



## Article

# Dongchuanite, a new phosphate mineral with a new structure, from Dongchuan copper mine, Yunnan Province, China

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### Abstract

Dongchuanite, ideally  $\text{Pb}_4^{\text{VI}}\text{Zn}^{\text{IV}}\text{Zn}_2(\text{PO}_4)_2(\text{PO}_4)_2(\text{OH})_2$ , is a new phosphate mineral with a new type of structure. It was found at the Dongchuan copper mine, Yunnan Province, People's Republic of China. Dongchuanite generally occurs as spherical aggregates with microscopic lamellar crystals, characterised by a turquoise–greenish blue colour. It is transparent, with a colourless streak and has a vitreous lustre without fluorescence. It is brittle with a Mohs hardness of 2–2½, and has good parallel cleavage to {011}, with insignificant parting and even fracture. According to the empirical formula and cell volume, it has a calculated density of 6.06 g/cm<sup>3</sup>. It easily dissolves in acid without gas being emitted. The mineral is biaxial (–), calculated  $n = 1.90$  and maximum birefringence:  $\delta = 0.010$  and  $2V = 70^\circ$ . Dispersion of the optical axes  $r < v$  is very weak. The mineral is pale blue to light blue and very weakly pleochroic in transmitted light. Dongchuanite crystallises in the triclinic space group  $P\bar{1}$ , with unit-cell parameters  $a = 4.7620(10)$  Å,  $b = 8.5070(20)$  Å,  $c = 10.3641(19)$  Å,  $\alpha = 97.110(17)^\circ$ ,  $\beta = 101.465(17)^\circ$ ,  $\gamma = 92.273(18)^\circ$ ,  $V = 407.44(15)$  Å<sup>3</sup> and  $Z = 1$ . The eight strongest reflections in the powder X-ray diffraction pattern [ $d_{\text{obs}}$ , Å ( $hkl$ )] are: 3.442 (100) ( $\bar{1}12$ ), 3.035 (50) (120), 4.652 (45) (100), 2.923 (40) ( $\bar{1}\bar{1}3$ ), 2.384 (35) ( $\bar{2}01$ ), 3.130 (30) ( $\bar{1}21$ ), 2.811 (30) (030) and 2.316 (18) (032). The crystal structure (solved and refined from single-crystal X-ray diffraction data,  $R_1 = 0.07$ ) is a new layered structure consisting of corner-sharing tetrahedrons and octahedrons, where  $[\text{PO}_4]$  tetrahedra and  $[\text{ZnO}_4]$  tetrahedra share corners to form a double chain, and the another  $[\text{PO}_4]$  tetrahedra is connected by corner-sharing with a  $[\text{ZnO}_4(\text{OH})_2]$  octahedra to form a tetrahedral–octahedral chain, extending along the  $a$ -axis direction. The two types of chains are connected by corner-sharing between  $[\text{ZnO}_4]$  and  $[\text{PO}_4]$  tetrahedra forming a wrinkled layer parallel to (011). The Pb atoms occupy two independent sites between the wrinkled layers, both of which have typical lopsided coordination of  $\text{Pb}^{2+}$  with stereoactive  $6s^2$  lone-pair electrons.

**Keywords:** dongchuanite, new mineral species, phosphate, supergene mineral, crystal structure, Dongchuan copper mine

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### Introduction

Located in the northeast of Yunnan Province, 160 km north of Kunming City, the Dongchuan copper mine, an important Chinese copper ore deposit, has been made famous for copper production and the supply of raw materials for minting coins for ancient dynasties. Owing to its unique geological conditions and deposit characteristics, the Dongchuan copper mine has become well known within China for its rare layered super-large sediment-hosted stratiform copper deposits (Leach and Song, 2019). Our recent findings have revealed several new supergene arsenate–phosphate minerals in the region including dongchuanite (IMA2021-058, Li *et al.*, 2021), cuprodongchuanite (IMA2021-065, Sun *et al.*, 2021), zheshengite (IMA2022-011,

Li *et al.*, 2022) and cuprozshengite (IMA2021-095a, Sun *et al.*, 2022). All have the same general crystal chemical formula and crystal structure type and have no natural or synthetic analogues. The first of these minerals is dongchuanite.

The new mineral species and its name (symbol Dc) have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2021-058, Li *et al.*, 2021). The holotype specimen of dongchuanite is under catalogue number No. M26148 at the Geological Museum of China (Xisi Yangrou Hutong No. 15, Xicheng District, Beijing), P.R. China.

### Occurrence and associated minerals

Dongchuanite was found at Sanguozhuang Village, Tangdan Town, Dongchuan District, Kunming City, Yunnan Province, P.R. China (26°8'14"N, 102°59'36"E), and located in the east of the Dongchuan copper ore field.

The Dongchuan copper ore field is composed of multiple spatially independent deposits with the same origin. The proven

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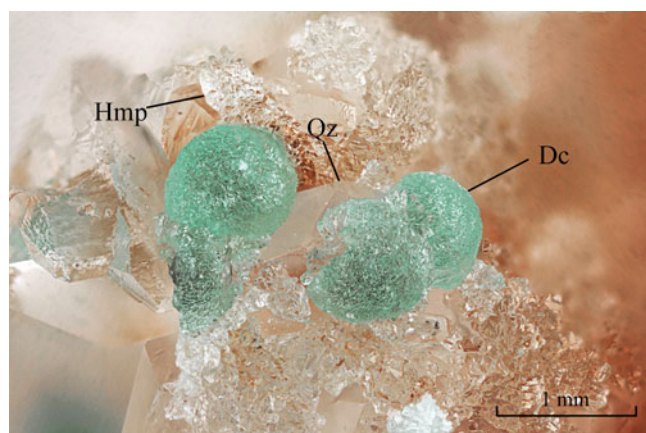
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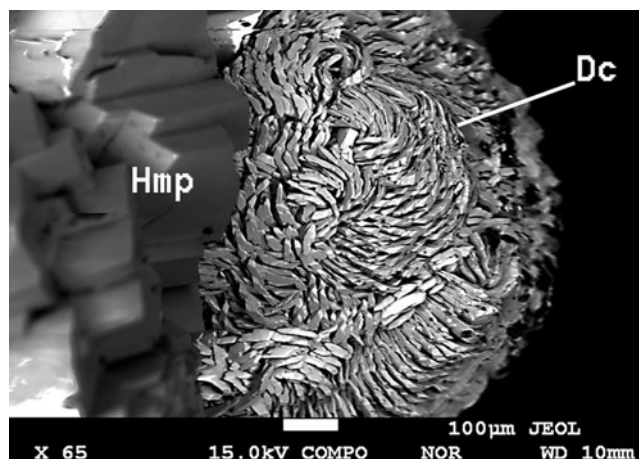
copper deposits are Sikeshu, Yikesu, Yinming, Luoxue, Sijiangjun, Baixina, Lanniping, Tangdan and Xintang (Zhang *et al.*, 2021). The surrounding ore-bearing rock is from the Mesoproterozoic Dongchuan Group and a small number of Shinian Doushantuo Formation strata. There are different views as to the origin of the ore deposit. However, it is generally believed that it was formed by sedimentation–hydrothermal transformation (Zeng *et al.*, 2021; He, 1996). There are a wide variety of mineral species in the deposits, with more than 20 species of polymetallic sulfide minerals and more than 30 supergene minerals identified so far. Dongchuanite was found in an abandoned mine shaft, which is ~1.7 km northwest of Sanguozhuang Village, where the altitude is over 3000 metres. This mine is located on the southern limb of the Huangcaoling syncline. Dongchuanite occurs on a sandstone fracture around Cu-sulfide ore veins, and are clearly of supergene origin. The new minerals may have been formed by the weathering of copper, lead and zinc sulfides under the action of surface water. Associated minerals are quartz, theisite, veszelyite, kipushite, tangdanite, tyrolite, arsenoveszelyite, bayldonite, cuprodongchuanite and hemimorphite.

### Morphology and physical properties

Dongchuanite is composed of spherical aggregates of microscopic lamellar crystals. The size of the spherical aggregates range from 0.5 to 1 mm (Fig. 1). The thickness of single lamellar crystals ranges from 5 to 20  $\mu\text{m}$  (Fig. 2). The crystal habit of the radial aggregates of tiny lamellar crystals is parallel to  $\{010\}$  with chisel-like terminations of  $\{011\}$ ; the forms are  $\{100\}$ ,  $\{010\}$ ,  $\{011\}$  and  $\{0\bar{1}1\}$  (Fig. 3) with unobserved twinning. It is characteristically turquoise–greenish blue and transparent, with a colourless streak, a vitreous lustre and is non-fluorescent. Dongchuanite is brittle with a Mohs hardness of 2–2½, and a micro-hardness (VHN load in 10 g) mean of 91.3 and a range of 85.7–96.4 ( $\text{kg}/\text{mm}^2$ ). It has good cleavage parallel to  $\{011\}$ , parting was not observed and the fracture is even. The density could not be measured directly because of the small size of individual crystals. Based on the empirical formula and cell volume, the calculated density is  $6.06 \text{ g}/\text{cm}^3$ . Dongchuanite is dissolved easily in dilute hydrochloric acid and without gas evolution. The mineral is biaxial (-). The anisotropic refractive index was not measured as that



**Figure 1.** Spherical radial aggregates of dongchuanite (Dc) associated with hemimorphite (Hmp) and quartz (Qz) (#M26148, holotype DC-1).

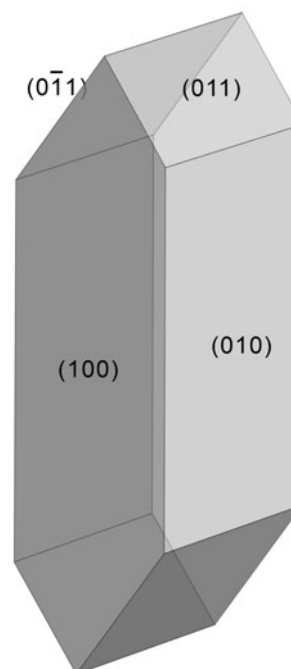


**Figure 2.** Scanning electron microscopy image of the crystal for dongchuanite (#M26148, holotype DC-1) on hemimorphite (Hmp).

of the mineral is higher than that of the highest refractive oil. The calculated Gladstone–Dale relation is  $n = 1.90$  by  $N = K_d + 1$  (Mandarino, 1981). The maximum birefringence:  $\delta = 0.010$  (estimation from the highest interference colour from a section of 30  $\mu\text{m}$  thickness) and  $2V_{\text{meas.}} = 70^\circ$ . Dispersion of the optical axes  $r < v$  is very weak. Optical axes could not be determined due to the form of the microcrystal aggregates. In transmitted light, the mineral is pale blue to light blue and is very weakly pleochroic.

### Chemical composition

The chemical composition of dongchuanite was determined using a JXA-8230 electron microprobe (wavelength dispersive mode) with settings of: acceleration voltage = 15 kV, beam current =



**Figure 3.** The ideal lamellar crystal shape for for dongchuanite.

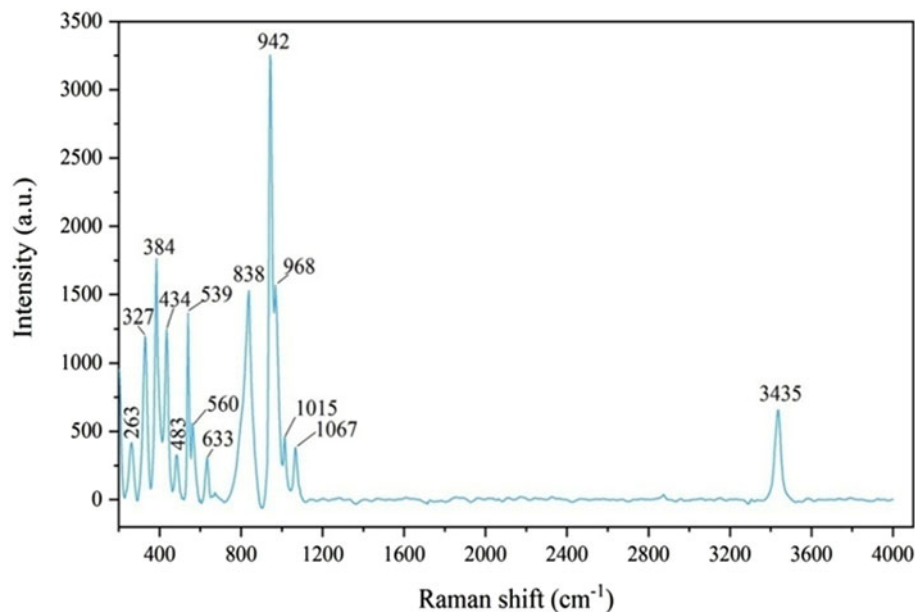


Figure 4. Raman spectrum of dongchuanite.

5 nA, beam diameter = 5  $\mu\text{m}$  and number of analyses = 8 points on one grain. The average component of the dongchuanite aggregate for the following structure refinement is acceptable. We did not collect a sufficient amount of material for direct determination of  $\text{H}_2\text{O}$ , so it was confirmed by Raman spectrum analysis, as shown in Fig. 4. Crystal structure refinement and bond-valence sum analysis showed that O9 is the only oxygen in the form of  $\text{OH}^-$ . Subsequently, we calculated the  $\text{H}_2\text{O}$  amount based on the O9 site as fully occupied by  $\text{OH}^-$ . The chemical composition and compositional ranges of dongchuanite are shown in Table 1. The empirical formula (based on O = 18 atoms per formula unit) is  $(\text{Pb}_{3.92}\text{Cd}_{0.02})_{\Sigma 3.94}(\text{Zn}_{0.69}\text{Cu}_{0.45})_{\Sigma 1.14}\text{Zn}_2[(\text{P}_{0.67}\text{As}_{0.29}\text{S}_{0.01})_{\Sigma 0.97}\text{O}_4]_2(\text{PO}_4)_2(\text{OH})_2$ . The simplified formula is:  $\text{Pb}_4(\text{Zn,Cu})\text{Zn}_2[(\text{P,As})\text{O}_4]_2(\text{PO}_4)_2(\text{OH})_2$ . The ideal formula is:  $\text{Pb}_4^{\text{VI}}\text{Zn}^{\text{IV}}\text{Zn}_2(\text{PO}_4)_2(\text{PO}_4)_2(\text{OH})_2$ , which requires PbO 62.05, ZnO 16.97,  $\text{P}_2\text{O}_5$  19.73,  $\text{H}_2\text{O}$  1.25, total 100 wt.%.

### Raman spectroscopy

The Raman spectrum of dongchuanite was obtained by using a Horiba Via-Reflex, in a reflection mode with a laser excitation

Table 1. Chemical data (in wt.%) for dongchuanite.

Constituent	Mean	Range	S.D. ( $\sigma$ )	Reference material
BaO	0.05	0.00–0.16	0.06	BaSO <sub>4</sub>
CdO	0.21	0.15–0.29	0.05	Cd
As <sub>2</sub> O <sub>5</sub>	4.62	3.92–5.2	0.52	FeAsS
SiO <sub>2</sub>	0.03	0.00–0.08	0.03	SiO <sub>2</sub>
ZnO	14.91	14.35–15.44	0.31	(ZnMn) <sub>2</sub> SiO <sub>4</sub>
CuO	2.45	2.13–2.72	0.20	CuFeS <sub>2</sub>
FeO	0.02	0.00–0.06	0.02	Fe <sub>2</sub> O <sub>3</sub>
V <sub>2</sub> O <sub>3</sub>	0.01	0.00–0.05	0.02	V
PbO	59.59	58.55–60.62	0.67	PbCrO <sub>4</sub>
SO <sub>3</sub>	0.05	0.00–0.09	0.03	SrSO <sub>4</sub>
P <sub>2</sub> O <sub>5</sub>	16.19	15.46–16.93	0.49	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F
H <sub>2</sub> O*	1.23			
Total	99.37	98.27–100.67	0.74	

\*Calculated from crystal structure refinement.  
S.D. – standard deviation.

wavelength of 532 nm and 600 gr/mm. The spectrum in the 200–4000  $\text{cm}^{-1}$  region was obtained using the collection time of 20 s and 2 scans with a resolution of 4  $\text{cm}^{-1}$ .

The Raman spectrum pattern is shown in Fig. 4. Bands in the range 600 to 200  $\text{cm}^{-1}$  comprise partially overlapped bands assigned to the  $\nu_4$  (and  $\nu_2$ ) vibrations of the  $\text{PO}_4$  ( $\text{AsO}_4$ ) tetrahedrons, vibrations of the  $\text{ZnO}_4$  tetrahedra, Zn-, Pb-centred polyhedrons and lattice modes. The bands at 560, 539 and 483  $\text{cm}^{-1}$  can be assigned to  $\nu_4(\text{O-P-O})$ . Bands at 384 and 327  $\text{cm}^{-1}$  corresponded to  $\nu_2(\text{O-P-O})$  (Frost *et al.*, 2002). The band at 434  $\text{cm}^{-1}$  probably corresponds to  $\text{ZnO}_4$  tetrahedra vibration, the symmetric stretching mode of the  $\text{ZnO}_4$  tetrahedron (Hawthorne *et al.*, 2012). The band at 263  $\text{cm}^{-1}$  can be assigned to M(Pb,Zn,Cu)–O vibration (Frost *et al.*, 2002; Ciesielczuk *et al.*, 2016).

Bands in the range of 1100–600  $\text{cm}^{-1}$  are ascribed to the stretching vibrations of  $(\text{PO}_4)^{3-}$  and  $(\text{AsO}_4)^{3-}$  (Farmer, 1974). Two groups of splitting peaks related to  $(\text{PO}_4)^{3-}$  are confirmed to be  $\nu_3$  (1067 and 1015  $\text{cm}^{-1}$ ) and  $\nu_1$  (968 and 942  $\text{cm}^{-1}$ ) modes respectively. The existence of  $\nu$ -splitting peaks indicates two different positions of the phosphate ion. The peak at 838  $\text{cm}^{-1}$  is assigned to the  $\nu_3$  mode of  $(\text{AsO}_4)^{3-}$ , and the weak peak at 633  $\text{cm}^{-1}$  ascribed to  $\nu_2$   $(\text{PO}_4)^{3-}$  vibration.

Sharp stretching vibrations corresponding to hydroxyl ions are found at 3435  $\text{cm}^{-1}$ . However there are no  $\text{H}_2\text{O}$ -molecule bending modes in the 1600–1700  $\text{cm}^{-1}$  region, which proves that  $\text{OH}^-$  is the only water present (Grey *et al.*, 2017).

### Powder X-ray diffraction

The powder X-ray diffraction pattern for dongchuanite was recorded using a Rigaku-Oxford diffraction XtaLAB PRO-007HF single-crystal diffractometer equipped with a hybrid pixel array plane detector, with the method of rotating a crystal using a 20  $\mu\text{m}$  grain. A Gandolfi-like motion on the  $\varphi$  and  $\omega$  axes was used to randomise the sample. The detector was set to a distance of 114 mm, and with detector  $2\theta$ -axis  $0^\circ$  and  $\pm 35^\circ$  images superposition, to improve the resolution of powder diffraction lines. The observed  $d$  values and intensities were derived by profile fitting using Search-Match software (Siegrist, 1997).

**Table 2.** Powder X-ray diffraction data ( $d$  in Å) for dongchuanite.\*

$l_{\text{obs}}$	$l_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$h$	$k$	$l$	$l_{\text{obs}}$	$l_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$h$	$k$	$l$	$l_{\text{obs}}$	$l_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$h$	$k$	$l$
2	2	8.3605	8.4197	0	$\bar{1}$	0	1	7	2.1644	2.1682	2	0	1	3	4	1.2724	1.2785	0	$\bar{5}$	6
3	8	6.9780	6.9382	0	$\bar{1}$	1	4	8	2.1200	2.1186	0	$\bar{4}$	1	5	2	1.2393	1.2395	$\bar{1}$	3	7
10	31	6.0947	6.0689	0	1	1	12	11	2.0237	2.0236	1	2	3	4	2	1.2092	1.2100	$\bar{1}$	$\bar{6}$	5
1	8	5.0500	5.0364	0	0	2	5	12	1.9629	1.9619	2	0	2	4	2	1.1836	1.1831	$\bar{3}$	$\bar{5}$	1
<b>45</b>	<b>53</b>	<b>4.6519</b>	<b>4.5921</b>	<b><math>\bar{1}</math></b>	<b>0</b>	<b>1</b>	8	9	1.9027	1.9030	0	$\bar{4}$	3	3	2	1.1603	1.1602	$\bar{2}$	6	3
13	21	4.2330	4.2098	0	2	0	<b>17</b>	<b>17</b>	<b>1.8582</b>	<b>1.8647</b>	<b>2</b>	<b>1</b>	<b>2</b>	1	2	1.1335	1.1341	$\bar{3}$	4	5
14	4	4.0808	4.0856	0	1	2	9	7	1.7810	1.7938	$\bar{1}$	$\bar{4}$	3	1	1	1.1168	1.1158	0	5	6
5	15	3.9279	3.9237	1	0	1	6	12	1.7433	1.7452	1	2	4	<1	1	1.1103	1.1101	$\bar{4}$	2	4
3	8	3.7159	3.7099	0	2	1	6	12	1.7166	1.7176	$\bar{1}$	$\bar{3}$	5	1	1	1.0923	1.0948	0	3	8
<b>100</b>	<b>100</b>	<b>3.4419</b>	<b>3.4288</b>	$\bar{1}$	<b>1</b>	<b>2</b>	10	2	1.6804	1.6812	1	$\bar{2}$	5	1	1	1.0712	1.0712	$\bar{4}$	2	5
6	45	3.2782	3.2748	0	$\bar{1}$	3	8	9	1.6419	1.6415	2	3	1	<1	2	1.0638	1.0625	$\bar{4}$	0	6
<b>30</b>	<b>65</b>	<b>3.1302</b>	<b>3.1170</b>	$\bar{1}$	<b>2</b>	<b>1</b>	3	2	1.5809	1.5801	$\bar{3}$	0	1	3	2	1.0479	1.0487	0	$\bar{4}$	9
<b>50</b>	<b>54</b>	<b>3.0347</b>	<b>3.0519</b>	<b>1</b>	$\bar{1}$	<b>2</b>	4	6	1.5482	1.5481	1	5	0	1	2	1.0227	1.0215	0	$\bar{8}$	4
<b>40</b>	<b>66</b>	<b>2.9231</b>	<b>2.9244</b>	$\bar{1}$	$\bar{1}$	<b>3</b>	7	4	1.5050	1.4989	$\bar{2}$	$\bar{3}$	5	1	2	1.0081	1.0022	$\bar{2}$	$\bar{1}$	10
<b>30</b>	<b>44</b>	<b>2.8106</b>	<b>2.8066</b>	<b>0</b>	<b>3</b>	<b>0</b>	4	2	1.4924	1.4915	0	2	6	1	1	0.9960	0.9960	$\bar{3}$	3	8
<1	1	2.7054	2.7211	1	2	1	4	7	1.4562	1.4548	$\bar{3}$	$\bar{2}$	1	2	1	0.9771	0.9846	3	$\bar{7}$	0
9	13	2.6130	2.6060	0	$\bar{3}$	2	3	2	1.4435	1.4427	$\bar{3}$	$\bar{2}$	3	1	1	0.9605	0.9604	4	$\bar{3}$	4
6	21	2.4934	2.4828	1	$\bar{1}$	3	6	5	4029	1.4083	$\bar{3}$	3	1	2	1	0.9443	0.9435	$\bar{1}$	$\bar{6}$	9
<b>35</b>	<b>59</b>	<b>2.3843</b>	<b>2.3725</b>	<b><math>\bar{2}</math></b>	<b>0</b>	<b>1</b>	4	1	3604	1.3605	2	4	2	1	1	0.9371	0.9371	0	4	9
18	4	2.3165	2.3127	0	$\bar{3}$	3	2	3	1.3494	1.3414	1	2	6							
6	6	2.2195	2.2202	$\bar{2}$	1	2	6	4	1.3146	1.3119	$\bar{1}$	$\bar{6}$	3							

\*The strongest lines are given in bold.

Table 2 shows the powder X-ray diffraction data (for 1.2 kW micro focus rotating anode X-ray source, MoK $\alpha$ ,  $\lambda = 0.71073$  Å; 50 kV/24 mA), along with the indexing and calculated intensities from the crystal structure. Unit-cell parameters refined from the powder data using *CheckCell* are:  $a = 7515(1)$  Å,  $b = 8.5064(2)$  Å,  $c = 10.3710(2)$  Å,  $\alpha = 97.090(2)^\circ$ ,  $\beta = 101.410(2)^\circ$ ,  $\gamma = 92.580(2)^\circ$  and  $V = 406.7(3)$  Å<sup>3</sup>, which are in good agreement with those obtained from the single-crystal study (Table 2).

### Single-crystal X-ray data collection and structure refinement

The single crystal X-ray diffraction data for dongchuanite were collected by using a Rigaku-Oxford diffraction XtaLAB PRO-007HF single-crystal diffractometer equipped with a rotating anode micro-focus X-ray source (1.2 kW MoK $\alpha$  and  $\lambda = 0.71073$  Å) and a hybrid pixel array detector. Similar results were obtained from two single-crystal fragments. The reflections obtained were from one single crystal fragment of excellent quality  $0.02 \times 0.01 \times 0.01$  mm in size, with  $-6 < h < 6$ ,  $-11 < k < 9$ ,  $-13 < l < 14$  with fair  $R_{\text{int}} = 0.0709$ . Intensity data was corrected for Lorentz polarisation and multi-scan absorption. The space group was obtained by conducting the system extinction statistics and was found to be  $P\bar{1}$ . The crystal structure determination and refinement were performed using *OLEX2-1.3* (Dolomanov et al., 2010) with *SHELXT* (Sheldrick, 2015). The crystal structure was solved by direct methods, which found all of the heavy atoms and part of the O atoms. According to differential-Fourier transform calculations, all O atoms were found.

The structure was refined to  $R_1 = 0.07$  on the basis of 1360 independent reflections with  $I > 2\sigma(I)$ . The crystallographic characteristics, the experimental parameters of data collection and structure refinement are summarised in Table 3. Atom coordinates, site occupancies and geometric parameters are listed in Tables 4, 5 and 6. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

**Table 3.** Crystal information and details of X-ray data collection and refinement.

<b>Crystal data</b>	
Structural formula	Pb <sub>4</sub> (Zn,Cu)Zn <sub>2</sub> [(P,As)O <sub>4</sub> ] <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Crystal dimensions (mm)	0.02 × 0.01 × 0.01
Crystal system, space group	$P\bar{1}$ (#2), triclinic
Temperature (K)	296(2)
$a, b, c$ (Å)	4.7620(10), 8.5070(20), 10.3641(19)
$\alpha, \beta, \gamma$ (°)	97.110(17), 101.465(17), 92.273(18)
$V$ (Å <sup>3</sup> )	407.44(15)
$Z$	1
Absorption $\mu$ (mm <sup>-1</sup> )	47.315
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	6.06
<b>Data collection</b>	
Crystal description	turquoise–greenish blue, brittle
Diffractometer	Rigaku-Oxford diffraction XtaLAB PRO-007HF
Radiation type, wavelength (Å)	MoK $\alpha$ (0.71073)
Scanning mode	$\omega$ scan, $\delta\omega = 0.5^\circ$
max $\theta$ (°)	29.319
Absorption correction	multi-scan absorption
$T_{\text{min}}, T_{\text{max}}$	0.576, 0.627
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4234, 1896, 1360
$R_{\text{int}}$	0.0709
Indices range of $h, k, l$	$-6 \leq h \leq 6, -11 \leq k \leq 9, -13 \leq l \leq 14$
<b>Refinement</b>	
No. of refined parameters	135
Residuals $R$ [ $I > 2\sigma(I)$ ]	0.07
$wR_2$ [ $I > 2\sigma(I)$ ]	0.143
Goodness of fit, $S$	1.059
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2]$
where $P = [\max(F_o^2) + 2(F_c)^2]/3$	
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e <sup>-</sup> Å <sup>-3</sup> )	5.74/-2.99

### Site-population assignment for dongchuanite

The Pb cations occupy two independent 8-coordinate sites in the interlayer region. Although the difference-Fourier map displays several  $\sim 5e^-$  residuals at  $\sim 1$  Å around these (heavy) Pb atoms,

**Table 4.** Atomic coordinates and site occupancies\* for dongchuanite.

Atom	Wyk.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
Pb1	2i	0.1497(2)	0.48048(11)	0.32941(9)	0.0221(3)
Pb2	2i	-0.1109(2)	0.10508(12)	-0.16008(10)	0.0280(3)
Zn1*	1c	0	½	0	0.0209(9)
Zn2	2i	0.6689(6)	0.1280(3)	0.3826(3)	0.0203(6)
P1*	2i	0.4891(8)	0.2494(5)	0.0886(4)	0.0181(14)
P2	2i	1.2414(12)	0.2207(7)	0.5660(6)	0.0143(12)
O1	2i	1.317(4)	0.103(2)	0.6637(16)	0.026(4)
O2	2i	1.382(4)	0.388(2)	0.6212(17)	0.032(5)
O3	2i	1.293(4)	0.162(2)	0.4251(16)	0.031(4)
O4	2i	0.908(4)	0.241(2)	0.5435(17)	0.031(4)
O5	2i	0.696(4)	0.212(2)	0.2193(18)	0.035(5)
O6	2i	0.675(3)	0.281(2)	-0.0190(16)	0.021(4)
O7	2i	0.263(4)	0.107(2)	0.0329(17)	0.028(4)
O8	2i	0.324(4)	0.403(2)	0.1253(16)	0.029(4)
O9(OH)	2i	-0.078(3)	0.6180(19)	0.1640(16)	0.022(4)

\*Occupancies for Zn1 = 0.55Zn + 0.45Cu and for P1 = 0.64(2)P + 0.364(19)As.

Wyk. = Wyckoff position.

**Table 5.** Anisotropic displacement parameters (in Å<sup>2</sup>) for dongchuanite.

Atom	<i>U<sup>11</sup></i>	<i>U<sup>22</sup></i>	<i>U<sup>33</sup></i>	<i>U<sup>23</sup></i>	<i>U<sup>13</sup></i>	<i>U<sup>12</sup></i>
Pb1	0.0193(5)	0.0262(5)	0.0216(5)	0.0030(4)	0.0056(4)	0.0052(4)
Pb2	0.0235(5)	0.0300(6)	0.0293(6)	0.0000(4)	0.0042(4)	0.0047(4)
Zn1	0.020(2)	0.029(2)	0.0138(18)	0.0005(17)	0.0038(16)	0.0104(17)
Zn2	0.0172(14)	0.0276(16)	0.0175(13)	0.0021(12)	0.0063(11)	0.0062(11)
P1	0.015(2)	0.025(2)	0.016(2)	0.0028(17)	0.0046(15)	0.0079(16)
P2	0.008(3)	0.021(3)	0.015(3)	0.000(2)	0.006(2)	0.006(2)
O1	0.024(9)	0.027(10)	0.025(9)	0.008(8)	-0.005(7)	0.013(8)
O2	0.018(9)	0.048(12)	0.028(9)	-0.010(9)	0.007(8)	0.008(8)
O3	0.018(9)	0.049(12)	0.025(9)	-0.009(9)	0.007(8)	0.009(8)
O4	0.021(7)	0.033(8)	0.035(8)	-0.014(6)	0.005(6)	0.011(6)
O5	0.033(11)	0.043(12)	0.030(10)	0.012(9)	0.004(8)	0.002(9)
O6	0.013(6)	0.026(7)	0.027(7)	0.001(6)	0.008(6)	0.008(6)
O7	0.019(9)	0.044(11)	0.029(9)	0.008(8)	0.013(7)	0.023(8)
O8	0.023(10)	0.039(11)	0.022(8)	-0.007(8)	0.005(7)	0.007(8)
O9(OH)	0.022(9)	0.021(9)	0.025(9)	-0.006(7)	0.010(7)	0.011(7)

which might suggest some slight disorder, they are probably simply 'ripples' resulting from series termination effects due to the average quality of the data.

Zinc has two different crystal chemical locations in dongchuanite. Zn1 (Wyckoff position 1c) and Zn2 (Wyckoff 2i). Zn1 (Wyckoff 1c) has [6]-coordinates (<sup>VI</sup>Zn) with O and OH forming [Zn1O<sub>4</sub>(OH)<sub>2</sub>] octahedra, whose average bond length is 2.126 Å. The substantial Cu content of the octahedral Zn1 site, as indicated by the empirical formula based on the electron microprobe analysis, was clearly supported by the significant Jahn-Teller distortion observed (see Table 6). The average bond valences involved in linkage to Zn1 cation is 0.33. Zn2 (Wyckoff 2i) has [4]-coordinates (<sup>IV</sup>Zn) with O forming [ZnO<sub>4</sub>] tetrahedral coordination and is fully occupied by Zn. The average bond length of Zn is 1.950 Å, and the average bond valences involved in linkage to the Zn2 cation is 0.50.

Phosphorus also has two crystal chemical locations. [P1O<sub>4</sub>] tetrahedra share corners with [Zn2O<sub>4</sub>] tetrahedra and two [Zn1O<sub>4</sub>(OH)<sub>2</sub>] octahedra. [P2O<sub>4</sub>] tetrahedra share corners with three [Zn2O<sub>4</sub>] tetrahedra. The results of the free refinement of these two positions using P show that the occupancy of P2 is 1.06P, whereas the occupancy of P1 is 1.51P, which indicates that isomorphic substitution mainly occurs at the P1 site with heavier atoms. The final free refined occupancy of the P1 site is

**Table 6.** Selected interatomic distances (Å) for dongchuanite.

Pb1-O <sup>i</sup>	2.385 (17)	Pb2-O <sup>iv</sup>	2.994 (17)
Pb1-O <sup>ii</sup>	3.210 (19)	Pb2-O <sup>v</sup>	2.961 (16)
Pb1-O <sup>iii</sup>	2.917 (17)	Pb2-O <sup>vi</sup>	3.289 (16)
Pb1-O <sup>3ii</sup>	3.050 (20)	Pb2-O <sup>4iv</sup>	3.429 (19)
Pb1-O <sup>4iii</sup>	2.616 (17)	Pb2-O <sup>6ii</sup>	2.364 (15)
Pb1-O <sup>5ii</sup>	3.030 (18)	Pb2-O <sup>7</sup>	2.397 (17)
Pb1-O <sup>8</sup>	2.449 (16)	Pb2-O <sup>7vii</sup>	2.526 (18)
Pb1-O <sup>9</sup>	2.312 (18)	Pb2-O <sup>9viii</sup>	2.496 (16)
<Pb1-O>	2.746	<Pb2-O>	2.807
Zn1-O <sup>6ii</sup>	2.339 (16)	Zn2-O <sup>1x</sup>	1.970 (17)
Zn1-O <sup>6ix</sup>	2.339 (16)	Zn2-O <sup>3ii</sup>	1.951 (17)
Zn1-O <sup>8</sup>	2.078 (18)	Zn2-O <sup>4</sup>	1.939 (17)
Zn1-O <sup>8viii</sup>	2.078 (18)	Zn2-O <sup>5</sup>	1.940 (19)
Zn1-O <sup>9viii</sup>	1.974 (15)	<Zn2-O>	1.950
Zn1-O <sup>9</sup>	1.974 (15)		
<Zn1-O>	2.130		
P1-O <sup>5</sup>	1.586 (19)	P2-O <sup>1</sup>	1.514 (18)
P1-O <sup>6</sup>	1.595 (16)	P2-O <sup>2</sup>	1.543 (19)
P1-O <sup>7</sup>	1.561 (19)	P2-O <sup>3</sup>	1.553 (17)
P1-O <sup>8</sup>	1.596 (18)	P2-O <sup>4</sup>	1.580 (18)
<P1-O>	1.585	<P2-O>	1.548

Symmetry codes: (i) -x+2, -y+1, -z+1; (ii) x-1, y, z; (iii) -x+1, -y+1, -z+1; (iv) x-1, y, z-1; (v) x-2, y, z-1; (vi) -x+1, -y, -z; (vii) -x, -y, -z; (viii) -x, -y+1, -z; (ix) -x+1, -y+1, -z; (x) -x+2, -y, -z+1; (xi) x+1, y, z; (xii) x+2, y, z+1; (xiii) x+1, y, z+1.

0.65P + 0.35As. The average bond length of P1-O (1.581 Å) is higher than P2-O (1.539 Å). Raman spectra shows splitting peaks of (PO<sub>4</sub>)<sup>3-</sup> indicating two different crystal chemical environments. P tends to occupy the crystal chemical position of the P2 site, while As tends to be predominantly at the P1 site. The results are close to the chemical composition and gave reasonable bond-valence sums (Table 7).

Although the coordinates of H are not refined in the crystal structure (due to interference of the heavy atom Pb), the Raman spectrum (Fig. 4) and bond-valence sums (Table 7) confirm that H is attached to O9 as OH<sup>-</sup>.

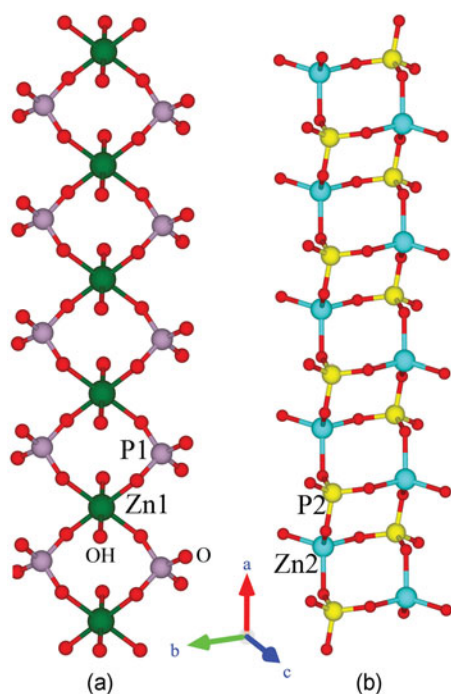
### Crystal structure description

Dongchuanite has a chain-layer structure, composed of a tetrahedral double chain and a tetrahedral-octahedral chain in a unit layer (Fig. 5). The tetrahedral double chain is formed by the connection of [PO<sub>4</sub>] tetrahedra and [ZnO<sub>4</sub>] tetrahedra along the [100] direction (Fig. 5b). Each tetrahedron is 3-connected with other tetrahedra in the chain. The P-O mean bond-length is 1.539 Å in the [PO<sub>4</sub>] tetrahedra, and the Zn-O mean bond length is 1.950 Å in the [ZnO<sub>4</sub>] tetrahedra. The tetrahedral-octahedral chain is formed by the [PO<sub>4</sub>] tetrahedra that share corners with [ZnO<sub>4</sub>(OH)<sub>2</sub>] octahedra, along the [100] direction. The alternating [ZnO<sub>4</sub>(OH)<sub>2</sub>] octahedra and pairs of corner-connected [PO<sub>4</sub>] tetrahedra are shown in Fig. 5a. The hydroxyl group is located on both sides of the centre of the Zn cation. In this chain, both the P-O and Zn-O bonds have longer distances than those bonds in the tetrahedral double chain, with an average P-O distance of 1.581 Å and a Zn-O distance of 2.126 Å. The same type of chains are present in drugmanite where PO<sub>4</sub> tetrahedra share corners with (Fe,Al)O<sub>6</sub> octahedra (King and Sengier-Roberts, 1988). Along the [100] direction, the tetrahedra [ZnO<sub>4</sub>]-[PO<sub>4</sub>]-[ZnO<sub>4</sub>] length matches the [PO<sub>4</sub>]-[ZnO<sub>4</sub>(OH)<sub>2</sub>]-[PO<sub>4</sub>] length exactly, so that the two types of chains can be connected by corner-sharing between [ZnO<sub>4</sub>] and [PO<sub>4</sub>] tetrahedra, as illustrated in Fig. 6, to form wrinkled layers parallel to (011) (Fig. 7).

**Table 7.** Bond-valence sum for dongchuanite.

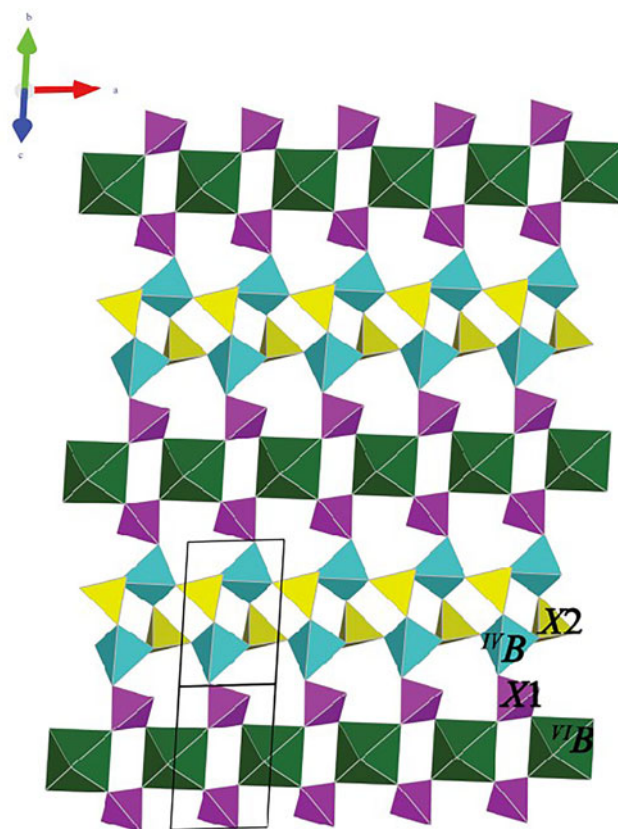
	Pb1	Pb2	Zn1	Zn2	P1	P2	O sum
O1		0.12+0.13 $\leftarrow$		0.47 $\leftarrow$		1.32 $\leftarrow$	2.04
O2	0.42+0.14+0.08 $\leftarrow$					1.23 $\leftarrow$	1.87
O3	0.11 $\leftarrow$	0.07 $\leftarrow$		0.49 $\leftarrow$		1.29 $\leftarrow$	1.86
O4	0.26 $\leftarrow$	0.05 $\leftarrow$		0.51 $\leftarrow$		1.12 $\leftarrow$	1.94
O5	0.11 $\leftarrow$			0.51 $\leftarrow$	1.29 $\leftarrow$		1.91
O6		0.44 $\leftarrow$	0.17 $\times 2 \rightarrow$		1.26 $\leftarrow$		2.04
O7		0.41+0.32 $\leftarrow$			1.38 $\leftarrow$		2.11
O8	0.37 $\leftarrow$		0.35 $\times 2 \uparrow \times 1 \rightarrow$		1.26 $\leftarrow$		1.98
O9	0.49 $\leftarrow$	0.34 $\leftarrow$	0.46 $\times 2 \uparrow \times 1 \rightarrow$				1.29
Sum	1.99	1.88	1.95	1.98	5.19	4.85	

Note: Bond strength for Zn1 site occupancy of  $0.55\text{Zn}^{2+}+0.45\text{Cu}^{2+}$ ; P1 site occupancy of  $0.64\text{P}^{5+}+0.36\text{As}^{5+}$ . The bond-valence calculations were done using the equation and constants of Brown (1977),  $S = \exp[R_0 - d_0]/b$ . Bond parameters:  $\text{Pb}^{2+}-\text{O}^{2-}$  from Krivovichev and Brown (2001);  $\text{Cu}^{2+}-\text{O}^{2-}$  Krivovichev (2012);  $\text{P}^{5+}-\text{O}^{2-}$  from Gagné and Hawthorne (2015) and  $\text{As}^{5+}-\text{O}^{2-}$  Brown and Altermatt (1985).



**Figure 5.** (a) Alternating  $\text{ZnO}_4(\text{OH})_2$  octahedra and pairs of corner-connected  $\text{PO}_4$  tetrahedra forming a tetrahedral-octahedral chain. (b) Double chain of corner-linked  $\text{ZnO}_4$  and  $\text{PO}_4$  tetrahedra. Each tetrahedron is 3-connected with other tetrahedra in the chain. Key: green= Zn1, blue=Zn2, purple=P1 and yellow = P2.

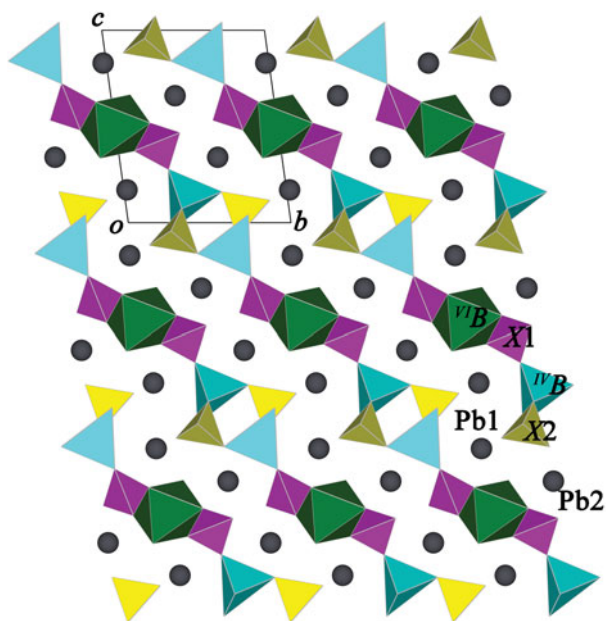
The  $\text{Pb}^{2+}$  cations have lone-electron pairs and typically are positioned off-centre in their polyhedral coordination. In dongchuanite (Fig. 7), the stereochemically active  $6s^2$  lone-electron-pair of  $\text{Pb}^{2+}$  results in a ‘one-sided’ distorted 8-fold coordination, with the  $\text{Pb}-\text{O}$  distance on one side of the ion being longer than on the other. The  $\text{PbO}_8$  eight-fold coordination polyhedra are modified square antiprisms with short bonds to four O atoms and much longer bonds to four O atoms. The  $\text{Pb1}-\text{O}$  bond distances have four shorter bonds to anions in the range of 2.32 to 2.61 Å and four longer bonds in the range of 2.91 to 3.05 Å. The  $\text{Pb2}-\text{O}$  has four shorter bonds in the range of 2.36 to 2.53 Å and four longer bonds in the range of 2.96 and 3.42 Å. The shorter bonds are to oxygen ligands of the  $\text{P1O}_4$  tetrahedra, whilst the longer bonds are to those of the  $\text{P2O}_4$  tetrahedra. Similar bonding has been reported for Pb in a synthetic lead hydrated phosphate (Mills *et al.*, 2010).



**Figure 6.** The parallel (011) layer in dongchuanite; the two types of chains are connected by corner-sharing between  $[\text{ZnO}_4]$  and  $[\text{PO}_4]$  tetrahedra forming wrinkled layers parallel to (011). Legend:  $^{\text{VI}}\text{B}$ : Zn1 octahedra;  $^{\text{VII}}\text{B}$ : Zn2 tetrahedra; X1: P1 tetrahedra; X2: P2 tetrahedra.

## Discussion

On the basis of crystal structure refinement and composition analysis of multiple samples from the mine, we found at least four mineral species with different compositions and similar structure. We propose the use of ‘dongchuanite group’ to systematically describe such mineral species. We have submitted the proposal to the CNMNC and it is under review. The general crystal chemistry formula of the ‘dongchuanite group’ minerals exhibit a generalised formula:  $A_4^{\text{VI}}\text{B}^{\text{IV}}\text{B}_2(\text{X1O}_4)_2(\text{X2O}_4)_2(\text{OH})_2$ , where A is an interlayer cation with dominant Pb; B are transition metals with two

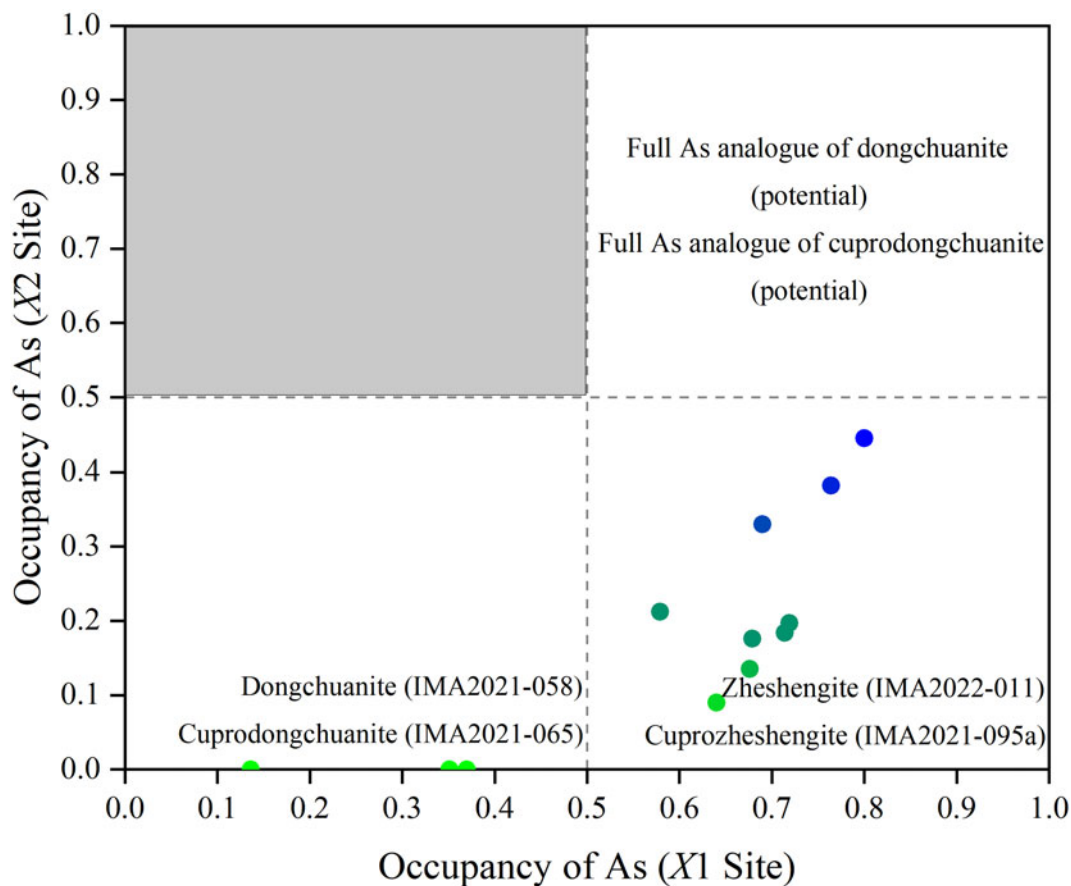


**Figure 7.** The structure for dongchuanite showing a wrinkled layer. The Pb is located in the wrinkled interlayers. Legend as in Fig. 6.

crystallographic positions;  $^{IV}B$  is in tetrahedral coordination, fully occupied by Zn, whereas  $^{VI}B$  has an octahedral coordination, occupied by Zn, Cu and Fe; and X1 and X2 are cations in complex anions, which are tetrahedrally coordinated and occupied by P and As.

The distributions of P and As at the X1 and X2 sites can be calculated from our study of the X-ray crystal structure refinement of the 'dongchuanite group' minerals. As shown in Fig. 8, As-atoms tend to preferentially occupy the X1 site. A similar pattern of occupation was also determined in the philipsburgite–kipushite series (Krivovichev *et al.*, 2018). Therefore, to avoid multiple occupancies, As (arsenic) was first assigned to the X1 position, although this may be slightly different from the occupancy of the crystal structure refinement.

The dominant elements in the crystallographic sites are the most important criterion for the definition of a mineral species. In the crystal structure, the X1 and X2 sites are two different crystallographic locations.  $[X1O_4]$  tetrahedra share corners with  $[^{IV}BO_4]$  tetrahedra and  $[^{VI}BO_4(OH)_2]$  octahedra.  $[X2O_4]$  tetrahedra share corners with two  $[^{IV}BO_4]$  tetrahedra. X-ray single-structure refinement shows that As occupies the X1 site more preferentially than the X2 site. When the atoms per formula unit (apfu) of As is  $< 0.8$ , no As atom is observed at the X2 site and nearly all As atoms occupy the X1 site. When the apfu of As is  $> 1.0$ , a small amount of As begins to occupy the position X2, and the total As at position X2 is always lower than that of X1. Consistently, the end-members with dominant As at X2 and dominant P at X1 probably do not exist. Moreover, only when the content of As is high enough (upper right corner area



**Figure 8.** The distribution of As atoms at X1 and X2 sites based on crystal structure X-ray refinement of 'dongchuanite group' minerals. The results show As atoms tend to occupy the X1 position preferentially. The dark grey area is vacant.

in Fig. 8), can it become dominant at both X1 and X2 sites, whose end-member formula is  $A_4^{VI}B^{IV}B_2(AsO_4)_2(AsO_4)_2(OH)_2$ . Therefore, the mineral species of this group can be divided into three ideal end-member formulae. Where P is dominant at both the X1 and X2 sites gives:  $A_4^{VI}B^{IV}B_2(PO_4)_2(PO_4)_2(OH)_2$ . The mineral species currently approved by the IMA–CNMNC are dongchuanite,  $Pb_4ZnZn_2(PO_4)_2(PO_4)_2(OH)_2$  and cuprodongchuanite,  $Pb_4CuZn_2(PO_4)_2(PO_4)_2(OH)_2$ . Where As is dominant at the X1, and P at the X2, the formula is  $A_4^{VI}B^{IV}B_2(AsO_4)_2(PO_4)_2(OH)_2$ . So far, the approved mineral species are zheshengite,  $Pb_4ZnZn_2(AsO_4)_2(PO_4)_2(OH)_2$  and cuprozheshengite,  $Pb_4CuZn_2(AsO_4)_2(PO_4)_2(OH)_2$ . Where As is dominant at both the X1 and X2 sites, e.g.  $A_4^{VI}B^{IV}B_2(AsO_4)_2(AsO_4)_2(OH)_2$ , are potential new minerals.

## Summary

Dongchuanite is triclinic. The space group of  $P\bar{1}$  exhibits unit-cell parameters:  $a = 4.7620(10)$  Å,  $b = 8.5070(20)$  Å,  $c = 10.3641(19)$  Å,  $\alpha = 97.110(17)^\circ$ ,  $\beta = 101.465(17)^\circ$ ,  $\gamma = 92.273(18)^\circ$ ,  $V = 407.44(15)$  Å<sup>3</sup> and  $Z = 1$ . The crystal structure is a wrinkled layer parallel to (011) formed of corner-sharing tetrahedra and octahedra. The ideal and simplified formulae of dongchuanite are  $Pb_4ZnZn_2(PO_4)_2(PO_4)_2(OH)_2$  and  $Pb_4(Zn,Cu)Zn_2[(P,As)O_4]_2(PO_4)_2(OH)_2$  respectively.

Dongchuanite is not an isolated mineral species. Instead, it is one species in a new group consisting of many mineral species. The general crystal-chemical formula of the mineral group is  $A_4^{VI}B^{IV}B_2(X1O_4)_2(X2O_4)_2(OH)_2$ . The structural study demonstrates that the dongchuanite structure type allows for the selective As–P substitution being induced by different crystal chemical environments of two tetrahedral sites, of which the X2 site is more preferable for P, whereas the X1 site is more suitable for As. The classification and nomenclature of the ‘dongchuanite group’ will be detailed in a later paper following CNMNC approval.

**Supplementary material.** The supplementary material for this article can be found at <https://doi.org/10.1180/mgm.2023.16>.

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**Competing interests.** The authors declare none.

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