

Lucabindiite, (K,NH₄)As₄O₆(Cl,Br), a new fumarole mineral from the “La Fossa” crater at Vulcano, Aeolian Islands, Italy

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ABSTRACT

Lucabindiite, ideally (K,NH₄)As₄O₆(Cl,Br), is a new mineral found as a medium-temperature fumarole encrustation ($T = 170\text{ }^{\circ}\text{C}$) at “La Fossa” crater of Vulcano, Aeolian Islands, Italy. The mineral deposited as aggregates of micrometer-sized hexagonal and platy crystals on the surface of the pyroclastic breccia in association with arsenolite, sal ammoniac, sulfur, and amorphous arsenic-rich sulfurite. The new mineral is colorless to white, transparent, non-fluorescent, has a vitreous luster and a white streak. The calculated density is 3.68 g/cm^3 . Lucabindiite is hexagonal, space group $P6/mmm$, with $a = 5.2386(7)\text{ \AA}$, $c = 9.014(2)\text{ \AA}$, $V = 214.23(7)\text{ \AA}^3$, and $Z = 1$. The eight strongest reflections in the X-ray powder-diffraction data [d in \AA (hkl)] are: 3.20 (100) (102), 2.62 (67) (110), 4.51 (52) (002), 4.54 (30) (100), 1.97 (28) (113), 1.49 (21) (115), 1.60 (21) (212), 2.26 (19) (112). Lucabindiite’s average chemical composition is (wt%): K₂O 5.14, As₂O₃ 84.71, Cl 3.63, Br 6.92, F 0.77, (NH₄)₂O 2.73, O=F,Cl,Br –1.84, total 102.06. The empirical chemical formula, calculated on the basis of 7 anions pfu, is $[\text{K}_{0.51}(\text{NH}_4)_{0.49}]_{\Sigma 1.00}\text{As}_{4.00}\text{O}_{5.93}(\text{Cl}_{0.48}\text{Br}_{0.40}\text{F}_{0.19})_{\Sigma 1.07}$. According to chemical analyses and X-ray data, lucabindiite is the natural analog of synthetic phases with general formula $M\text{As}_4\text{O}_6X$ where $M = \text{K}, \text{NH}_4$ and $X = \text{Cl}, \text{Br}, \text{I}$. The crystal structure is characterized by neutral As₂O₃ sheets arranged parallel to (001). The As atoms of two neighboring sheets point at each other and the sheets are separated by interlayer $M (= \text{K}, \text{NH}_4)$ and $X (= \text{Cl}, \text{Br}, \text{F})$ atoms. The name is in honor of Luca Bindi (b. 1971), Professor of Mineralogy and former Head of the Division of Mineralogy of the Natural History Museum of the University of Florence. Both the mineral and the mineral name have been approved by the IMA-CNMNC Commission (IMA 2011-010).

Keywords: Lucabindiite, As-oxychlorides, new mineral, sublimates, fumaroles, crystal structure, Vulcano, Aeolian Islands, Italy

INTRODUCTION

The history of the discovery of lucabindiite began at the beginning of the nineties, during the years of the Ph.D. studies of one of us (Garavelli 1994). At that time Vulcano was in a thermal-increase period reflecting the increase in activity at the “La Fossa” crater (Garavelli et al. 1997 and references therein). Temperature values rose quickly and the maximum temperature of the fumaroles reached $700\text{ }^{\circ}\text{C}$ in October 1992. To contribute to the understanding of the genesis and evolution both of fluids and depositional environments of sublimates at Vulcano, with the aim also to give a contribution to volcanic surveillance, the fumarolic products and encrustations at La Fossa crater have been studied systematically from a mineralogical and geochemical point of view (Garavelli 1994; Garavelli and Vurro 1994; Vurro et al. 1999; Cheynet et al. 2000; Borodaev et al. 1998, 2000, 2001, 2003; Garavelli et al. 2005; Pinto et al. 2006a, 2006b, 2006c, 2008, 2011; Mitolo et al. 2009, 2011). Sublimates and encrustations were collected directly from the ground, but also by means of quartz tubes inserted as deep as possible into the fumarolic vents (Cheynet et al. 2000; Garavelli et al. 1997). Volcanic fluids vented freely through the tubes and gradually deposited sublimates on the tube inner walls. In this way we could

collect a large variety of volcanic sublimates, some of which are known as minerals, others not; the latter have been considered new potential minerals. Of particular interest was the finding, in the sampling tubes, of an unidentified compound containing As, Cl, and S in typical rose-like aggregates of hexagonal crystals. We suspected that the lack of this phase among sublimates collected from the ground was due to its metastability. In any case, we never stopped looking for this phase among sublimates from the ground, with no success until the discovery of a similar phase containing As and Cl, with no sulfur but with K, NH₄, and O: here it is; lucabindiite!

The mineral and its name were approved by the IMA Commission on New Minerals, Nomenclature and Classification, CNMNC (2011-010). It was named “lucabindiite” in honor of Luca Bindi (b. 1971), Professor of Mineralogy and former Head of the Division of Mineralogy of the Natural History Museum of the University of Florence, in acknowledgment of his major contribution to the study of the structural complexity in minerals (i.e., incommensurate structures, superstructures, twinned structures), integrating together mineralogy and the most advanced fields of crystallography. In the most recent years, he covered the field of quasicrystals. In this context of investigations, his recent discovery of the first natural quasicrystal, icosahedrite (Bindi et al. 2009, 2011, 2012; Bindi and Steinhardt 2012), is remarkable.

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The holotype of lucabindiite is deposited in the mineral collection of the Museum “C.L. Garavelli”, Dipartimento di Scienze della Terra e Geoambientali, Università di Bari, Italy, under the catalog number 11/nm-V28.

OCCURRENCE AND PHYSICAL PROPERTIES

Lucabindiite was found as a fumarole encrustation collected in 1998, during a sampling trip at the “La Fossa” crater (Vulcano island, Aeolian archipelago, Italy), from the fumarole F1 ($T = 170\text{ }^\circ\text{C}$), sited on the crater rim of the volcano (Fig. 1). The micrometer-sized, hexagonal, and platy crystals, were directly deposited on the surface of the pyroclastic breccia of the “La Fossa” cone, and were covered by a vitreous reddish crust containing mainly sulfur and arsenic. Associated minerals are sal ammoniac, sulfur, and an amorphous arsenic-rich sulfurite (Fig. 2). Arsenolite (Fig. 3), was found in the same sample in which lucabindiite occurs, but no clear paragenetic relation between the two arsenic minerals could be observed. Geological and metallogenic data for the “La Fossa” crater area are given in previous papers (Garavelli et al. 1997; Campostrini et al. 2011 and references therein). Individual single crystals of lucabindiite are very rare. Generally, the mineral occurs as aggregates of minute, hexagonal, and platy crystals (Figs. 4 and 5) up to $70 \times 70 \times 3\text{ }\mu\text{m}$ in size. The very small dimensions, as well as the softness and friability of the crystals, made it difficult to handle the crystals of the new phase and to measure some of its physical properties.

Lucabindiite is colorless to white in color, with a white streak and a vitreous luster. Minute crystals are transparent to translucent. Unfortunately, the direct measure of refractive index could not be done due to the minute size of the crystals available. The mean refractive index was calculated using the method proposed by Korotkov and Atuchin (2008). Taking into account the empirical chemical formula, the mean refractive index of lucabindiite should be 1.88. This is in good agreement with the value of 1.92 obtained using the method proposed by Mandarino (1981).

Density was not measured because of the scarcity of available material; the calculated density is 3.68 g/cm^3 .

Lucabindiite is brittle. No cleavage, parting or fracture could be observed. Mohs hardness could not be directly measured because of the small crystal size.

CHEMICAL AND SPECTROSCOPIC STUDIES

The presence of ammonium in lucabindiite was first suspected, and later proved by combining SEM-EDS chemical analysis, crystal structure solution and FTIR spectroscopy. At a first step, the chemical analyses showed the presence of K, As, Cl, Br, and F as the only significant elements. The crystal structure study then indicated a formula close to stoichiometric KAs_4O_6Cl , but with a deficit on the occupancy of the K site (and thus a deficit of positive charges), suggesting the additional presence of another monovalent cation. Ammonium was considered as the most probable candidate. At Vulcano island the abundance of ammonium minerals has been reported since the end of the last eruption in 1888–1890 (Panichi 1924 and references therein), and in more recent years a notable quantity of ammonium minerals have been investigated and/or identified (Garavelli and Vurro 1994; Coradossi et al. 1996; Demartin et al.

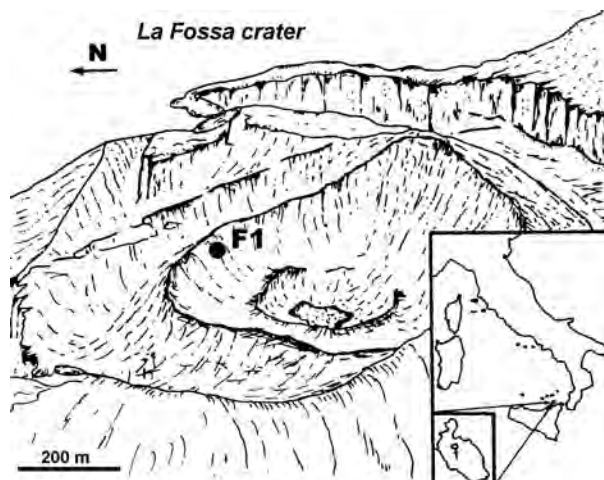


FIGURE 1. Location of fumarole F1 at Vulcano: the sampling site of lucabindiite.

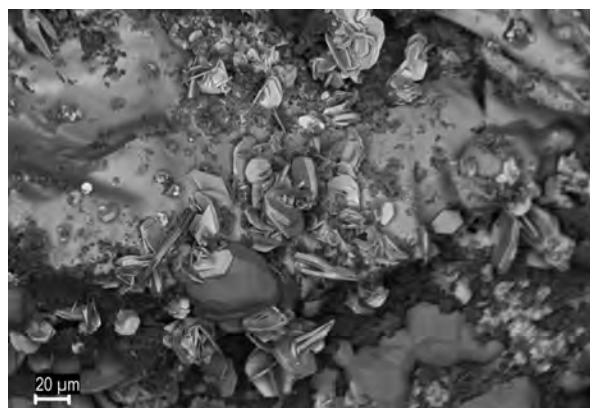


FIGURE 2. SEM-BSD image of lucabindiite aggregates with well formed sulfur crystals on an amorphous arsenic-rich sulfurite.

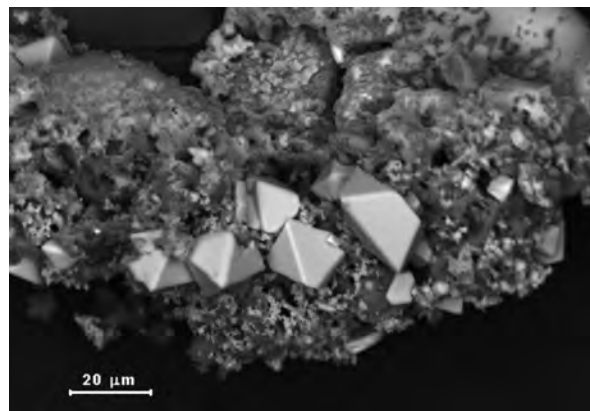


FIGURE 3. SEM-BSD image of arsenolite crystals, As_2O_3 , associated with rare plates of lucabindiite on a base of amorphous arsenic-rich sulfurite.

2009a, 2009b; Campostrini et al. 2010; Demartin et al. 2010a, 2010b, 2012; Mitolo et al. 2013). A subsequent FTIR study on lucabindiite confirmed qualitatively the presence of NH_4^+ ions.

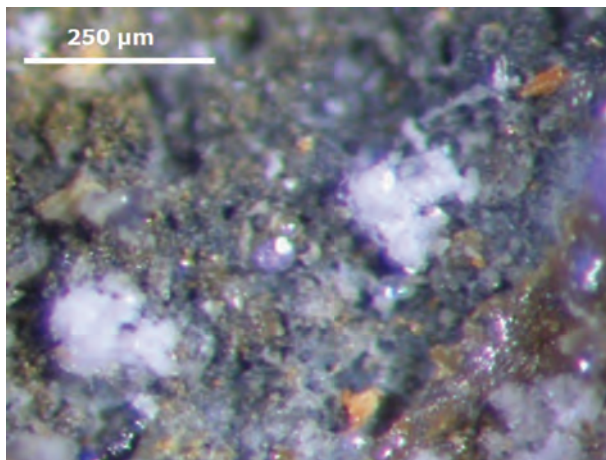


FIGURE 4. Microscope-optical image of transparent-white aggregates of lucabindiite crystals associated with a reddish arsenic-rich sulfidite. (Color online.)

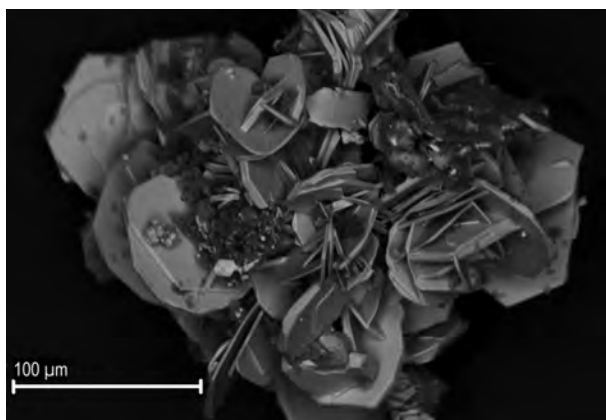


FIGURE 5. SEM-BSD image of an aggregate of lucabindiite crystals.

SEM-EDS chemical analyses

Quantitative chemical analyses were obtained by SEM-EDS methods. The instrument used for this research was a S360 Cambridge scanning electron microscope coupled with an Oxford-Link Ge ISIS energy-dispersive spectrometer equipped with a Super Atmosphere Thin Window, since this allows better detection of light elements. An ED spectrometer was chosen for quantitative analyses of the small sized crystals instead of a WD detector. The investigated sample consisted of a lucabindiite crystal aggregate, 100 μm in size (Fig. 5), sputtered with a 30 nm thick carbon film. Operating conditions were: 15 kV accelerating potential, 500 pA probe current, 2500 cps as average count rate on the whole spectrum, typical counting time 100 s. X-ray intensities were converted to wt% by ZAF4/FLS quantitative analysis software support of Oxford-Link Analytical (U.K.). This allows to match the peaks (heights and areas) of the standards with the ones of the analyzed mineral, taking into account the relative contribution of the matrix and also partial or complete overlaps among peaks of different elements. The ED detector gives accurate analyses of small volumes of investigated sample also with a probe current lower than 1 nA. Moreover the ED

detector gives good results also when collecting X-rays emitted from a non perfectly flat surface of the specimen: this is due to its capability to give quantitative analytical data also with a “non-critical” working distance (Ruste 1979; Acquafredda and Paglionico 2004). The standards employed were: orthoclase (K), halite (Cl), synthetic InAs (As), synthetic KBr (Br), and synthetic LiF (F). The analytical results (mean of 12 analyses) are represented in Table 1. The empirical chemical formula, calculated on the basis of 7 anions per formula unit, is [(K_{0.51}(NH₄)_{0.49})_{Σ1.00}As_{4.00}O_{5.93}(Cl_{0.48}Br_{0.40}F_{0.19})_{Σ1.07}]. The ammonium content was deduced from the K content, taking into account the (K,NH₄)As₄O₆(Cl,Br) stoichiometry (K+NH₄ = 1 apfu). The presence of ammonium was confirmed by FTIR spectroscopy and from the structure refinement. The simplified formula of lucabindiite is (K,NH₄)As₄O₆(Cl,Br), which requires: K₂O 4.89, (NH₄)₂O 2.70 As₂O₃ 82.10, Cl 3.68, Br 8.29 O=Cl,Br 1.66, total 100.00 wt%.

FTIR spectroscopy

The infrared spectrum of lucabindiite was collected in the range of 4000–400 cm⁻¹ using a Nicolet Avatar FTIR spectrometer with a nominal resolution of 4 cm⁻¹, equipped with a Continuum microscope, a MCT nitrogen-cooled detector, and a KBr beamsplitter. The measurement was performed on a single crystal mounted on glass capillary. The observed IR-patterns resulted from the average of 400 scans. The single-crystal FTIR spectra provided evidence for the presence of ammonium in the lucabindiite structure (Farmer 1974). The NH₄⁺ stretching regions (3350–2750 and 1550–1250 cm⁻¹) were modeled using the program PeakFit (by Jandel Scientific), assuming Gaussian functions to describe the peak shape as $y = A \exp[-0.5(x - P/W)^2]$ where A is the amplitude, P is the peak centroid, and W is the full-width at half maximum (FWHM).

Figure 6 illustrates the FTIR spectra of the lucabindiite crystal in the range of 4000–800 cm⁻¹. Band position and FWHM were derived from the interactive optimization and least-squares refinement of the digitized IR absorption spectra.

Band assignments for vibrational features are given in Table 2. In the 3350–1250 cm⁻¹ region, a group of well-defined bands

TABLE 1. SEM-EDS chemical data for lucabindiite (average of 12 point analyses)

Constituent	wt%	Range	St.dev.
K ₂ O	5.14	3.67–6.70	0.70
As ₂ O ₃	84.71	80.52–88.84	2.90
Cl	3.63	1.90–5.81	1.41
Br	6.92	3.70–10.31	2.24
F	0.77	0.27–1.21	0.27
(NH ₄) ₂ O*	2.73	1.72–3.13	0.35
	103.90		
O=F,Cl,Br	-1.84		
Total	102.06		

*The ammonium content was deduced from the K content, taking into account the (K,NH₄)As₄O₆(Cl,Br) stoichiometry (K+NH₄ = 1 apfu).

TABLE 2. Band position and assignment for the bands in the FTIR spectrum of the lucabindiite single crystal

Position (cm ⁻¹)	Absorbance (a.u.)	Assignment NH ₄ ⁺
3257	0.608	ν ₃
3159	0.434	2ν ₂
3045	0.389	ν ₂ + ν ₄
2926	0.303	ν ₁
2850	0.280	2ν ₄
1417	0.716	ν ₄

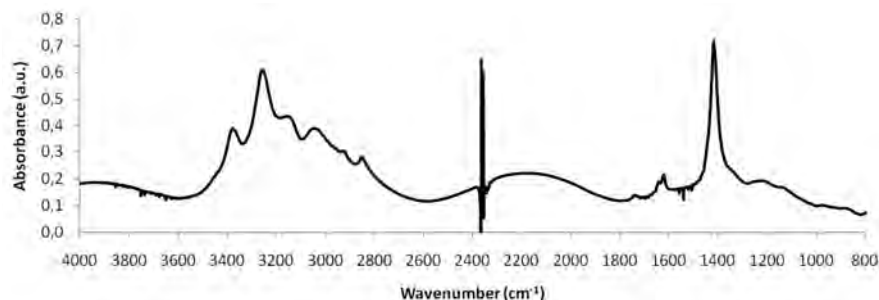


FIGURE 6. FTIR spectrum of lucabindiite in the range 4000–800 cm⁻¹.

at 3257, 3159, 3045, 2926, 2850, and 1417 cm⁻¹ were assigned to ν NH₄⁺ vibrations (Fig. 7, Table 2, Farmer 1974). The additional band at 3375 cm⁻¹ could be related to a minor OH⁻ incorporation.

X-RAY DIFFRACTION STUDIES

X-ray powder diffraction

Gandolfi powder-pattern for lucabindiite (Table 3) was obtained using a CCD-equipped single-crystal diffractometer (CuK α radiation). Calculated powder pattern and indexing of the reflections was done on the basis of $a = 5.2386(7)$ Å, $c = 9.014(2)$ Å, and with the atomic coordinates and occupancies reported in Table 4. Intensities were calculated using XPOW software version 2.0 (Downs et al. 1993).

The refined unit-cell parameters, based on 15 reflections between 4.54 and 1.310 Å, are: $a = 5.2372(2)$ Å, $c = 9.0085(7)$ Å, $V = 213.98(2)$ Å³.

Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data were collected from a selected crystal fragment (110 × 150 × 50 μ m) using a Bruker AXS X8 APEX2 CCD automated diffractometer equipped with a κ -geometry goniometer and graphite monochromated MoK α radiation (50 kV and 30 mA operating conditions). The *Miracol* fiber optics capillary collimator (0.3 mm size) was used to enhance the intensity of the MoK α radiation and to reduce X-ray beam divergence. Five sets of 19 frames were used for initial cell determination, whereas complete data collection was accomplished by several φ and ω scans with 0.5° frame width, 120 s exposure time per frame and a crystal-to-detector distance of 40 mm. The collection strategy was optimized by the Apex suite program (Bruker 2003a). Details about data collection and refinement are summarized in Table 5.

Data reduction, including intensity integration, correction for Lorentz, polarization, background effects, and scale variation, was done using the package SAINT-IRIX (Bruker 2003b). A semi-empirical absorption correction (Blessing 1995) was applied using the SADABS program (Sheldrick 2008). The minimum and maximum X-ray transmission-factors were 0.4136 and 0.7454, respectively.

The structure refinement was performed in the space group $P6/mmm$ using the SHELX program (Sheldrick 2008), starting from the atomic coordinates of synthetic KAs₄O₆Cl (Pertlik 1988). Indeed the synthetic compounds MAs_4O_6X ($M = K, NH_4$; $X = Cl, Br, I$) described by Pertlik (1988) were ascribed to the acentric space group $P622$, although there was no clear reason

given as to why the crystal-structures of these compounds should be non-centrosymmetric.

Taking into account the results of chemical data, the two substitutions $K^+ \leftrightarrow NH_4^+$ and $Cl^- \leftrightarrow (Br^-, F^-)$ were considered during the structure refinement. The presence of NH₄⁺ substituting for K⁺ was confirmed by the refinement although it was not possible to locate the H atoms of the NH₄⁺ group. Refinement of the occupancy of the *M* site gave 0.52(4) K and 0.48(4) NH₄, in good agreement with the chemical data. The occupancies for Cl, Br, and F were assigned in the anion site *X* on the basis of the

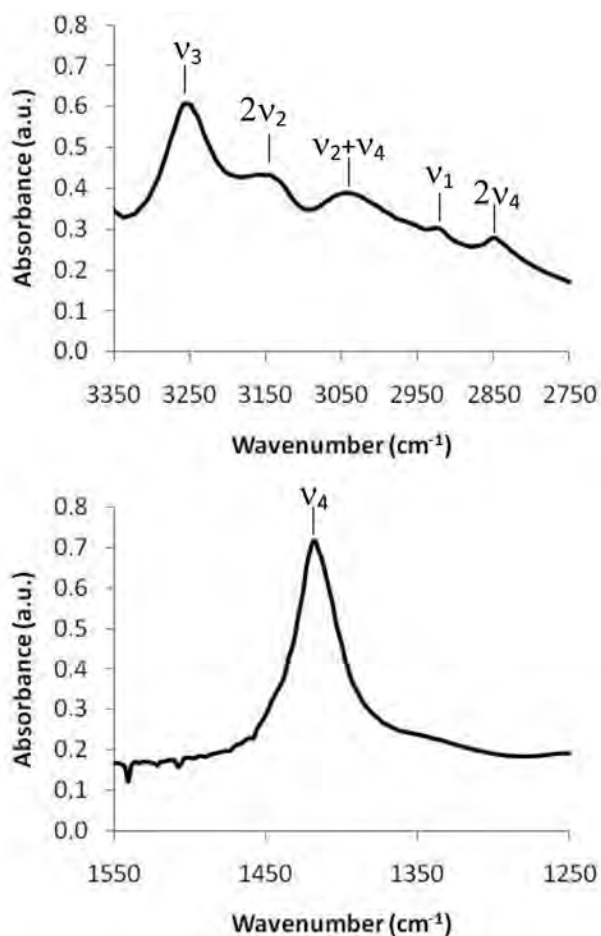


FIGURE 7. Detailed FTIR spectra of lucabindiite with absorption bands due to NH₄⁺.

TABLE 3. X-ray powder diffraction pattern for lucabindiite

<i>hkl</i>	<i>d</i> _{calc} (Å)	<i>I</i> _{calc}	<i>d</i> _{obs} (Å)	<i>I</i> _{meas}
001	9.0140	16.30	—	—
100	4.5368	30.49	4.54(1)	35
002	4.5070	51.64	4.50(1)	50
102	3.1974	100.00	3.200(3)	100
003	3.0047	4.33	—	—
110	2.6193	66.57	2.613(4)	60
111	2.5153	14.14	2.516(4)	10
103	2.5051	11.28	2.501(5)	10
112	2.2646	18.89	2.262(4)	20
004	2.2535	4.35	—	—
202	2.0262	8.78	2.021(3)	5
113	1.9744	28.01	1.973(2)	25
203	1.8104	15.97	1.809(3)	15
005	1.8028	3.45	—	—
210	1.7147	3.81	—	—
114	1.7083	9.42	1.707(3)	10
105	1.6754	3.13	—	—
212	1.6027	20.28	1.602(2)	20
300	1.5123	11.04	1.513(2)	10
213	1.4893	4.67	—	—
115	1.4850	20.99	1.486(1)	20
302	1.4337	4.65	—	—
205	1.4114	5.78	—	—
303	1.3508	6.93	—	—
220	1.3096	10.34	1.310(1)	10
222	1.2576	5.47	—	—
312	1.2119	6.81	—	—
305	1.1586	8.37	—	—
117	1.1556	4.69	—	—
225	1.0596	3.91	—	—
322	1.0141	3.89	—	—
410	0.9900	5.57	—	—
307	0.9804	3.05	—	—
218	0.9417	3.01	—	—
413	0.9403	4.77	—	—
415	0.8678	10.69	—	—
1.1.10	0.8523	5.64	—	—
318	0.8394	3.39	—	—

results of the chemical analysis as the simultaneous refinement of these three atoms in the same position is not expected to give any reliable result.

The refinement converged to the agreement *R* value of 0.0384 for 136 reflections with $F_o > 4\sigma(F_o)$ [$R = 0.0617$ for all the 174 unique reflections]. Scattering factors for neutral atoms were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). In the final refinement anisotropic displacement factors were used for all the atoms.

Fractional atomic coordinates, occupancies, and anisotropic displacement parameters are presented in Table 4, whereas selected interatomic distances are in Table 6.

The CIF file with structure data of lucabindiite can be download from the *Inorganic Crystal Structure Database* at FIZ Karlsruhe, Germany (CSD number 424826). (CIF is also available on deposit¹.)

DESCRIPTION OF THE STRUCTURE AND RELATION WITH SYNTHETIC SPECIES

The crystal structure of lucabindiite is topologically identical to that of the synthetic compounds MA_sO_6X ($M = K, NH_4; X$

TABLE 4. Fractional atomic coordinates, anisotropic displacement parameters, and occupancies for lucabindiite

Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> _{eq}
<i>M</i>	0	0	1/2	0.041(5)	0.041(5)	0.047(9)	0.020(3)	0.043(5)
<i>As</i>	1/3	2/3	0.7969(2)	0.0078(4)	0.0078(4)	0.0278(8)	0.0039(2)	0.0145(4)
<i>O</i>	1/2	0	0.6894(9)	0.0165(5)	0.007(3)	0.031(4)	0.003(1)	0.019(2)
<i>X</i>	0	0	0	0.0206(16)	0.0206(16)	0.069(5)	0.0103(8)	0.037(2)

Notes: The anisotropic displacement parameters are defined as: $\exp[-2\pi^2\sum_i \sigma_i^2 = \sum_{ij} a_i^* a_j^* h_i h_j]$, U_{eq} according to Fischer and Tillmanns (1988). U_{23} and U_{13} are equal to 0. Sites scattering: $M = 0.52(4)$ K, $0.48(4)$ NH₄ (from the refinement); $X = 0.5$ Cl, 0.3 Br, 0.2 F (fixed on the basis of the chemical data).

TABLE 5. Summary of parameters describing data collection and refinement for lucabindiite

Empirical structural formula	[K _{0.52} (NH ₄) _{0.48}]As ₄ O ₆ (Cl _{0.5} Br _{0.3} F _{0.2})
Crystal dimensions (mm)	0.05 x 0.11 x 0.15
Crystal system, space group	Hexagonal, <i>P6/mmm</i>
<i>a</i> (Å)	5.2386
<i>c</i> (Å)	9.014(2)
<i>V</i> (Å ³)	214.23(7)
<i>Z</i>	1
Temperature (K)	293
<i>D</i> _x (g/cm ³)	3.645
X-ray conditions (kV, mA)	50, 30
Wavelength of radiation (Å)	0.71073
Detector to sample distance (mm)	40
Number of frames	1095
Rotation width per frame (°)	0.5
Measuring time (s)	120
Maximum covered 2θ (°)	61 ($d = 0.70 \text{ \AA}$)
Independent reflections	174
Reflections with $F_o > 4\sigma(F_o)$	136
<i>R</i> _{int}	0.0998
<i>R</i> _σ	0.0392
Ranges of <i>h, k, l</i>	-6 ≤ <i>h</i> ≤ 7 -7 ≤ <i>k</i> ≤ 5 -12 ≤ <i>l</i> ≤ 12
<i>R</i> [$F_o > 4\sigma(F_o)$]	0.0384
<i>R</i> (all data)	0.0617
w <i>R</i> [$F_o > 4\sigma(F_o)$]	0.0969
w <i>R</i> (all data)	0.1102
Goof	1.15
Refined parameters	13
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 1.0076P]$ where $P = [\max(F_o)^2 + 2(F_o)^2]/3$
<i>Dp</i> _{min} <i>Dp</i> _{max} (e/Å ³)	-1.58, 3.06

TABLE 6. Selected interatomic distances (Å) and angles (°) in lucabindiite

	This study		Pertlik (1988)			
	lucabindiite	KAs ₄ O ₆ Cl	KAs ₄ O ₆ Br	NH ₄ As ₄ O ₆ Br	NH ₄ As ₄ O ₆ I	
M-O (12x)	3.127(5)	3.104(3)	3.097(2)	3.109(2)	3.158(1)	3.165(2)
As-O (3x)	1.796(5)	1.795(2)	1.805(2)	1.807(2)	1.801(1)	1.806(2)
O-O (3x)	2.619(1)	2.626(2)	2.629(2)	2.640(9)	2.632(1)	2.645(2)
X-As (12x)	3.535(1)	3.538(3)	3.561(2)	3.631(2)	3.564(1)	3.632(2)
O-As-O (3x)	93.6(3)	94.01(1)	93.45(9)	93.86(9)	93.87(9)	94.15(8)

= Cl, Br, I) reported by Pertlik (1988). The structure (Fig. 8) is characterized by (001) layers consisting of neutral As₂O₃ sheets. Each As₂O₃ sheet is formed by AsO₃ pyramids connected by shared oxygen atoms. The As atoms of two neighboring sheets point at each other and the sheets are connected by interlayer *M* (=K, NH₄) and *X* (=Cl, Br, F) atoms. The *M* atoms are coordinated to 12 O atoms in the form of a regular hexagonal prism, with *M*-O distances almost intermediate between K-O and NH₄-O distances (Table 6) in the synthetic phases described by Pertlik (1988). As the symmetry of the *M* site is higher than the symmetry of an NH₄ molecule, Pertlik (1988) suggested that each H atom is statistically distributed over at least three symmetry equivalent sites in the structure framework of the NH₄As₄O₆X ($X = Cl, Br,$

¹ Deposit item AM-13-018, data set and CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

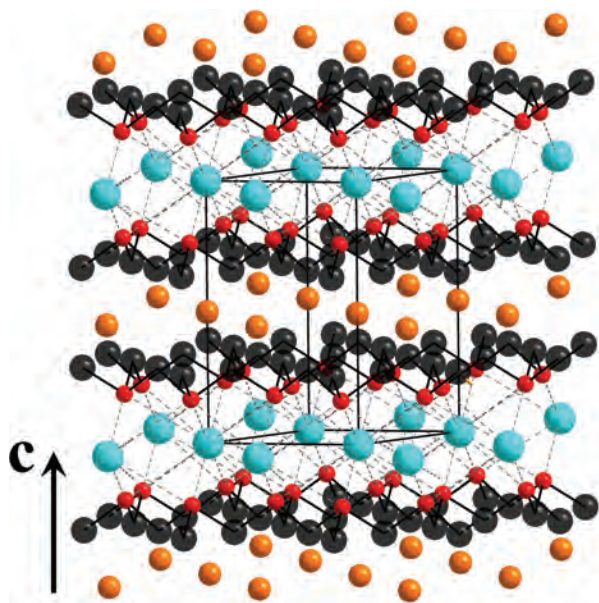


FIGURE 8. The crystal structure of lucabindiite. In order of decreasing size : *X* (light blue), O (dark), *M* (orange), and As (red) atoms. Dashed bonds indicate long As-(Cl,Br) contacts. (Color online.)

D) compounds. This explains the impossibility to locate the H atoms of the NH₄⁺ group by X-ray diffraction.

The apices of the As₂O₃ sheets, the As atoms, point toward the *X* atoms, and 12 As atoms form the first coordination sphere around the *X* atoms (hexagonal prisms). The coordination of As atoms is thus characterized by three typical short As-O distances [1.796(5)] against three opposite long As-X contacts [3.536(1)]. According to Pertlik (1988) the As-O and O-O first-neighbor distances in the *M*As₄O₆*X* compounds (Table 6) are greatly influenced by the site occupancy of *X*. As a matter of fact, Pertlik noticed that both the As-O and O-O distances increase systematically from Cl through Br to I containing compounds, whereas they are equal within limits of error for the compounds containing the same halogen (the two Br in respect to the two I compounds) and independent of the occupancy of the *M* site [note that synthetic NH₄As₄O₆Cl could not be synthesized by Pertlik (1988) and therefore no structural data are known for it]. The above evidence suggests that the values of the As-O and O-O distances observed

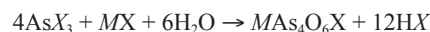
in the structure of lucabindiite, which are practically equal to those of the compound KAs₄O₆Cl (Table 6), are related to the simultaneous occurrence of F and Br, in addition to Cl, in the *X* site. The same is also true for the *X*-As bond lengths (Table 6). As expected, in the *M*As₄O₆*X* compounds the *X*-As distances increase systematically from Cl through Br to I containing compounds and are not influenced by the occupancy of *M* (Pertlik 1988). The values of *X*-As distances in the structure of lucabindiite are very close to those of the compound KAs₄O₆Cl.

GENETIC FEATURES AND DISCUSSION

Lucabindiite, ideally (K,NH₄)As₄O₆(Cl,Br), is an arsenic oxychloride, which was found as a sublimate phase at “La Fossa” crater, Vulcano islands, Aeolian archipelago, Italy. It corresponds to the synthetic phase with general formula *M*As₄O₆*X* (Pertlik 1988), where *M* = K, NH₄ and *X* = Cl, Br, I. In Table 7, chemical and crystallographic data of lucabindiite are compared with those of the related synthetic phases (Pertlik 1988).

In laboratory, the synthetic analogues of lucabindiite were obtained by thermal treatments of cubic As₂O₃ and potassium or ammonium halides in a saturated aqueous solution of potassium acetate or ammonia (Pertlik 1988). Although both arsenolite and K and NH₄ halides are present at Vulcano, it is not probable that lucabindiite formed by a similar reaction, for which an earlier formation of arsenolite, As₂O₃, is required. As a matter of fact, arsenolite was found in association with lucabindiite (Fig. 3), but it was not in a clear paragenetic sequence with the new mineral. On the contrary, their mode of appearance suggests a simultaneous deposition of the two arsenic phases.

At Vulcano, the lucabindiite and arsenolite occurrence is most probably due to the simultaneous presence in the steam of hydrogen halogenides and arsenic, whose transport as AsCl₃ has been hypothesized to happen in the La Fossa crater fumaroles (Garavelli et al. 1997). In this context, possible reactions explaining their formation in the cooling of the halogen-rich volcanic gases are:



or

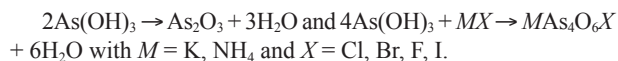


TABLE 7. Crystal lattice parameters of lucabindiite and the strongest powder diffraction lines compared with those of the related synthetic phases

Chemical formula	This study	Pertlik (1988)				
	[K _{0.51} (NH ₄) _{0.45}] _{Σ10.96} As _{4.01} O _{5.95} (Cl _{0.48} Br _{0.41} F _{0.19}) _{Σ1.08}	KAs ₄ O ₆ Cl	KAs ₄ O ₆ Br	KAs ₄ O ₆ I	NH ₄ As ₄ O ₆ Br	NH ₄ As ₄ O ₆ I
Space group	<i>P6/mmm</i>	<i>P622</i>	<i>P622</i>	<i>P622</i>	<i>P622</i>	<i>P622</i>
Unit-cell parameters (Å)	<i>a</i> = 5.2386(7) <i>c</i> = 9.014(2)	<i>a</i> = 5.252(1) <i>c</i> = 8.880(2)	<i>a</i> = 5.257(1) <i>c</i> = 8.955(2)	<i>a</i> = 5.281(1) <i>c</i> = 9.169(2)	<i>a</i> = 5.265(1) <i>c</i> = 9.148(2)	<i>a</i> = 5.290(1) <i>c</i> = 9.338(2)
Strongest powder lines <i>d</i> (Å)// (related to 10)	9.014/2 4.537/3 4.507/5 3.197/10 2.619/7 2.265/2 1.974/3 1.603/2 1.485/2	4.548/3 4.440/5 3.177/10 2.626/6 2.260/2 1.964/3	8.955/2 4.477/3 3.192/10 2.628/5 1.606/2	9.169/2 3.238/10 2.640/5 2.537/2 1.617/2	9.148/5 4.574/5 4.560/5 3.230/10 2.632/6 2.530/3 1.826/2	9.338/6 4.669/2 4.113/2 3.270/10 2.645/5 2.575/2 2.545/2

Arsenic minerals at Vulcano are relatively abundant. The occurrence of orpiment, As_2S_3 , and realgar, As_4S_4 , has been reported for the area by several authors throughout the nineteenth and the first 20 yr of the twentieth century (Stromeyer 1824; Sainte-Claire Deville 1856; Jervis 1873; Bellini 1918; Panichi 1924), but modern investigations (Campostrini et al. 2011 and references therein) do not confirm their presence. On the contrary, an amorphous arsenic-rich sulfurate, often containing selenium and/or tellurium, is still very abundant today around medium temperature fumaroles and has been often described (Garavelli 1958, 1994; Campostrini et al. 2011). Solid phases containing As-S-Cl that look morphologically very similar to lucabindiite have been found as sublimate collected in silica sampling tubes deeply inserted in high-temperature fumarole vents at Vulcano (Garavelli 1994; Garavelli et al. 1997). It is not excluded that such phases could be related to lucabindiite by a substitution of S-O in the structure and the total substitution of NH_4 in place of K. This hypothesis is also supported by our recent finding of several “lucabindiites” from the ground around fumarole F5AT (sampling year 2009) containing As, but no traces of K, I, and Br substituting for Cl, and/or S partially substituting for O. Investigations on these phases are still in progress. Around high-temperature fumaroles of Vulcano, further minerals containing arsenic are represented by sulfosalts like kirkiite, $Pb_{10}(Bi, As)_6(S, Se)_{19}$ (Borodaev et al. 1998) and vuroite $Pb_{20}Sn_2(Bi, As)_{22}S_{54}Cl_{16}$ (Garavelli et al. 2005), whose occurrence is related both to the high fugacity of sulfur and to the high activity of hydrogen halogenides in fumarolic fluids discharging from fumaroles (Borodaev et al. 1998; Garavelli et al. 1997).

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MANUSCRIPT RECEIVED MARCH 28, 2012

MANUSCRIPT ACCEPTED OCTOBER 9, 2012

MANUSCRIPT HANDLED BY ANDREW McDONALD

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_computing_molecular_graphics	?
_computing_publication_material	?

```

_refine_special_details
;
Refinement of F^2^ against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F^2^, conventional R-factors R are based
on F, with F set to zero for negative F^2^. The threshold expression of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type          full
_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.0608P)^2^+1.0076P] where P=(Fo^2^+2Fc^2^)/3'
```

_atom_sites_solution_primary	direct
_atom_sites_solution_secondary	difmap
_atom_sites_solution_hydrogens	'.'
_refine_ls_hydrogen_treatment	'none'
_refine_ls_extinction_method	none
_refine_ls_extinction_coef	?
_refine_ls_number_reflns	174
_refine_ls_number_parameters	13
_refine_ls_number_restraints	0

_refine_ls_R_factor_all	0.0617
_refine_ls_R_factor_gt	0.0384
_refine_ls_wR_factor_ref	0.1102
_refine_ls_wR_factor_gt	0.0969
_refine_ls_goodness_of_fit_ref	1.150
_refine_ls_restrained_S_all	1.150
_refine_ls_shift/su_max	0.000
_refine_ls_shift/su_mean	0.000

loop_

_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group

As1	As	0.3333	0.6667	0.20309(16)	0.0145(4)	Uani	1	6	d	S	.	.	.
O	O	0.5000	0.0000	0.3106(10)	0.0192(16)	Uani	1	4	d	S	.	.	.
K	K	0.0000	0.0000	0.5000	0.043(5)	Uani	0.52(5)	24	d	SP	.	.	.
N	N	0.0000	0.0000	0.5000	0.043(5)	Uani	0.48(5)	24	d	SP	.	.	.
Br1	Br	0.0000	0.0000	0.0000	0.0366(16)	Uani	0.30	24	d	SP	.	.	.
Cl1	Cl	0.0000	0.0000	0.0000	0.0366(16)	Uani	0.50	24	d	SP	.	.	.
F1	F	0.0000	0.0000	0.0000	0.0366(16)	Uani	0.20	24	d	SP	.	.	.

loop_

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_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12

As1	0.0078(4)	0.0078(4)	0.0278(8)	0.000	0.000	0.0039(2)
O	0.016(2)	0.007(3)	0.031(4)	0.000	0.000	0.0034(15)
K	0.041(5)	0.041(5)	0.047(9)	0.000	0.000	0.020(3)
N	0.041(5)	0.041(5)	0.047(9)	0.000	0.000	0.020(3)
Br1	0.0206(16)	0.0206(16)	0.069(5)	0.000	0.000	0.0103(8)
Cl1	0.0206(16)	0.0206(16)	0.069(5)	0.000	0.000	0.0103(8)
F1	0.0206(16)	0.0206(16)	0.069(5)	0.000	0.000	0.0103(8)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

;

loop_

_geom_bond_atom_site_label_1
_geom_bond_atom_site_label_2
_geom_bond_distance
_geom_bond_site_symmetry_2
_geom_bond_publ_flag
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As1 O 1.796(5) 3 ?
As1 O 1.796(5) 2 ?
O As1 1.796(5) 1_545 ?
O As1 1.796(5) 2_655 ?
O K 3.127(5) 1_655 ?
O K 3.127(5) . ?
K O 3.127(5) 14_666 ?
K O 3.127(5) 2_445 ?
K O 3.127(5) 15_566 ?
K O 3.127(5) 3_545 ?
K O 3.127(5) 13_656 ?
K O 3.127(5) 1_455 ?
K O 3.127(5) 2 ?
K O 3.127(5) 14_556 ?
K O 3.127(5) 13_556 ?
K O 3.127(5) 3 ?
K O 3.127(5) 15_556 ?

loop_

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_geom_angle_atom_site_label_2
_geom_angle_atom_site_label_3
_geom_angle
_geom_angle_site_symmetry_1
_geom_angle_site_symmetry_3
_geom_angle_publ_flag
O As1 O 93.6(3) 1_565 3 ?
O As1 O 93.6(3) 1_565 2 ?
O As1 O 93.6(3) 3 2 ?
As1 O As1 114.7(5) 1_545 2_655 ?
As1 O K 107.13(6) 1_545 1_655 ?
As1 O K 107.13(6) 2_655 1_655 ?
As1 O K 107.13(6) 1_545 . ?
As1 O K 107.13(6) 2_655 . ?
K O K 113.8(3) 1_655 . ?
O K O 180.0 14_666 2_445 ?
O K O 49.53(8) 14_666 15_566 ?
O K O 130.47(8) 2_445 15_566 ?
O K O 130.47(8) 14_666 3_545 ?
O K O 49.53(8) 2_445 3_545 ?
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O K O 49.53(8) 14_666 13_656 ?
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O K O 86.98(19) 3_545 13_656 ?
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O K O 93.02(19) 3_545 1_455 ?
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O K O 113.8(3) 2_445 2 ?
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O K O 93.02(19) 3_545 2 ?
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O K O 66.2(3) 2_445 14_556 ?
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O K O 86.98(19) 3_545 14_556 ?
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O K O 93.02(19) 14_666 13_556 ?
O K O 86.98(19) 2_445 13_556 ?
O K O 49.53(8) 15_566 13_556 ?
O K O 130.47(8) 3_545 13_556 ?
O K O 113.8(3) 13_656 13_556 ?
O K O 66.2(3) 1_455 13_556 ?
O K O 130.47(8) 2 13_556 ?
O K O 49.53(8) 14_556 13_556 ?
O K O 86.98(19) 14_666 . ?
O K O 93.02(19) 2_445 . ?
O K O 130.47(8) 15_566 . ?
O K O 49.53(8) 3_545 . ?
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O K O 113.8(3) 1_455 . ?
O K O 49.53(8) 2 . ?
O K O 130.47(8) 14_556 . ?
O K O 180.0 13_556 . ?
O K O 86.98(19) 14_666 3 ?
O K O 93.02(19) 2_445 3 ?
O K O 66.2(3) 15_566 3 ?
O K O 113.8(3) 3_545 3 ?
O K O 130.47(8) 13_656 3 ?
O K O 49.53(8) 1_455 3 ?
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O K O 130.47(8) 14_556 3 ?
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O K O 93.02(19) . 3 ?
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O K O 86.98(19) 2_445 15_556 ?
O K O 113.8(3) 15_566 15_556 ?
O K O 66.2(3) 3_545 15_556 ?
O K O 49.53(8) 13_656 15_556 ?
O K O 130.47(8) 1_455 15_556 ?
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O K O 49.53(8) 14_556 15_556 ?
O K O 93.02(19) 13_556 15_556 ?
O K O 86.98(19) . 15_556 ?
O K O 180.0 3 15_556 ?

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_diffraction_reflns_theta_full	30.31
_diffraction_measured_fraction_theta_full	1.000
_refine_diff_density_max	3.062
_refine_diff_density_min	-1.583
_refine_diff_density_rms	0.293

List of observed and calculated structure factors (to be deposited)

<u>refln_index_h</u>	<u>refln_index_k</u>	<u>refln_index_l</u>	<u>refln_F_squared_calc</u>	<u>refln_F_squared_meas</u>	<u>refln_F_squared_sigma</u>	<u>refln_observed_status</u>
0	1	0	1963.26	2002.78	41.18	o
-1	2	0	13581.21	15202.77	275.19	o
0	2	0	14.02	28.90	7.88	o
-1	3	0	1180.41	1300.56	25.51	o
0	3	0	8333.62	8777.28	195.61	o
-2	4	0	10778.05	11345.43	221.51	o
-1	4	0	888.16	938.09	30.76	o
0	4	0	91.59	88.10	21.80	o
-2	5	0	599.70	637.11	22.63	o
-1	5	0	3981.19	4003.78	76.98	o
0	5	0	441.76	453.07	48.56	o
-3	6	0	2832.44	2895.69	76.12	o
-2	6	0	91.64	95.14	22.01	o
-1	6	0	411.36	475.49	28.10	o
0	6	0	2793.68	2736.42	115.66	o
-3	7	0	295.88	315.91	29.75	o
-2	7	0	1743.01	1755.96	55.17	o
0	0	1	749.90	655.21	23.78	o
0	1	1	25.69	19.38	5.28	o
-1	2	1	1615.17	1608.03	23.70	o
0	2	1	361.98	371.76	10.75	o
-1	3	1	17.86	20.18	5.16	o
0	3	1	961.14	975.88	31.61	o
-2	4	1	419.62	497.19	24.04	o
-1	4	1	11.20	26.67	8.55	o
0	4	1	95.79	105.58	14.28	o
-2	5	1	11.25	28.33	10.95	o
-1	5	1	489.62	632.21	19.76	o
0	5	1	9.80	15.30	23.59	o
-3	6	1	373.15	485.47	28.61	o
-2	6	1	45.66	53.80	14.64	o
-1	6	1	4.93	20.64	17.48	o
0	6	1	144.87	187.92	28.93	o
-3	7	1	5.66	81.02	20.89	o
-2	7	1	198.47	303.88	25.71	o
0	0	2	9788.41	9752.24	301.72	o
0	1	2	6280.22	5881.73	89.65	o
-1	2	2	2772.64	2546.56	36.83	o
0	2	2	1478.00	1320.33	23.14	o
-1	3	2	3037.58	2978.01	29.95	o
0	3	2	2208.45	2159.62	33.57	o
-2	4	2	3381.44	3328.33	49.37	o
-1	4	2	1923.07	1870.01	23.67	o
0	4	2	741.95	706.57	21.69	o
-2	5	2	1239.08	1216.13	20.48	o
-1	5	2	1272.95	1230.15	24.20	o
0	5	2	855.56	814.03	33.91	o
-3	6	2	958.01	944.26	29.46	o
-2	6	2	393.33	452.39	17.85	o
-1	6	2	678.70	663.79	24.16	o
0	6	2	1081.32	963.07	43.87	o
-3	7	2	475.87	517.42	22.33	o

-2	7	2	662.60	677.85	24.72	o
0	0	3	1932.17	1959.13	120.14	o
0	1	3	1143.82	1055.38	20.98	o
-1	2	3	5289.30	4991.97	67.41	o
0	2	3	3547.12	3434.50	47.01	o
-1	3	3	840.75	785.14	14.07	o
0	3	3	3192.32	3004.00	43.08	o
-2	4	3	1223.52	1202.87	26.17	o
-1	4	3	605.75	605.42	14.50	o
0	4	3	1391.64	1344.01	30.07	o
-2	5	3	498.66	503.20	14.68	o
-1	5	3	1623.37	1556.67	26.30	o
0	5	3	392.28	333.21	23.11	o
-3	6	3	1258.26	1267.70	35.34	o
-2	6	3	727.99	696.66	21.97	o
-1	6	3	255.65	214.47	19.41	o
0	6	3	439.03	469.28	38.60	o
-3	7	3	220.25	197.82	21.43	o
-2	7	3	681.06	642.78	26.84	o
0	0	4	3052.92	3460.57	192.93	o
0	1	4	0.52	-1.67	10.48	o
-1	2	4	2085.26	1990.96	33.44	o
0	2	4	0.45	10.74	9.33	o
-1	3	4	4.29	9.57	8.72	o
0	3	4	1296.14	1294.08	28.59	o
-2	4	4	1108.20	1130.19	26.82	o
-1	4	4	7.84	1.84	10.79	o
0	4	4	5.26	-13.66	15.79	o
-2	5	4	8.99	3.87	12.88	o
-1	5	4	616.64	648.41	18.63	o
0	5	4	9.35	-20.30	20.30	o
-3	6	4	445.58	480.04	31.54	o
-2	6	4	7.09	2.43	16.16	o
-1	6	4	9.74	-18.97	18.97	o
0	6	4	299.55	347.76	42.73	o
-3	7	4	9.20	-17.25	22.62	o
0	0	5	3821.47	4646.20	255.02	o
0	1	5	837.68	780.97	25.34	o
-1	2	5	6438.16	6128.07	88.07	o
0	2	5	2204.60	2101.03	37.60	o
-1	3	5	596.24	589.36	14.86	o
0	3	5	4353.02	4352.23	69.52	o
-2	4	5	2275.26	2217.14	43.02	o
-1	4	5	417.39	440.86	15.04	o
0	4	5	951.08	973.87	29.12	o
-2	5	5	341.20	353.72	15.83	o
-1	5	5	2374.17	2282.47	35.56	o
0	5	5	271.13	267.51	26.17	o
-3	6	5	1851.01	1790.76	50.05	o
-2	6	5	521.33	540.63	21.74	o
-1	6	5	178.33	170.79	20.16	o
0	0	6	1278.93	1349.70	110.41	o
0	1	6	0.54	-17.83	17.83	o
-1	2	6	346.70	316.41	19.27	o
0	2	6	137.27	137.49	19.39	o
-1	3	6	0.02	12.26	13.29	o
0	3	6	240.50	229.37	22.00	o
-2	4	6	474.98	438.08	21.52	o
-1	4	6	0.61	-15.43	15.43	o
0	4	6	39.10	28.48	21.65	o
-2	5	6	0.33	7.48	17.36	o
-1	5	6	111.85	71.64	17.17	o
0	5	6	0.37	-27.36	29.02	o

-3	6	6	74.22	57.60	33.42	o
-2	6	6	15.46	-19.90	19.90	o
-1	6	6	2.29	-21.53	21.64	o
0	0	7	1917.14	2197.94	148.67	o
0	1	7	602.19	644.44	27.04	o
-1	2	7	2219.90	2281.84	54.27	o
0	2	7	850.48	877.16	32.78	o
-1	3	7	449.98	501.06	20.34	o
0	3	7	1569.82	1622.15	50.33	o
-2	4	7	1034.62	1081.49	39.08	o
-1	4	7	333.84	311.33	19.66	o
0	4	7	454.59	496.68	32.98	o
-2	5	7	264.53	194.57	21.57	o
-1	5	7	888.67	905.28	29.13	o
0	5	7	208.63	180.79	32.01	o
-3	6	7	698.86	683.12	43.97	o
-2	6	7	268.61	215.11	25.35	o
0	0	8	1432.44	1726.48	135.54	o
0	1	8	663.87	694.50	35.16	o
-1	2	8	537.90	535.90	31.38	o
0	2	8	154.06	166.98	27.39	o
-1	3	8	455.20	434.16	21.48	o
0	3	8	436.99	444.87	30.37	o
-2	4	8	774.94	822.93	43.75	o
-1	4	8	336.02	320.25	22.83	o
0	4	8	84.38	89.37	33.50	o
-2	5	8	230.70	217.81	25.93	o
-1	5	8	266.57	246.89	24.91	o
0	5	8	166.78	139.37	37.22	o
0	0	9	453.33	566.31	88.68	o
0	1	9	86.18	58.85	32.51	o
-1	2	9	295.10	346.87	34.21	o
0	2	9	36.71	-22.16	29.57	o
-1	3	9	61.74	18.54	22.73	o
0	3	9	228.18	168.17	34.70	o
-2	4	9	257.91	176.32	37.45	o
-1	4	9	46.74	-11.81	23.66	o
0	4	9	20.68	-31.85	37.95	o
-2	5	9	34.13	4.37	27.88	o
-1	5	9	137.45	82.93	27.59	o
0	0	10	1556.03	2173.13	157.42	o
0	1	10	189.09	204.32	37.33	o
-1	2	10	948.22	1236.48	55.01	o
0	2	10	56.44	49.61	40.77	o
-1	3	10	148.91	107.52	27.23	o
0	3	10	722.48	714.59	44.65	o
-2	4	10	867.93	874.50	64.97	o
-1	4	10	122.78	104.52	36.50	o
0	4	10	39.84	15.55	41.91	o
0	0	11	2.48	31.29	87.55	o
0	1	11	0.01	-43.41	43.41	o
-1	2	11	13.64	-6.53	41.43	o
0	2	11	22.73	-43.75	43.75	o
-1	3	11	0.02	-30.13	30.13	o
0	3	11	9.91	-25.77	42.75	o
0	0	12	309.12	78.63	118.84	o
0	1	12	116.23	77.14	69.65	o
-1	2	12	254.36	195.25	51.64	o
0	2	12	88.95	-26.31	59.81	o