was X-ray mapped for Mn, Fe, Si, and Mg and the four maps are shown in Fig. 2. The composition of the crystal was measured at 25 points from its outside edge to the centre in a line shown in Fig. 2. These results are shown graphically in Fig. 3. The manganese map shows growth associated zoning (lighter areas represent an increase in concentration) while the iron map shows similar but inverse zoning such that the sum of iron and manganese remains relatively constant. However, the absence of abrupt changes in crystal chemistry suggests the two minerals are intimately intergrown.

Specimens from Penberthy Croft Mine are preserved at the Natural History Museum, (accession numbers BM 1997,60 and BM 1997,61). Specimens from Hingston Downs Quarry are preserved at The Manchester Museum (accession numbers MANCH:N12926 and N13580 to N13584).

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