

The crystal structure of parnaute: a copper arsenate–sulphate with translational disorder of structural rods

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Abstract: New data for parnaute from the type locality, Majuba Hill, Nevada, USA (MH; type specimen), and also from Cap Garonne, Var, France (CG), and the Clara Mine, Baden-Württemberg, Germany, are presented. The average chemical composition of MH material is $(\text{Cu}_{8.82}\text{Al}_{0.16}\text{Fe}_{0.02})_{\Sigma 9.00}(\text{As}_{1.78}\text{Al}_{0.07}\text{Si}_{0.08}\text{S}_{0.07})_{\Sigma 2.00}\text{O}_8(\text{SO}_4)(\text{OH})_{10} \cdot 7\text{H}_2\text{O}$ and that of CG parnaute, $(\text{Cu}_{8.42}\text{Al}_{0.21}\text{Zn}_{0.10})_{\Sigma 8.73}(\text{AsO}_4)_2[(\text{S}_{0.97}\text{As}_{0.10})_{\Sigma 1.07}\text{O}_4](\text{OH}_{9.23}\text{Cl}_{0.77})_{\Sigma 10.00} \cdot 7\text{H}_2\text{O}$. Both of these formulae confirm the 9:2:1 Cu:As:S ratio obtained from earlier descriptions of parnaute. Raman spectra for parnaute from both localities are very similar. Bands are assigned, but show no evidence of the presence of CO_3 , in contrast to previous studies, and no distinct Cu–Cl stretching mode. It appears that neither the minor CO_3 and PO_4 previously reported nor Cl are essential constituents of parnaute.

Single-crystal XRD analysis indicates a primitive orthorhombic unit cell with dimensions $6 \times 14 \times 15 \text{ \AA}$, similar to previous studies, but $h = \text{odd}$ reflections were heavily streaked and diffuse, preventing full refinement. A $3 \text{ \AA}$ substructure was refined, with space group $Pmn2_1$, to $R_1(F) = 0.0750$ (MH). For a MH crystal, the subcell had $a = 3.0113(4)$, $b = 14.259(3)$, $c = 14.932(2) \text{ \AA}$, $V = 641.13(16) \text{ \AA}^3$ and $Z = 1$. The structure is of a new type, and contains Cu in 6 distinct sites, forming two three-polyhedron wide ribbons of edge-sharing Cu–O polyhedra extended parallel to the a -axis. The two ribbons lie back-to-back and are bridged by two AsO_4 tetrahedra. The collection of $6\text{Cu} + 2\text{As}$ cations plus ligands forms a rod-like moiety extended $\parallel a$. These rods link through polyhedral corners to form complex, corrugated (010) layers. The interlayer space is occupied by H_2O molecules. Thus, the disorder observed by XRD is of an unusual type, in which the shape of the unit mesh within layers is variable, rather than the stacking of the layers.

Disorder arises because each AsO_4 tetrahedron shares a face with a $\text{Cu}(\text{O},\text{OH},\text{H}_2\text{O})_{5-6}$ polyhedron in the substructure, necessitating partial occupancy of both As and Cu sites. The S atoms were not located in the refinement, but four electron-density maxima in the interlayer region were interpreted as H_2O molecules. Hence, the simplified structural formula derived from the substructure is $(\text{Cu}_{10}\square_2)(\text{As}_2\square_2)\text{O}_8(\text{OH})_{14} \cdot 8\text{H}_2\text{O}$, deviating from that obtained in chemical analyses. The discrepancy presumably arises due to strong delocalisation of the sulphur and the apical oxygen of the SO_4 tetrahedron in the substructure. Short-range order of Cu–As and Cu–S $\parallel a$ can occur independently in the relevant structural rods, which accounts for the observed long-range disorder.

Cell parameters and substructures obtained from CG and Clara material are similar to those from the MH crystal. Site splitting of OH positions in the CG refinement indicates that Cl is distributed over several sites in the $3 \text{ \AA}$ substructure, making the mineral a Cl-rich variety of parnaute rather than a distinct mineral species.

Key-words: parnaute, crystal structure, disorder, chemical analysis, Raman spectroscopy, Majuba Hill, Cap Garonne.

1. Introduction

Parnaute is a secondary copper mineral originally described by Wise (1978) as $\text{Cu}_{8.76}\text{Al}_{0.10}(\text{AsO}_4)_{1.43}$

$(\text{SO}_4)_{0.94}(\text{PO}_4)_{0.43}(\text{CO}_3)_{0.19}(\text{OH})_{9.98} \cdot 6.81\text{H}_2\text{O}$, or ideally $\text{Cu}_9(\text{AsO}_4)_2(\text{SO}_4)(\text{OH})_{10} \cdot 7\text{H}_2\text{O}$, from the Majuba Hill Mine, Pershing County, Nevada, USA (Sec 8, T32N R32E). Parnaute is most renowned for its occurrence in

stacks of bright green-blue to greenish, thin platy crystals, often reaching up to a centimetre across. Despite it being discovered in a number of deposits worldwide (cf. www.mindat.org), the crystal structure and definitive chemistry have proved elusive. In particular, there has been some debate in the literature regarding the definitive formula for the mineral, and whether it contains essential carbonate (*e.g.*, Walenta, 1981; Lai *et al.*, 1997; Frost & Keeffe, 2011), the premise for which began with the work of Wise (1978), who remarked that the “mineral dissolves readily in dilute HCl with the evolution of CO₂ bubbles”. We address this issue below.

In order to better understand the crystal chemistry of parnaute we have reinvestigated the type specimen from Majuba Hill [designated as MH henceforth] (Department of Earth Science, University of California, Santa Barbara, collection number 8090) and a Cl-rich specimen from the Cap Garonne mine, Var, France [designated as CG henceforth] (Natural History Museum of Los Angeles County, specimen 64056). Here we report the results of the energy-dispersive spectrometry (EDS), single-crystal X-ray diffraction (XRD) and Raman spectroscopic investigations undertaken on both the type material and that from CG. In addition, the crystal structure of a sample from the Clara mine, Black Forest, Germany, was studied by single-crystal XRD.

2. Occurrence and paragenesis

Wise (1978) provided a brief description of the Majuba Hill mine, including its geology and mineralogy. The mine exploited a small copper ore body that was oxidized to a depth of about 75 m. The type specimen of parnaute was collected by Jack Parnau (a local mineral collector) in the lower part of the oxidation zone in the vicinity of the largest mining stope, known as the Copper Stope. Secondary minerals found in or near the Copper Stope are: arthurite, azurite, brochantite, chalcantite, chalcophyllite, chrysocolla, clinoclase, cornwallite, malachite, metazeunerite, pharmacosiderite, olivenite, scorodite, spangolite and strashimirite.

The Cap Garonne mine, Var, Provence-Alpes-Côte d’Azur, France (43°6′23″N, 6°1′26″E), is the type locality for 14 minerals (Sarp *et al.*, 1997; Mari & Sarp, 2006; Mills *et al.*, 2011; 2012). Parnaute was first found at the mine more than a century ago, but was originally described as tyrolite by Lacroix (1910), then by Guillemin (1952) who made some chemical analyses. Parnaute was first recognized in CG as a new mineral by Sarp *et al.* in 1978, shortly after the discovery of the species at Majuba Hill (Wise, 1978).

In the Cap Garonne mine, parnaute is a widespread mineral occurring chiefly as coatings of thin pearly plates, which are occasionally grouped as compact aggregates rarely reaching 2 mm. The most frequently associated mineral is cyanotrichite, with needles sitting on parnaute plates or supporting tiny oriented parnaute crystals. Associated noteworthy minerals include sulphates

(brochantite, spangolite) and arsenates (pharmacosiderite and members of the scorodite–mansfieldite series), with the arsenates often altered.

The parnaute specimen analysed in this study was found during one prospecting session organized in cooperation between l’Association des Amis de la Mine de Cap Garonne (AAMCG) and the mine museum. The material was collected by GF in a chamber of the south mine located near the entrance, called “Annex S”, at the same time as co-type specimens of forêtite were found (Mills *et al.*, 2012). Parnaute occurs in the same horizontal bed as the forêtite. The host rock is a fine-grained quartz conglomerate rich in reddish baryte plates, cut by numerous fractures containing olivenite and minor zeunerite. Some of the specimens are characterised by chalcophyllite that has been extensively altered to fragile white mansfieldite. Parnaute occurs on these specimens as bluish green translucent balls with pearly lustre (up to 1 mm across), quite different from the usual parnaute specimens previously recovered from the mine. It is associated with a suite of secondary Al-bearing minerals, including: forêtite (Mills *et al.*, 2012), bariopharmacoalumite (Mills *et al.*, 2011), cyanotrichite and chalcophyllite.

3. Chemical composition

Chemical analyses were carried out using a JEOL 6400 SEM equipped with an Oxford X-Link (80 mm²) energy-dispersive spectrometer. Energy-dispersive data were collected at 20 kV, with a beam current of 1 nA, an estimated beam diameter of 1 µm and a live time of 120 s. The data were quantified using a series of natural standards (chalcopyrite for CuKα, FeKα, SKα; arsenopyrite, AsKα; albite, AlKα, SiKα; sylvite, ClKα; sphalerite, ZnKα) and reduced using a ZAF correction. In addition to these elements, trace amounts of P and Sb were also noted, but found to be below detection limits (3σ level); beyond these, no other elements were detected. Insufficient material was available for direct water determination; therefore, the H₂O content was calculated by difference. The presence of H₂O, OH, AsO₄ and SO₄ were also confirmed by Raman spectroscopy (see below). Analytical data collected on both the MH and CG parnaute are given in Table 1.

For MH parnaute, 63 analyses of ten crystals were made and for CG parnaute, 13 analyses of five crystals were made. Based on 29 (O + OH + Cl + H₂O), the average empirical formula for the MH parnaute is (Cu_{8.82}Al_{0.16}Fe_{0.02})Σ_{9.00}[(As_{1.78}Al_{0.07}Si_{0.08}S_{0.07})Σ_{2.00}O₈(SO₄)(OH)₁₀ · 7H₂O and, for CG parnaute, (Cu_{8.42}Al_{0.21}Zn_{0.10})Σ_{8.73}(AsO₄)₂[(S_{0.97}As_{0.10})Σ_{1.07}O₄](OH_{9.23}Cl_{0.77})Σ_{10.00} · 7H₂O. Both of these formulae conform well to that originally proposed by Wise (1978). The calculated cationic sums (12.00 for MH parnaute and 11.80 for CG parnaute) strongly attest to the correct assumption of the sum of the anionic components, with differences in the ideal cationic contents likely being attributable to a combination of trace elements not analysed for, variations in assumed valences in the metals and semi-

Table 1. Analytical data for parnaute.

Constituent	MH parnaute		CG parnaute	
	Avg. (wt. %)	Range (wt. %)	Avg. (wt. %)	Range (wt. %)
CuO	56.10	51.65–59.11	54.04	51.90–55.63
Fe ₂ O ₃	0.12	<i>b.d.</i> –0.61	<i>b.d.</i>	–
ZnO	<i>b.d.</i>	–	0.68	0.36–0.92
As ₂ O ₅	16.34	15.22–17.18	19.42	18.21–21.14
SO ₃	6.83	5.74–7.54	6.29	5.34–7.12
Al ₂ O ₃	0.95	0.34–2.29	0.87	0.62–1.27
SiO ₂	0.40	0.11–1.39	<i>b.d.</i>	<i>b.d.</i> –0.13
Cl	<i>b.d.</i>	–	2.19	1.53–2.89
H ₂ O _{calc.}	17.30		16.88	
O = Cl	–		–0.49	
Total	98.04		99.88	
# of atoms				
Cu ²⁺	8.82		8.42	
Fe ³⁺	0.02		–	
Zn ²⁺	–		0.10	
As ⁵⁺	1.78		2.10	
S ⁶⁺	1.07		0.97	
Al ³⁺	0.23		0.21	
Si ⁴⁺	0.08		–	
Cl [–]	–		0.77	
H	24.00		23.23	
O	29.00		28.23	
Cation sum	12.00		11.80	

metals present, *etc.* Note that for simplification in the case of MH, the excess Al (0.07 *pfu*) has been assigned to the As site. It is noteworthy that neither the new data for the MH parnaute nor those for the CG parnaute show PO₄ to be present in concentrations originally given for the mineral (P₂O₅ 2.56 wt. %; Wise, 1978) nor do they provide any convincing (albeit, indirect) evidence for additional CO₃ (*i.e.*, significant deviations of cationic sums from ideal values). PO₄-free parnaute has also been described in detail by Walenta (1972, 1981).

In order to investigate further the possible presence of CO₂, we also tested type and non-type parnaute from MH and some crystals from CG for effervescence in dilute HCl. In some cases, aggregates of stacked parnaute plates were observed to evolve a small amount of gas bubbles initially, but no bubbles were seen during later stages of dissolution. We note that the aggregates were not entirely pure parnaute: a small amount of an unidentified white phase could sometimes be observed between plates within the stacks. Interestingly, no effervescence was observed from individual thin plates of parnaute, except when an adhering white aggregate was visible. We interpret this as implying that the effervescence can be attributed to the unidentified white phase (possibly a carbonate), that is either interleaved with plates of parnaute in the aggregates, or forms as coatings on individual plates. The white phase is present in very low concentrations and appears to be X-ray amorphous, both of which would explain its lack of any contribution to the observed

PXRD pattern. While it is also possible that the parnaute crystal structure (see below) could accommodate some CO₃ between structural layers or replacing AsO₄ or SO₄, it does not appear to be an essential constituent of the mineral. Parnaute dissolved completely in a few seconds in 10 % HCl. The solution obtained by dissolution of the type parnaute precipitated micrometre-scale pale blue needles on evaporation, which were found to consist of CuCl₂ · 2H₂O (synthetic “eriochalcite”) by PXRD.

Probably the most notable difference between the empirical formulae of MH and CG parnaute is in the respective amounts of Cl present. Initially, it was strongly considered that the CG material might be a distinct species containing essential Cl, in light of its high and approximately stoichiometric Cl content (~1 *apfu* Cl); however, evidence to support this conclusion (Raman spectroscopy, single-crystal XRD; discussed below) is far from being unequivocal and, on this basis, we prefer to consider the CG parnaute as being a Cl-rich variety of parnaute. The CG Cl-rich parnaute can, however, be distinguished optically from MH parnaute, and has distinctly higher refractive indices: $\alpha_{\text{calc}} = 1.714$, $\beta = 1.740(5)$, $\gamma = 1.750(5)$, biaxial (–) and $2V = 63(1)^\circ$, measured in white light, by comparison to those of MH (Wise, 1978): $\alpha = 1.680(3)$, $\beta = 1.704(3)$, $\gamma = 1.712(3)$, biaxial (–) and $2V = 60(5)^\circ$, with no observable dispersion. Partial optical data for a sample from MH (supplied by Wise) measured by Walenta (1981) are: $\alpha = 1.670(3)$, $\gamma = 1.726(3)$, biaxial (–), $2V = 55^\circ$ and $r < v$, while those of material from the Clara mine are: $\alpha = 1.667(3)$, $\beta = 1.720(3)$, $\gamma = 1.737(3)$, biaxial (–), $2V = 60^\circ$ and $r > v$ (Walenta, 1981). Minor impurities (Ca, Fe, Si and Cl) were noted by Walenta (1981) in some of the studied samples from the Clara mine. For CO₃-bearing (and Cl-free) parnaute from China, Lai *et al.* (1997) report: $\alpha = 1.709$, $\beta = 1.732$, $\gamma = 1.738$, biaxial (–) and $2V = 55^\circ$. Optical properties of a sample from CG studied by Sarp *et al.* (1978) are: $\alpha = 1.682(2)$, $\beta = 1.706(2)$, $\gamma = 1.715(2)$, biaxial (–) and $2V = 63^\circ$. All these datasets reflect flexibility in the chemical composition of parnaute. In this regard, it is noteworthy that a Ni-bearing parnaute from Leogang, Austria, is mentioned by Pöeverlein (2008).

4. Raman spectroscopy

The Raman spectra (average of five 30 s spectra) of both MH and CG parnaute were obtained over the range 100 to 4000 cm^{–1} (Fig. 1a,b). Although the crystals used were unoriented, analyses were preferentially made on surfaces perpendicular to the {010} cleavage. Data were collected in backscattered mode with a HORIBA Jobin Yvon XploRA spectrometer interfaced with an Olympus BX 41 microscope (100× magnification, estimated spot size 2 µm, 1200 grating, and excitation radiation 532 nm). Calibration was made using the 521 cm^{–1} line of silicon metal. The Raman spectra of the MH and CG parnaute are remarkably similar both in terms of their general appearance and the bands present (Fig. 1a,b), suggesting that both MH and CG parnaute, despite apparent

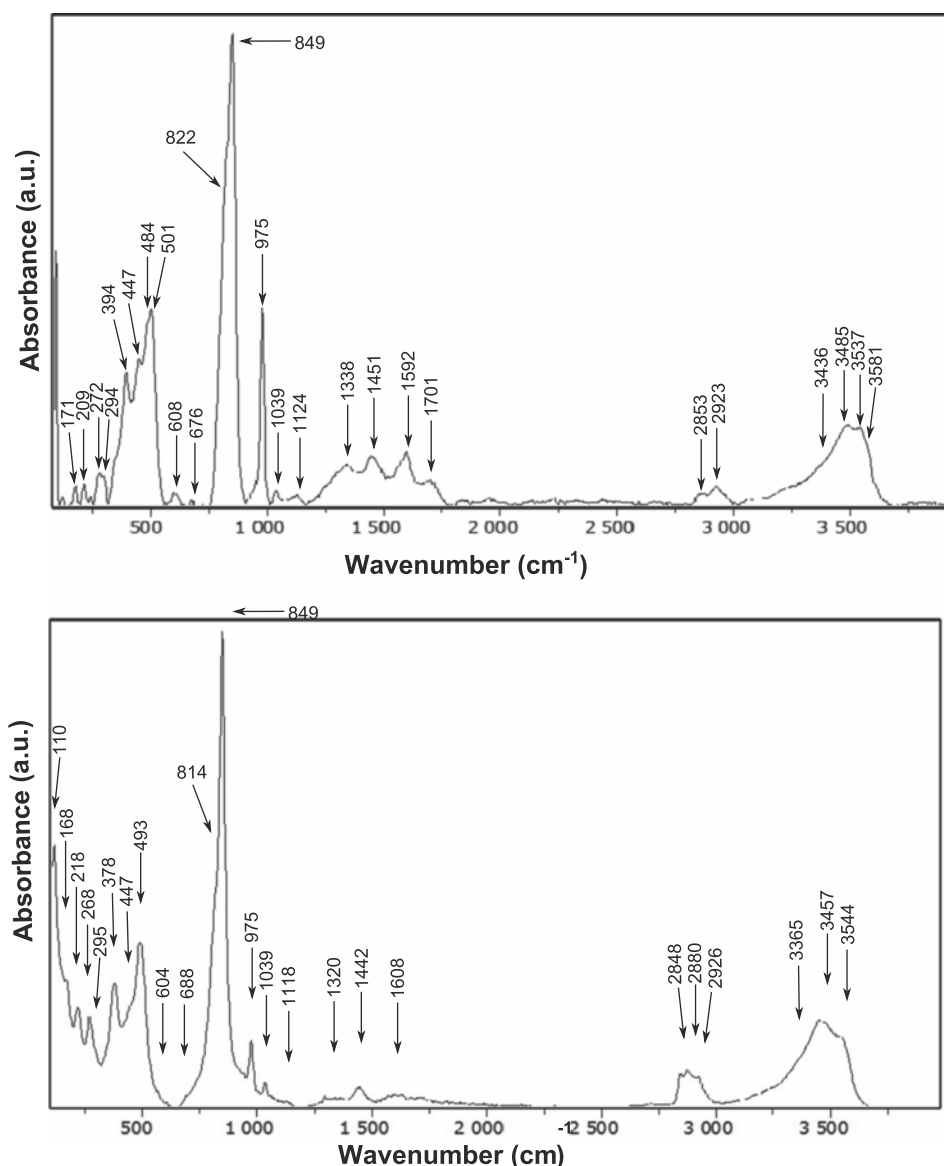


Fig. 1. Raman spectrum of MH (top) and CG (bottom) parnaute.

chemical differences (notably in their respective Cl contents), must be crystallochemically very similar. It was noted, however, that the Raman spectrum of the MH parnaute was considerably stronger in terms of signal-to-noise and was characterized by stronger, sharper bands than those in the Raman spectrum of the CG parnaute; the differences may be partially attributed to differences in the orientation of the crystals being analyzed. In terms of the general features of the spectra, both possess: (1) a very strong doublet in the range of $\sim 820\text{--}850\text{ cm}^{-1}$, attributable to AsO_4 stretches; (2) several medium to weak bands in the range of $\sim 970\text{--}1125\text{ cm}^{-1}$ attributable to SO_4 stretches; (3) several medium to weak bands in the range of $\sim 1320\text{--}1700\text{ cm}^{-1}$ attributable to H–O–H bending; and (4) several medium bands in the range of $\sim 2850\text{--}3580\text{ cm}^{-1}$, attributable to O–H stretches (the latter are further subdivided into two groups, those centred at $\sim 2900\text{ cm}^{-1}$, attributable to stretches associated with H_2O groups and those $\sim 3450\text{ cm}^{-1}$, attributable to stretches

associated with (OH) groups). There are also several peaks in the region $<500\text{ cm}^{-1}$, which are predominantly attributable to a variety of stretches and bends associated with both AsO_4 and SO_4 groups, as well as Cu–O vibrations (*cf.* Schmidt & Lutz, 1993) and lattice modes. All of the observed peak positions and band assignments for both MH and CG parnaute are given in Table 2. It is noteworthy that our data agree closely with those presented by Frost & Keeffe (2011). However, with respect to the possibility of CO_3 being present in parnaute, Frost & Keeffe (2011) attribute the bands present at 1107 and 1126 cm^{-1} to C–O symmetric stretching (ν_1), thus implying the presence of carbonate in the parnaute structure. While C–O ν_1 bands would be predicted to be present in this general range, such bands also fall squarely within the region corresponding to SO_4 antisymmetric stretches (ν_3) (*e.g.*, White, 2009), and given that all analytical data show considerable SO_4 to be present in the mineral, it is more logical to assign them to SO_4 antisymmetric stretches.

Table 2. Raman band assignments for parnaute*.

MH parnaute		CG parnaute
Raman Absorption Band (cm^{-1})	Suggested Band Assignments	Raman Absorption Band (cm^{-1})
3581, 3537, 3485, 3436 m	Stretching mode of (OH) groups	3544, 3457, 3365 m
2923, 2853 m	Stretching mode of H_2O molecules	2926, 2880, 2849 m
1701, 1592, 1451, 1338 m	H-O-H bending	1608, 1442, 1320 w
1124, 1039 w	$\nu_3(\text{SO}_4)$, antisymmetric stretch	1118, 1039 w
975 m-s	$\nu_1(\text{SO}_4)$, symmetric stretch	975 w
935 w	$\nu_1(\text{SO}_4)$, symmetric stretch	943 vw
849 vs	$\nu_1(\text{AsO}_4)$, symmetric stretch	849 s
822 s	$\nu_1(\text{AsO}_4)$, symmetric stretch	814 s
676, 608 w	$\nu_3(\text{AsO}_4)$, antisymmetric stretch	688, 604 vw
501, 484, 447 m-s	$\nu_4(\text{SO}_4)$, antisymmetric bend; Cu-O	493, 444 m
394, 346 m-s	$\nu_2(\text{AsO}_4)$, symmetric bend	378 m
294, 272 w-m	Lattice modes	295, 268 w
236, 209, 171, 119 vw	Lattice modes	218, 168, 110 w

*vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

Furthermore, the Raman spectra of carbonates are also typically associated with bands at $\sim 700 \text{ cm}^{-1}$, corresponding to CO_3 in-plane bends (ν_4); in the spectra obtained for both MH and CG parnaute, there is no unequivocal evidence for bands in this area. Thus, we suggest that based on the Raman spectra of both MH and CG parnaute, CO_3 is not present. It is curious that the study of Frost & Keeffe (2011) did note the presence of peaks at 725 and 777 cm^{-1} which would be consistent with the C–O ν_4 bends. However, Frost & Keeffe (2011) actually attribute these bands to AsO_4 antisymmetric stretches rather than C–O bends. As no bands in the region $\sim 700\text{--}780 \text{ cm}^{-1}$ are evident in the spectra obtained in this study, we cannot comment on them further. Beyond this finding, we also find no compelling evidence on the basis of the obtained Raman spectra to conclude that the CG parnaute in fact represents a potential Cl-analogue. There are no clear differences in the observed absorption bands between the two specimens studied and thus, no evidence for any bands that could be suggestive of unique Cu–Cl bonds. In the case of atacamite and paratacamite for example, Cu–Cl vibrational bands are present in the region $< 500 \text{ cm}^{-1}$, typically $\sim 350\text{--}390 \text{ cm}^{-1}$ (Frost *et al.*, 2002). While the spectra for both MH and CG parnaute exhibit absorption bands in this region (attributable to AsO_4 bending), the observed bands are virtually identical for both, therefore there is no unambiguous evidence for unique Cu–Cl bands in the CG parnaute, as might be expected if it were to contain essential ordered, Cl. Thus, evidence from Raman spectroscopy suggests that the CG parnaute is just a Cl-rich variety of parnaute, rather than a potential Cl-analogue.

5. X-ray crystallography

Single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized $\text{MoK}\alpha$ radiation. The Rigaku CrystalClear software package was used for processing of the diffraction data, including the application

of an empirical multi-scan absorption correction using ABCOR (Higashi, 2001). Inspection of the frames revealed a very strong $a/2$ substructure, with severe streaking of reflections in layers with $h = \text{odd}$ (Fig. 2), indicating substantial disorder. The substructure with $a \approx 3 \text{ \AA}$ gave a total of 948 unique reflections. However, integrating the structure with $a \approx 6 \text{ \AA}$ (primitive orthorhombic cell) only yielded 987 unique reflections. Therefore, there was insufficient information from the parent structure to get a solution for the 6 $\text{\AA}$ structure, and structure determination and refinement were restricted to the 3 $\text{\AA}$ substructure. Various trial solutions in triclinic, monoclinic and orthorhombic space groups were only successful in the case of $Pmn2_1$. Racemic twinning was identified in both datasets (45:55 for MH and 81:19 for CG). The heavy Cu and As atoms were found using SHELXS-97 (Sheldrick, 2008). The oxy-

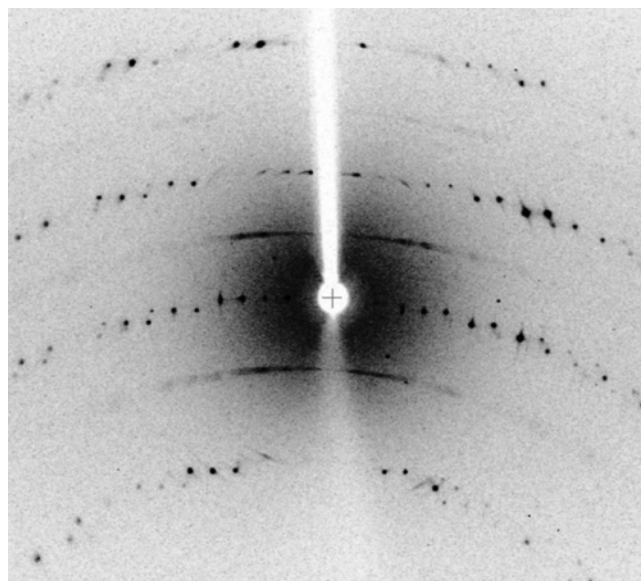


Fig. 2. Frame from the parnaute structure data collection (sample MH) showing severe streaking of reflections in layers with $h = \text{odd}$.

gen atoms were then located via subsequent difference-Fourier syntheses during the refinement, performed using SHELXL-97 (Sheldrick, 2008). Details concerning data collection and structure refinement are provided in Table 3. Fractional coordinates and atom displacement parameters are provided in Table 4, and selected interatomic distances in Table 5. It was apparent that some sites were not necessarily fully occupied, but that the data were of insufficient quality to obtain accurate, robust occupancy values. Therefore, occupancies for these sites were fixed at reasonable round-number values for the final refinement. Such constraints were applied for As1, As2, Cu5, and Cu6 (50 % occupancy in MH and CG refinements), and various anion/water sites which were fixed at 15 %, 35 %, 50 %, 85 % or 100 % occupancy, differently in the two refinements (Table 4). Note that with the sole exception of Cu2, bond-valence sums calculated for all Cu and As atoms using the parameters of Brese & O'Keeffe (1991) were significantly low. This is likely due to substitution of minor S and Si for As, inaccuracies in the refinement of the oxygen coordinates, possibly exacerbated by splitting of oxygen sites, and implies that the deviations away from expected values for some of the As–O bond distances should not be regarded as significant.

The refined substructure of parnaute shows six symmetrically distinct Cu sites. Five Cu are in sixfold coordination by (O, OH, H₂O); only Cu1 and Cu3 show significant Jahn-Teller elongation of the octahedron, while Cu2, Cu4 and Cu6 are in more regular environments than is usual for copper. The sixth Cu (Cu5) is in trigonal-bipyramidal coordination (Table 5). The Cu4–O polyhedron shares edges with those of Cu1 and Cu6 to form a three-

polyhedron wide ribbon of edge-sharing Cu–O polyhedra running parallel to **a**; the Cu2–O polyhedron shares edges with those of Cu3 and Cu5 to form a similar, but symmetrically independent, ribbon (Fig. 3). The two ribbons are orientated approximately parallel to one another, and are bridged by As1O₄ and As2O₄ tetrahedra. The pairs of ribbons bridged by these AsO₄ tetrahedra define structural rods that are then linked through polyhedral corners to form corrugated, complex layers parallel to (010) (Fig. 3). Based on the structure model, four water molecules per asymmetric unit are situated in the interlayer region. Since layers are connected only by hydrogen bonding through the water molecules, the “good” cleavage noted in the literature (Wise, 1978; Walenta, 1981) is presumably parallel to (010). Unusual for a layered structure, the disorder noted above does not appear to arise from variation of stacking of the structural layers, which would affect the periodicity along the **b** direction, but instead involves perturbations of the 6 Å periodicity by independent “shifting” of rods along the **a** direction, thus affecting the shape of the unit mesh in the plane of the layers. A similar style of disorder of chains of alternating SO₄ and H₂O groups has been observed in volaschioite, Fe³⁺₄(SO₄)O₂(OH)₆·2H₂O (Biagioni *et al.*, 2011). Stacking disorder of the layers would produce additional smearing of some diffraction spots parallel to **b**^{*}, and additional diffuse intensity at *k* = nonintegral positions, but we do not at present have any evidence for such phenomena.

Our initial substructure of parnaute showed the Cu5O₅ trigonal bipyramid sharing a triangular face with the As1O₄ tetrahedron, and the Cu6O₆ octahedron sharing a

Table 3. Data collection and structure refinement details for parnaute.

	MH parnaute	CG parnaute
Structural formula	Cu ₁₀ [AsO ₄] ₂ (OH) ₁₄ ·8H ₂ O	Cu ₁₀ [AsO ₄] ₂ Cl _{0.9} (OH) _{13.1} ·4.3H ₂ O
Space group	<i>Pmn</i> 2 ₁	<i>Pmn</i> 2 ₁
Unit-cell		
<i>a</i> (Å)	3.0113(4)	3.0088(4)
<i>b</i> (Å)	14.259(3)	14.212(3)
<i>c</i> (Å)	14.932(2)	14.890(2)
<i>V</i> (Å ³)	641.13(16)	636.69(16)
<i>Z</i>	1	1
Absorption coefficient	10.795 mm ^{−1}	10.943 mm ^{−1}
<i>F</i> (000)	596	574
Theta range (°)	3.08–24.98	3.09–25.02
Index ranges		
<i>h</i>	−3 ≤ <i>h</i> ≤ 3	−3 ≤ <i>h</i> ≤ 3
<i>k</i>	−16 ≤ <i>k</i> ≤ 16	−16 ≤ <i>k</i> ≤ 16
<i>l</i>	−17 ≤ <i>l</i> ≤ 15	−16 ≤ <i>l</i> ≤ 17
Reflections collected/unique	2719/1157	4871/1291
Reflections with <i>F</i> > 4σ(<i>F</i>)	945	888
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Parameters refined	95	110
GoF	1.111	1.309
Final <i>R</i> indices [<i>F</i> _o > 4σ(<i>F</i>)]	<i>R</i> ₁ = 0.0750, <i>wR</i> ₂ = 0.0912	<i>R</i> ₁ = 0.1571, <i>wR</i> ₂ = 0.1898
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1963, <i>wR</i> ₂ = 0.2144	<i>R</i> ₁ = 0.3567, <i>wR</i> ₂ = 0.3876
Extinction coefficient	0.0000(3)	0.0000(5)
Largest diff. peak/hole	2.73/−1.21 e/Å ³	4.42/−1.96 e/Å ³

Table 4. Atom coordinates and displacement parameters ($\text{\AA}^2$) for parnaute.

	<i>x</i>	<i>y</i>	<i>z</i>	occ.	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
MH parnaute											
Cu1	0	0.1379(2)	0.2337(2)	1	0.0170(8)	0.0096(15)	0.0332(18)	0.0082(18)	0.0020(16)	0	0
Cu2	0.5	−0.2549(2)	0.0515(2)	1	0.0244(8)	0.0228(16)	0.0326(18)	0.0176(16)	−0.0008(15)	0	0
Cu3	0	−0.3268(2)	0.8733(2)	1	0.0222(8)	0.0150(16)	0.0334(18)	0.0183(19)	0.0016(15)	0	0
Cu4	0.5	0.0716(2)	0.0548(2)	1	0.0242(9)	0.0135(15)	0.051(3)	0.0082(15)	−0.0035(19)	0	0
Cu5	0	−0.2118(6)	0.2232(6)	0.5*	0.048(2)	0.070(6)	0.047(5)	0.026(5)	−0.004(3)	0	0
Cu6	0	0.0423(4)	−0.1297(4)	0.5*	0.0180(15)	0.025(3)	0.028(4)	0.001(3)	−0.002(3)	0	0
As1	0	−0.1059(5)	0.1853(4)	0.5*	0.0257(15)	0.029(3)	0.030(3)	0.018(3)	−0.004(2)	0	0
As2	0	−0.0780(4)	−0.0789(4)	0.5*	0.0154(12)	0.012(2)	0.022(3)	0.012(3)	−0.001(2)	0	0
O1	0.5	0.1721(11)	0.1517(12)	1	0.016(4)						
O2	0	−0.0875(12)	−0.1905(15)	1	0.025(5)						
O3	0	0.0064(14)	0.1356(14)	1	0.029(5)						
O4	0	−0.1956(16)	−0.0236(16)	1	0.044(5)						
O5	0.5	−0.3575(12)	−0.0423(14)	1	0.026(4)						
O6	0.5	−0.1605(14)	0.1511(14)	1	0.033(5)						
O7	0	−0.298(2)	0.119(2)	1	0.084(10)						
O8	0.5	−0.0191(14)	−0.0467(13)	1	0.029(4)						
O9	0	−0.1060(18)	0.3002(17)	1	0.044(6)						
O10	0	0.2927(11)	0.2970(11)	1	0.017(4)						
O11	0	0.142(2)	−0.020(3)	1	0.087(11)						
OW1	0	0.396(4)	0.061(4)	1*	0.129(14)						
OW2	0	−0.500(3)	0.830(3)	1*	0.109(13)						
OW3	0	−0.503(4)	0.177(4)	1*	0.17(2)						
OW4	0	−0.316(4)	0.310(4)	1*	0.150(18)						
CG parnaute											
Cu1	0	0.1382(4)	0.2329(3)	1	0.0322(15)	0.019(3)	0.062(4)	0.015(3)	0.006(3)	0	0
Cu2	0.5	−0.2571(4)	0.0528(4)	1	0.0410(16)	0.043(4)	0.052(4)	0.028(3)	−0.005(3)	0	0
Cu3	0	−0.3280(5)	0.8717(3)	1	0.0380(17)	0.025(3)	0.074(4)	0.015(3)	−0.001(3)	0	0
Cu4	0.5	0.0714(5)	0.0559(4)	1	0.0431(19)	0.023(3)	0.090(5)	0.016(3)	0.000(4)	0	0
Cu5	0	−0.2135(11)	0.2260(11)	0.5*	0.062(4)	0.072(10)	0.073(9)	0.041(8)	0.006(7)	0	0
Cu6	0	0.0401(10)	−0.1313(8)	0.5*	0.051(4)	0.064(9)	0.072(10)	0.016(6)	−0.023(7)	0	0
As1	0	−0.1062(9)	0.1873(7)	0.5*	0.043(3)	0.037(6)	0.074(7)	0.019(6)	−0.007(5)	0	0
As2	0	−0.0777(7)	−0.0768(6)	0.5*	0.031(2)	0.038(6)	0.035(5)	0.019(5)	−0.003(3)	0	0
O1	0.5	0.164(2)	0.147(3)	1	0.037(8)						
O2	0	−0.085(2)	−0.186(2)	1	0.032(8)						
O3	0	0.014(2)	0.129(2)	1	0.036(7)						
O4	0	−0.187(3)	−0.019(3)	1	0.073(12)						
O5	0.5	−0.3589(15)	−0.0478(19)	1	0.017(6)						
O6	0.5	−0.168(3)	0.148(3)	1	0.053(10)						
O7	0	−0.309(4)	0.121(4)	1	0.082(15)						
O8	0.5	−0.021(2)	−0.049(2)	1	0.031(7)						
O9	0	−0.107(4)	0.303(3)	1	0.070(13)						
O10	0	0.294(2)	0.298(2)	1	0.039(8)						
O11A (Cl)	0	0.185(10)	−0.040(10)	0.15*	0.08(4)						
O11B	0	0.115(4)	−0.020(5)	0.85*	0.085(18)						
OW1	0	−0.320(10)	0.335(9)	0.5*	0.12(4)						
OW2	0	0.393(4)	0.051(5)	0.5*	0.036(13)						
OW3 (Cl)	0	−0.501(6)	0.823(6)	0.15*	0.044(19)						
OW4A (Cl)	0	−0.377(8)	0.146(8)	0.15*	0.06(3)						
OW4B	0	−0.482(6)	0.163(6)	0.35*	0.03(2)						
OW5	0.5	−0.453(4)	−0.120(4)	0.5*	0.034(14)						

* The occupancies of these sites have been fixed.

face with the As₂O₄ tetrahedron. Neither of these arrangements is crystallochemically feasible, since they would require unacceptably short distances (1.6–1.9 Å) between Cu²⁺ and As⁵⁺ cations. The real situation must be that the Cu site is vacant when the adjacent As site is occupied, and *vice versa*. This is consistent with the 50 % occupancy estimated for all these cation sites in the refinement (Table 4). Note that occupancy of either As site that is

greater than 50 % would imply that there is polymerisation of AsO₄ tetrahedra by corner linkage. Neither chemical analyses nor the structure refinement suggest that this is the case; the AsO₄ tetrahedra appear to remain isolated from one another in parnaute. Cu5 and As1 can alternate regularly in chains along the *a* direction, with a local 6 Å periodicity, as can Cu6 and As2. However, there is no requirement for nearby chains to correlate in phase with

Table 5. Selected bond distances (Å) and angles (°) in parnaute.

	Ligand in MH		MH	CG	Ligand in CG, if different from MH
Cu1	O1	×2	2.001(12)	2.01(2)	
Cu1	O2	×2	2.016(14)	2.07(2)	
Cu1	O3		2.38(2)	2.35(3)	
Cu1	O10		2.402(16)	2.42(3)	
<Cu–O>			2.136	2.16	
Cu2	O7	×2	1.91(2)	1.96(4)	
Cu2	O6		2.01(2)	1.90(4)	
Cu2	O5		2.026(19)	2.08(3)	
Cu2	O4	×2	2.059(16)	2.10(3)	
<Cu–O>			1.996	2.02	
Cu3	O10	×2	1.950(10)	1.92(2)	
Cu3	O5	×2	2.012(14)	1.973(18)	
Cu3	O4		2.42(2)	2.33(4)	OW5
Cu3	OW2		2.55(2)	2.56(9)	Cl
<Cu–O>			2.149	2.12	
Cu4	O8		1.99(2)	2.04(3)	
Cu4	O1		2.036(18)	1.89(4)	
Cu4	O11	×2	2.13(3)	1.98(5)	2.63(12) Cl
Cu4	O3	×2	2.142(15)	2.03(2)	
<Cu–O>			2.095	2.10	
Cu5	O9		1.90(3)	1.91(5)	
Cu5	OW4		1.97(5)	2.22(14)	OW1
Cu5	O7		1.99(3)	2.07(5)	
Cu5	O6	×2	1.990(15)	2.01(3)	
<Cu–O>			1.968	2.04	
Cu6	O9	×2	2.047(18)	2.02(3)	
Cu6	O2		2.06(2)	1.95(3)	
Cu6	O8	×2	2.137(15)	2.13(2)	
Cu6	O11		2.17(4)	2.46(14)	
<Cu–O>			2.099	2.12	
As1	O9		1.72(3)	1.73(5)	
As1	O3		1.77(2)	1.92(4)	
As1	O6	×2	1.770(11)	1.84(2)	
<As–O>			1.757	1.83	
As2	O2		1.67(2)	1.63(4)	
As2	O8	×2	1.790(11)	1.756(16)	
As2	O4		1.87(2)	1.77(5)	
<As–O>			1.78	1.73	

one another, whether they are symmetrically independent {Cu5, As1} and {Cu6, As2}, or whether they are chains that are equivalent in the substructure. The rest of the structure is compatible with any relative phasing of these chain elements, subject to minor relaxations of oxygen positions. Hence, the sharp Bragg reflections obtained from the 3 Å substructure convey no information about the state of order of these Cu and As atoms. The heavily streaked spots and diffuse scattering observed in $h = \text{odd}$ layers (6 Å cell) indicate that some short-range order does occur. The coexistence of a sharply defined, invariant sublattice in reciprocal space with diffuse superlattice scattering is characteristic of order-disorder (OD) structures (Đurovič, 1997; http://www.crystallography.fr/math-cryst/OD_structures.htm).

The overall composition deduced from the structure refinement, with 50 % occupancy of {Cu5, Cu6, As1, As2}, is $(\text{Cu}_{10}\square_2)(\text{As}_2\square_2)\text{O}_8(\text{OH})_{14}\cdot 8\text{H}_2\text{O}$. This is not in agreement with the formula determined by multiple

independent chemical analyses of type material (see section 3 above), which is close to $(\text{Cu}_9\square_3)(\text{As}_2\square_2)\text{SO}_{12}(\text{OH})_{10}\cdot 7\text{H}_2\text{O}$. In purely chemical terms, the latter is related to the former by the exchange of $(\square\text{SO}_4\square)$ for $(\text{Cu}\square(\text{OH})_4\text{H}_2\text{O})$, which implies that S, like As, partially occupies sites in a mutually exclusive relationship with nearby Cu atoms. The S atom cannot occupy the As1 and As2 sites, as this would entail an occupancy >50 % for these sites, and hence the presence of unstable As–O–S bonds. Structure models were investigated in which SO_4 groups attached to the Cu–(O,OH,H₂O) layer via only one oxygen, or in which isolated SO_4 groups in the interlayer region replaced OW1. None of these gave stable refinements, and all such models had very short non-bonded distances between oxygens. Furthermore, such models add a large number of oxygens into the interlayer region, while not providing a structural rationale for the additional vacancies which must be introduced into Cu sites in order to match the analysed stoichiometry. Hence, we deduce

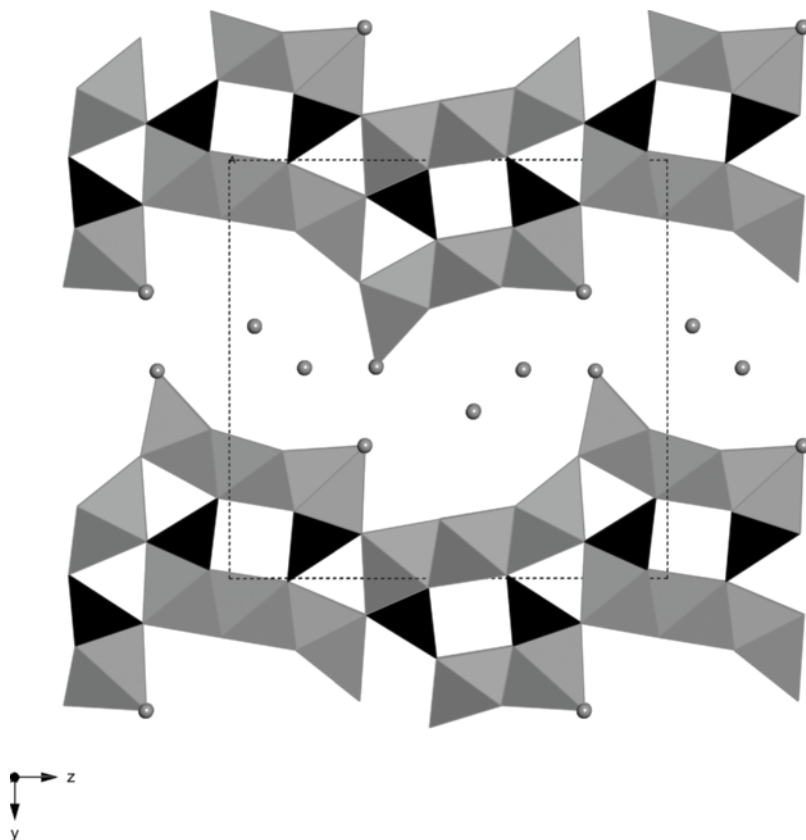


Fig. 3. The $3\text{\AA}$ substructure of parnauite viewed down **a**. Complex (010) structural layers composed from three-polyhedron wide ribbons of $\text{Cu}(\text{O},\text{OH},\text{H}_2\text{O})_{5-6}$ polyhedra (medium grey) surrounding partly occupied AsO_4 tetrahedra (black) are visible. H_2O molecules are indicated as small light grey spheres.

that any S site that is present shares faces with $\text{Cu}(\text{O},\text{OH})_n$ polyhedra, in such a way that it points into the interlayer, with an apical oxygen of SO_4 partly replacing a H_2O site. The five-coordinated Cu5 does not have a triangular polyhedron face available for attachment of SO_4 . Attachment to Cu6 would require formation of $\text{As}-\text{O}-\text{S}$ bonds. The polyhedra of Cu1 and Cu3 have available only very elongated $(\text{OH},\text{H}_2\text{O})_3$ faces for replacement by small O_3 triangles of SO_4 , which is unlikely. The most reasonable positions for face-sharing with an SO_4 tetrahedron would be the compact $(\text{OH})_3$ triangles formed by O5 and O7 ($\times 2$) on Cu2, and O1 and O11 ($\times 2$) on Cu4. The Cu–O bonds are short in all these cases (1.957–2.114 Å), as are the non-bonded O...O distances (2.972–3.011 Å). The bond-valence parameters of Brese & O’Keeffe (1991) imply that we should expect S–O of 1.470 Å, in good agreement with the empirical 1.473 Å “grand mean” distance of Hawthorne *et al.* (2000). Hence, we expect an O...O edge length of $\sqrt{8/3} \times 1.47 \text{ \AA} = 2.39 \text{ \AA}$. Since the oxygen sites are much further apart (close to 3 Å) in the substructure, considerable relaxation of oxygen positions towards S is still required, and oxygens {O1, O5, O7, O11} should show indications of site-splitting, such as unusually large displacement parameters in the substructure.

Structure refinements were attempted with a 50 % occupied S site located near both Cu2 and Cu4. All such attempts were unsuccessful, with the refinements either not staying

stable or the atoms moving away from the correct positions creating coordinations which were not crystallochemically sound. It seems most likely that the S occupies two sites in the substructure at 25 % occupancy, one near Cu2 and one near Cu4. These sites could not be refined stably, given their very low mean scattering factor and the presence of other split and partially occupied sites nearby.

If the model presented above is considered to be correct, then each “double ribbon” component of the parnauite structural layer contains four rod-like components elongated $\parallel \text{a}$ that may be translated relative to their surroundings without damaging the integrity of the structure. One of these units is a column of alternating Cu5 and As1 sites with their surrounding anions, and the other is a similar column containing Cu6 and As2. The other two translationally variable columns contain: (i) Cu2 + OW3 alternating with SO_4 in a 3:1 ratio, and (ii) Cu4 + OW1 alternating with SO_4 , also in a 3:1 ratio. Figure 4 shows the substructure of Fig. 3, with the addition of the 25 % occupied sulphur sites S1 and S2 and their surrounding tetrahedra. In one double ribbon, the four independently variable components and their cations have been indicated. Figure 5 indicates one possible local realisation of the true parnauite chemistry with theoretical atomic coordinates as presented in Table 6.

In the structure of parnauite from CG, severe splitting of O11, OW3 and OW4 is observed, possibly caused by these

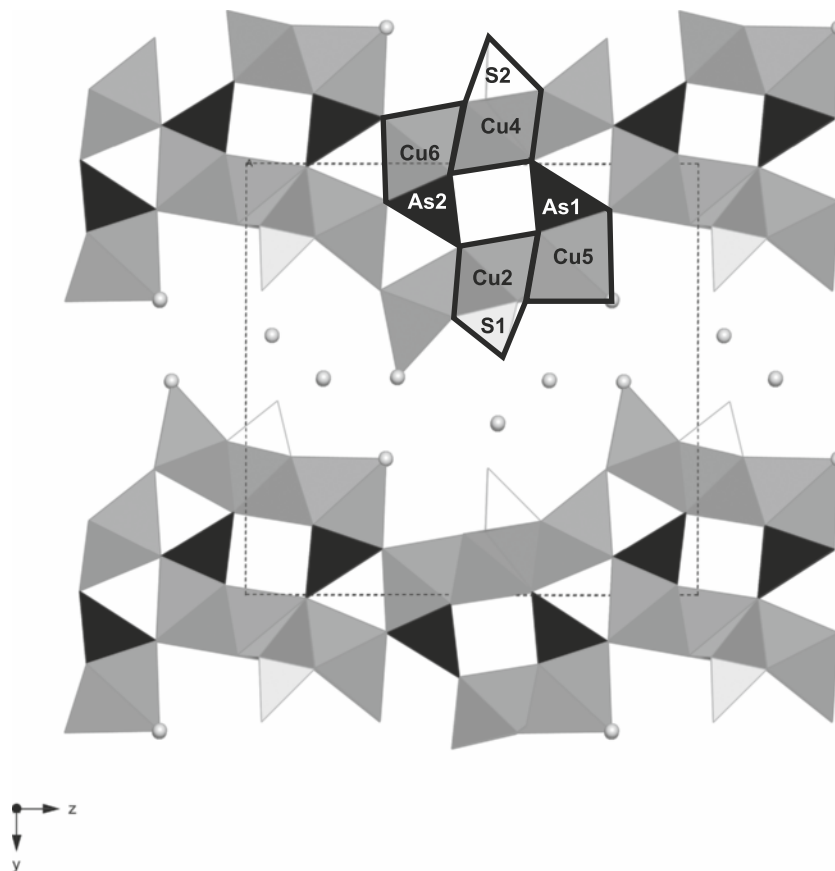


Fig. 4. Substructure of parnaute after Fig. 3, with the addition of partly occupied S1O_4 and S2O_4 tetrahedra. The four outlined structural elements have periodicities of $2a$ or $4a$, and may translate relative to one another and to the rest of the structure. On average, they contain 50 % Cu5 + 50 % As1, 50 % Cu6 + 50 % As2, 75 % Cu2 + 25 % S1 and 75 % Cu4 + 25 % S2.

sites being partially occupied by Cl (Table 4). Despite the presence of ≈ 0.9 apfu Cl in the asymmetric unit, $\text{Cu}_{10}[\text{AsO}_4]_2\text{Cl}_{0.9}(\text{OH})_{13.1} \cdot 4.3\text{H}_2\text{O}$, Cl does not appear to be ordered or dominant in any one of the three sites, and therefore there does not appear to be enough Cl in any one site to warrant separate species status, which is also consistent with the interpretation made from the Raman spectra. Future determination of the true structure of parnaute may reveal that Cl is indeed dominant in site(s) in a larger unit cell, but at this stage, poor crystal quality does not permit anything definite to be concluded about the structural role of Cl, except that it appears highly disordered in the 3 Å subcell. Furthermore, it is curious that the CG sample, with substitution of large Cl^- for relatively small OH^- (187 vs. 140 pm; Shannon, 1976), has very slightly smaller cell dimensions than the MH material (Table 3). However, the structural formula obtained from the refinement suggests that much interlayer H_2O may be missing in CG, possibly to make room for Cl. Loss of those molecules, changes to the hydrogen-bonding scheme, and the flexibility of the corrugated layers may all result in the counterintuitive dimensional change observed.

In the course of the study, we also studied a single crystal of parnaute from the Clara mine, which showed the same streaking parallel to $\mathbf{a}^*$, but fairly sharp reflections for

subcell and, to a lesser extent, real cell (nonetheless, the structure could not be solved in any model involving a 6 Å axis, independent of the chosen symmetry). The substructure unit cell ($Pmn2_1$) was $a = 3.011(1)$, $b = 14.009(2)$ and $c = 14.949(3)$ Å, with an $R_1 = 0.0612$ (SHELXL-97) for 2148 reflections with $F_o > 4\sigma(F_o)$. It is noteworthy that the b parameter, 14.009(2) Å is distinctly smaller than that of both MH and CG [14.259(3) and 14.212(3) Å, respectively]. A tentative explanation would be that this could be attributed to a reduced interlayer water content. The CO_3 -bearing parnaute from China described by Lai *et al.* (1997) shows an even longer b cell edge (cell parameters: $a = 15.052(18)$, $b = 14.320(7)$, $c = 6.002(6)$ Å). A similar, but low-accuracy unit cell for a Cap Garonne sample was reported by Sarp *et al.* (1978) $a = 15.10$, $b = 14.25$, $c = 6.03$ Å. Refinement of the substructure for the Clara sample did not shed any additional light on the structure (a *.cif file pertaining to this refinement can be obtained from UK). The “real” (large) unit cell of this crystal seemed to be either monoclinic P with $a = 6.02$ Å, $b = 14.00$ Å, $c = 15.25$ Å and $\beta = 101.4^\circ$ (related to the orthorhombic cell above by $\mathbf{c}_{\text{mon}} = \mathbf{c}_{\text{orth}} - \mathbf{a}_{\text{orth}}/2$) or orthorhombic/pseudo-orthorhombic B , $a = 6.02$ Å, $b = 13.99$ Å and $c = 29.84$ ($= 2 \times 14.92$ Å). The crystal structure could not be solved on the basis of either large cell.

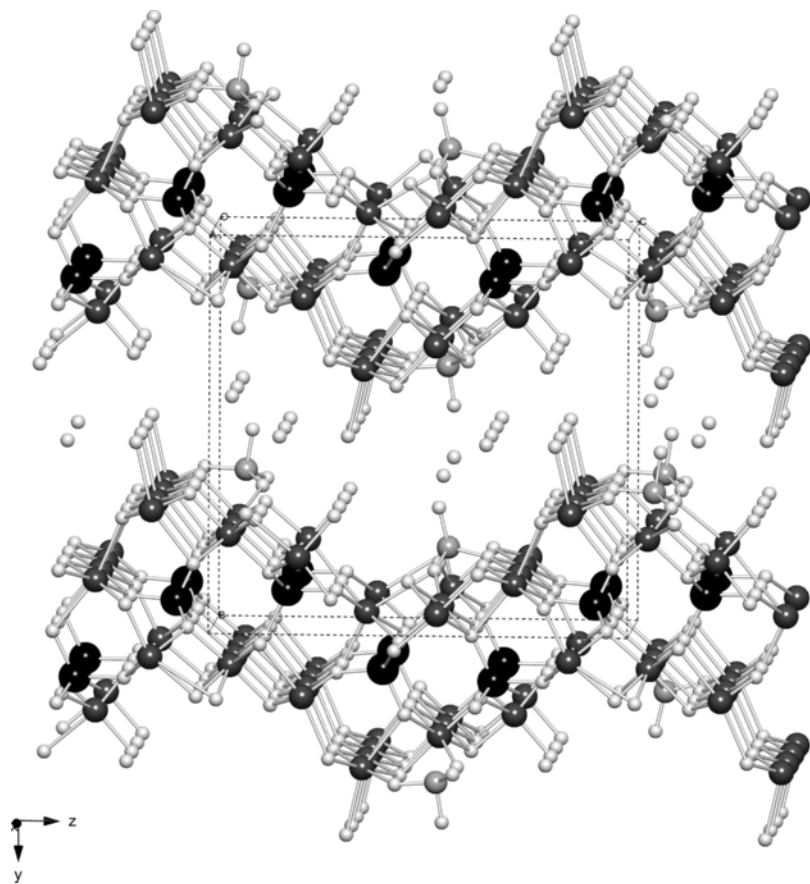


Fig. 5. An $a = 6 \text{ \AA}$ unit cell, showing a ball-and-stick representation of one possible local realisation of the true parnauite stoichiometry. Atoms are As (large, very dark), Cu (medium-large, medium-dark), S (medium-small, medium-pale) and O (very small and pale). In this example, As1 and As2 have been assigned the same x coordinate, and alternate along a with Cu5 and Cu6. At the same x as Cu5/6, half of the Cu2 and Cu4 are missing at random, since they have been replaced by S1 and S2 in nearby tetrahedral sites. The apical oxygens of the SO_4 tetrahedra replace water molecules which would otherwise have been present.

Table 6. Theoretical atomic coordinates for a model $6 \text{ \AA}$ parnauite structure. Unit-cell parameters as for MH structure in Table 3, but with a repeat doubled and change of origin. The (100) mirror plane of the $3 \text{ \AA}$ substructure has been removed, giving the monoclinic space group $P112_1$ but retaining an orthorhombic cell metric ($\gamma = 90^\circ$).

	occ.	x	y	z
As1	1	0.8750	0.8941	0.1856
As2	1	0.8750	0.9220	0.9215
Cu1	1	0.8750	0.1382	0.2334
Cu2	1	0.1250	0.7450	0.0516
Cu3	1	0.8750	0.6733	0.8732
Cu4	0.5	0.1250	0.0716	0.0551
Cu5	1	0.3750	0.7884	0.2232
Cu6	1	0.3750	0.0429	0.8701
Cu1a	1	0.3750	0.1382	0.2334
Cu2a	0.5	0.6250	0.7450	0.0516
Cu3a	1	0.3750	0.6733	0.8732
Cu4a	1	0.6250	0.0716	0.0551
O1	1	0.1250	0.1717	0.1526
O2	1	0.8750	0.9121	0.8114
O3	1	0.8750	0.0081	0.1330
O4	1	0.8750	0.8082	0.9732

(Continued)

Table 6. Continued.

	occ.	x	y	z
O5	1	0.1250	0.6438	0.9568
O6	1	0.1250	0.8391	0.1482
O7	0.5	0.8750	0.6960	0.1210
O8	1	0.1250	0.9784	0.9534
O9	1	0.8750	0.8931	0.3025
O10	1	0.8750	0.2934	0.2978
O11	0.5	0.8750	0.1410	0.9810
O12	0.5	0.6250	0.5500	0.0700
O13	0.5	0.6250	0.2950	0.0350
O1a	1	0.6250	0.1717	0.1526
O2a	1	0.3750	0.9121	0.8114
O3a	1	0.3750	0.0081	0.1330
O4a	1	0.3750	0.8082	0.9732
O5a	1	0.6250	0.6438	0.9568
O6a	1	0.6250	0.8391	0.1482
O7a	0.5	0.3750	0.6960	0.1210
O7ab	0.5	0.4250	0.6800	0.1000
O7b	1	0.8300	0.6800	0.1000
O8a	1	0.6250	0.9784	0.9534
O9a	1	0.3750	0.8931	0.3025
O10a	1	0.3750	0.2934	0.2978

(Continued)

Table 6. Continued.

	occ.	x	y	z
O11a	0.5	0.3750	0.1410	0.9810
O11ab	0.5	0.4250	0.1450	0.0300
O11b	0.5	0.8250	0.1450	0.0300
OW1	1	0.1250	0.3980	0.0580
OW2	1	0.8750	0.5050	0.8360
OW3	1	0.1250	0.4980	0.1720
OW4	1	0.8750	0.6838	0.3103
OW1a	0.5	0.6250	0.3980	0.0580
OW2a	1	0.3750	0.5050	0.8360
OW3a	0.5	0.6250	0.4980	0.1720
OW4a	1	0.3750	0.6838	0.3103
S1	0.5	0.6250	0.6500	0.0550
S2	0.5	0.6250	0.1950	0.0580

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