



Andersonite, ideally $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\frac{1}{3}\text{H}_2\text{O}$: crystal structure refinements, water content, and a puzzling defect

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Abstract

Four crystal structures of the uranyl carbonate mineral andersonite were refined from single-crystal X-ray diffraction data. One sample is a natural andersonite from the Monte Cristo mine, Utah, USA. Structure refinement at 297 K yielded the composition $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5.28\text{H}_2\text{O}$, space group $R\bar{3}m$, $a=17.9012(6)$ Å, $c=23.7978(12)$ Å, $Z=18$, and $R1=0.0139$ for $2283 F_o > 4\sigma(F_o)$. Three synthetic andersonite samples refined at $T=297, 200$, and 100 K in space group $R\bar{3}m$ ($R1=0.0122$ – 0.0144) have similar compositions with 5.27 – 5.29 structure-based H_2O per formula unit. Unlike the natural sample, they exhibit an additional electron-density peak (X) with $\rho_{\text{peak}}=1.8$ – 2.8 e[−]/Å³, attributed to an as-yet unidentified lattice defect. The crystal structure of andersonite consists of a framework with composition $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\text{H}_2\text{O}$, constructed from uranyl tricarbonate groups and $\text{CaO}_6(\text{H}_2\text{O})$ polyhedra organized into $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layers linked by $\text{NaO}_4(\text{H}_2\text{O})_2$ and $\text{NaO}_2(\text{H}_2\text{O})_4$ octahedra. The framework contains a distinctive closed cavity bounded by twelve Na-bonded H_2O groups forming a hexagonal prism and six carbonate oxygen atoms. Each cavity accommodates two symmetry-equivalent interstitial H_2O molecules, corresponding to $\frac{1}{3}$ H_2O per formula unit at full occupancy. The result is a unique water-in-water capsule. Site splitting affects approximately $\frac{1}{6}$ of the twelve H_2O groups surrounding the interstitial H_2O in all structures and is attributed to hydrogen-bond donation to the cavity water molecules. After providing deeper insight into the complexity of the andersonite structure and its close relationships to línekite and markeyite-type minerals, a comparison with existing crystal structures of andersonite is presented. It is shown that the idealized chemical formula of andersonite should be written as $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\frac{1}{3}\text{H}_2\text{O}$ and that there is no space to accommodate additional H_2O .

Keywords Andersonite · Crystal structures · Water content · Structural relationships · Defect structure

Introduction

Based on chemical composition and stability, andersonite is now the third most frequent uranyl tricarbonate mineral, after schrockingerite, $\text{NaCa}_3[(\text{UO}_2)(\text{CO}_3)_3](\text{SO}_4)\text{F} \cdot 10\text{H}_2\text{O}$, and liebigite, $\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_3] \cdot 11\text{H}_2\text{O}$ (Mindat.org 2025a; Ralph et al. 2025). Its formation as a secondary mineral

after primary uraninite and pitchblende is not restricted to mine tunnels and post-mining environments, but also occurs in undisturbed occurrences of the numerous sandstone-type uranium deposits of the Colorado Basin, USA.

Andersonite was first reported from the Hillside mine—a now abandoned vein type (Au)–Ag–Pb–Zn–deposit near the copper-mining town of Bagdad, Arizona, USA—where coatings of secondary uranium minerals (schrockingerite, bayleyite, swartzite, andersonite) on gypsum attracted the attention of scientists of the US Geological Survey (Axelrod et al. 1951). After an impure sample of andersonite analyzed by microchemical tests had shown that it is a sodium–calcium–uranylcarbonate, the mineral was subsequently synthesized from aqueous solutions of $\text{UO}_2(\text{NO}_3)_2$, Na_2CO_3 , K_2CO_3 , and $\text{Ca}(\text{NO}_3)_2$, studied by contemporary crystallographic methods [small cube-like crystals, trigonal, space group $R\bar{3}$ or $R3$,

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$a = 18.04(5)$ Å, $c = 23.90(5)$ Å, $Z = 18$, $d_{\text{meas}} = 2.8$ g cm⁻³, optically (+), $n_{\omega} = 1.520$ (colorless), $n_e = 1.540$ (pale-yellow)] and by a quantitative chemical analysis which led to the chemical formula $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 6\text{H}_2\text{O}$ (Axelrod et al. 1951).

The first X-ray structure determinations of synthetic andersonite by Coda (1963) and later by Coda et al. (1981) revealed a crystal structure corresponding to the formula $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\text{H}_2\text{O}$ (space group $R\bar{3}m$, $a = 17.902(4)$ Å, $c = 23.734(4)$ Å, $R_w = 0.049$ for 794 reflections). This structure was reported to contain a wide channel, in which – based on thermoanalytical investigations by other authors (Čejka 1969) – an additional amount of water was postulated. This assignment resulted in the chemical formula $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot x\text{H}_2\text{O}$ ($x \approx 5.6$) reported by Coda et al. (1981). Using synthetic material, Mereiter (1986) conducted a single-crystal X-ray study demonstrating that this additional interstitial H_2O is located on the threefold axis at $00z$, $z = 0.0862$. This assignment resulted in the chemical composition $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\frac{1}{3}\text{H}_2\text{O}$ (space group $R\bar{3}m$, $a = 17.904(2)$ Å, $c = 23.753(3)$ Å, $R1 = 0.028$ for 1860 reflections). Despite these findings, as well as further thermoanalytical investigations (Čejka et al. 1987; Čejka and Urbanec 1988; Vochten et al. 1993), the original chemical formula proposed by Axelrod et al. (1951), containing 6 H_2O , has persisted in the literature and continues to appear in recent publications and compendia.

Plášil and Čejka (2015) reported a crystal-structure analysis of andersonite from Jachymov, Czech Republic, with an idealized unrefined content of $5\frac{1}{3}\text{H}_2\text{O}$ per formula unit ($R1 = 0.029$ for 1657 reflections with $I > 3\sigma(I)$). They discussed this result in comparison with earlier analytical, spectroscopic and structural studies, and suggested that the molecular water content of andersonite varies slightly, approximately within the range 5.33–5.6 H_2O . More recently, Gurzhiy et al. (2018) reported a low-temperature ($T = 100$ K) structural study of andersonite from the Cane Springs Canyon, Utah, USA. As a new structural feature, they described a disorder of the Na-bonded H_2O surrounding the interstitial H_2O , manifested by an $\sim 88/12\%$ splitting into two adjacent sites. Two additional H_2O sites were also reported, leaving some ambiguity regarding the water content.

The present study reports crystal-structure determinations of a natural andersonite from the Monte Cristo mine, Lower Cane Creek District, Utah, USA, and of three synthetic andersonite samples. Based on these data, we provide new insights into the crystal structure of andersonite, analyze the role and amount of interstitial water, and discuss interpretations of a residual electron-density peak observed in some specimens.

Andersonite from the Monte Cristo mine (MCMA)

Structure determination

A well crystallized sample of andersonite from the Monte Cristo mine, Lower Cane Creek District, Utah, USA, was provided by The Natural History Museum Vienna, Austria (specimen L 6338; see supplementary material Fig. S1). A small rounded fragment (~ 0.20 mm) of a larger faceted crystal of tabular shape was prepared for X-ray single crystal diffraction. This sample is subsequently designated with the acronym MCMA. It is optically uniaxial (+) with $n_{\omega} = 1.5285$ and $n_e = 1.5431$ determined by λ -T-variation on a spindle stage (Mereiter 1986).

This crystal was investigated at $T = 297$ K on a Bruker Smart APEX CCD diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation from a sealed tube. A total of 49,917 reflections covering a complete Ewald sphere up to $2\theta_{\text{max}} = 60^\circ$ was collected. Unit cell dimensions and trigonal symmetry with a rhombohedral lattice were in agreement with previous investigations. No reflections due to obverse/reverse twinning or a superstructure were detected. After data integration with program SAINT (Bruker 2007), the reflection intensities were corrected for absorption by the multi-scan method using program SADABS (Bruker 2007) and applying at first Laue symmetry $\bar{3}$ and finally $\bar{3}m$.

In order to start the structure determination free from bias, the structure was determined ab-initio using program SHELXT (Sheldrick 2015a) taking the space groups $R3m$, $R\bar{3}$, $R3$, $R32$ and $R\bar{3}m$ into account. On subsequent least-squares refinement with program SHELXL (Sheldrick 2015b), all solutions converged rapidly to R values below 0.03, but produced structures practically indistinguishable from $R\bar{3}m$ symmetry. This space group was then used for all the further refinement steps of andersonite. The origin and the asymmetric unit of the structure chosen by Gurzhiy et al. (2018) was applied ($x, y, z > 0$). This setting is symmetry-equivalent with the parameter sets given by Coda et al. (1981) and Mereiter (1986), but not with the setting of Plášil and Čejka (2015), who used an origin shifted by $\Delta z = \frac{1}{2}$. Starting with an ordered structure model of composition $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\frac{1}{3}(\text{O})$ ($R1 = 0.017$, no hydrogen atoms), the difference-Fourier synthesis showed clearly that the Na2-bonded H_2O of W4 (W denotes H_2O oxygen atoms) is split into a main position W4 and a satellite position W4a with site occupancies of $\sim 86\%$ and $\sim 14\%$, respectively, and a W4...W4a distance of ~ 0.85 Å (see supplementary material, Fig. S2). This feature, detected previously for andersonite at $T = 100$ K (Gurzhiy et al. 2018), is not a low-temperature effect but persists essentially unchanged over a temperature range of ~ 200 K. It was overlooked in earlier investigations (Mereiter 1986;

Plášil and Čejka 2015) and is in context with the interstitial H_2O (see below). Subsequently, five H-atom positions of W1, W2, W3, and W4 could be clearly recognized in difference–Fourier syntheses. They were refined in x, y, z , U_{iso} with the restraints $\text{W}–\text{H}=0.80\text{ Å}$ and $\text{H}–\text{W}–\text{H}=106^\circ$. The remaining H atoms could not be directly located from the X-ray data (half occupied H4b and H4c of W4; H4aa, H4ab, H4ac of W4a; H5a of the interstitial H_2O of W5). They were inserted in calculated positions assuming linear hydrogen bonds and were then kept at fixed positions.

In the next step the interstitial H_2O of W5, which was located on a 3-fold axis ($x, y, z = \frac{2}{3}, \frac{1}{3}, 0.42$) and showed a large oblate displacement ellipsoid ($U_{11}=0.128$, $U_{33}=0.063\text{ Å}^2$) and a triangular electron density peak (see supplementary material, Fig. S3) with a peak height of $4.66\text{ e}^-/\text{Å}^3$ much lower than the electron density peaks of all other oxygen atoms ($\sim 15\text{--}17\text{ e}^-/\text{Å}^3$), was displaced from the axis and refined in a position $x, 1-x, z$ of point symmetry m . This off-axis position of W5 is designated W5m. It is located $\sim 0.34\text{ Å}$ from the 3-fold axis and shows smaller displacement parameters of much less anisotropy than W5. The rationale behind the off-axis position was that the oxygen atom of the polar H_2O is in symmetry conflict with a 3-fold axis and that the electron density peak was triangular. However, the introduction of W5m in off-axis position had minute effects on R

values and the refined occupancy. For the final refinement, the population parameters of W14a and W5m were treated as a single variable because the individual values were overlapping within their standard deviations, and $R1=0.0139$ for 2283 observed reflections was obtained. Crystallographic data and refinement parameters for *MCMA* are summarized in Table 1. Atomic parameters are given in Tables 2 and 3, selected geometric data in Table 4. The supplementary material contains further graphics, complete geometric data, a table of bond valences and a crystallographic information file (CIF). Structure graphics were generated with programs MERCURY (Macrae et al. 2020) and DIAMOND (Brandenburg 2016).

The crystal structure of andersonite

The crystal structure of andersonite is built up from a uranyl tricarbonate group (UTC group), a $\text{Ca}1\text{O}_6(\text{H}_2\text{O})$ polyhedron with the shape of a monocapped trigonal prism, a $\text{Na}1\text{O}_4(\text{H}_2\text{O})_2$ octahedron, and a $\text{Na}2\text{O}_2(\text{H}_2\text{O})_4$ octahedron. All these constituents have symmetry m with the metal atoms located on the mirror plane (Fig. 1). The UTC group shares two equatorial edges (O2 and O4) of the $(\text{UO}_2)\text{O}_6$ hexagonal bipyramid with two $\text{Ca}1\text{O}_6(\text{H}_2\text{O})$ polyhedra, while the third equatorial edge (O3 and O3($1-y, 1-x, z$)) is

Table 1 Details of single-crystal X-ray data collections and structure refinements for *MCMA* and *SYNA1*

Compound code	<i>MCMA</i>	<i>SYNA1</i> ^a
Sample source	Andersonite, Monte Cristo mine, USA	Andersonite, synthetic
Chemical formula	$\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3]\cdot 5.28\text{H}_2\text{O}$	$\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3]\cdot 5.29\text{H}_2\text{O}$
Diffractometer	Bruker-AXS Smart APEX CCD	Bruker-AXS Smart APEX CCD
Radiation, λ	Mo $K\alpha$, 0.71073 Å	Mo $K\alpha$, 0.71073 Å
Temperature (K)	297	297
Crystal size (mm)	$0.22 \times 0.20 \times 0.16$	$0.12 \times 0.12 \times 0.12$
Crystal description	yellow fragment	yellow cube
Crystal system, space group	Trigonal, $R\bar{3}m:H$ (#166)	Trigonal, $R\bar{3}m:H$ (#166)
a, c (Å)	17.9012 (6), 23.7978 (12)	17.9015 (6), 23.7752 (12)
V (Å ³)	6604.4 (6)	6598.3 (6)
Formula units Z	18	18
Formula weight	631.17	631.42
μ (mm ^{−1}), $F(000)$	11.55, 5270	11.56, 5272
D_x (g·cm ^{−3})	2.857	2.860
θ range (°)	2.16–30.00	2.16–30.09
Indices range	$-25 \leq h \leq 25, -25 \leq k \leq 25, -33 \leq l \leq 33$	$-25 \leq h \leq 25, -25 \leq k \leq 25, -33 \leq l \leq 33$
No. or measured, independent and observed reflections	49,917, 2346, 2283	35,109, 2365, 2190
R_{int}	0.025	0.028
Absorption correction	multi-scan	multi-scan
Transmission $T_{\text{min}}, T_{\text{max}}$	0.213, 0.384	0.376, 0.462
Refinement	Full-matrix least squares on F^2 using program SHELXL	
$R1$ [$F^2 > 2\sigma(F^2)$], $R1$ (all)	0.0139, 0.0145	0.0144, 0.0172
$wR(F^2)$, S	0.0365, 1.198	0.0361, 1.190
Parameters, restraints	149, 9	154, 9
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ / $\text{e}^-/\text{Å}^3$	0.80, −0.48	0.88, −1.17

^a Data for the low temperature structures of *SYNA2* and *SYNA3* are reported in the supplementary material and Table 4

Table 2 Atomic coordinates, isotropic displacement parameters, site occupancy factors (s.o.f.), and site symmetry information (s.s.i.) for *MCMA* and *SYNAI*

(a) Andersonite from Monte Cristo mine, <i>MCMA</i>						
Atom ^a	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}} [\text{\AA}^2]$	s.o.f. (<1)	s.s.i. ^b
Na1	0.51724 (4)	0.48276 (4)	0.82952 (5)	0.0229 (2)		18 <i>h m</i>
Na2	0.54053 (5)	0.45947 (5)	0.44249 (6)	0.0328 (3)		18 <i>h m</i>
Ca1	0.45580 (2)	0.54420 (2)	0.94396 (2)	0.01413 (9)		18 <i>h m</i>
U1	0.55701 (2)	0.44299 (2)	0.67840 (2)	0.01499 (4)		18 <i>h m</i>
C1	0.59020 (10)	0.40980 (10)	0.56601 (12)	0.0190 (5)		18 <i>h m</i>
C2	0.68349 (12)	0.59767 (12)	0.73487 (8)	0.0167 (3)		36 <i>i 1</i>
O1	0.59544 (8)	0.40456 (8)	0.51448 (9)	0.0259 (5)		18 <i>h m</i>
O2	0.52600 (10)	0.35340 (10)	0.59589 (6)	0.0267 (3)		36 <i>i 1</i>
O3	0.60429 (9)	0.55202 (10)	0.75204 (6)	0.0225 (3)		36 <i>i 1</i>
O4	0.69949 (10)	0.57384 (10)	0.68694 (6)	0.0223 (3)		36 <i>i 1</i>
O5	0.74053 (9)	0.65998 (9)	0.76228 (6)	0.0202 (3)		36 <i>i 1</i>
O6	0.60725 (7)	0.39275 (7)	0.71424 (10)	0.0261 (4)		18 <i>h m</i>
O7	0.50618 (8)	0.49382 (8)	0.64322 (10)	0.0285 (5)		18 <i>h m</i>
W1	0.44010 (7)	0.55990 (7)	0.83871 (10)	0.0223 (4)		18 <i>h m</i>
H1a ^d	0.46042 (13)	0.61108 (12)	0.8371 (14)	0.040 (9)		36 <i>i 1</i>
W2	0.58987 (8)	0.41013 (8)	0.86162 (11)	0.0303 (5)		18 <i>h m</i>
H2a ^d	0.5989 (10)	0.4011 (10)	0.8931 (5)	0.045 (14)		18 <i>h m</i>
H2b ^d	0.5644 (5)	0.3641 (5)	0.8465 (6)	0.05 (2)	0.5	36 <i>i 1</i>
W3	0.59340 (14)	0.59340 (14)	0.50000	0.0334 (5)		18 <i>g 2</i>
H3a ^d	0.6087 (7)	0.6318 (7)	0.4777 (6)	0.057 (12)		36 <i>i 1</i>
W4 ^f	0.47210 (18)	0.32224 (16)	0.39326 (10)	0.0422 (6)	0.862 (3)	36 <i>i 1</i>
H4a ^d	0.4207 (3)	0.296 (3)	0.396 (2)	0.063	0.862 (3)	36 <i>i 1</i>
H4b ^e	0.4752	0.3285	0.3599	0.063	0.431 (2)	36 <i>i 1</i>
H4c ^e	0.4721	0.2776	0.3933	0.063	0.431 (2)	36 <i>i 1</i>
W4a ^f	0.5243 (12)	0.3352 (11)	0.3884 (7)	0.041 (4)	0.138 (3)	36 <i>i 1</i>
H4aa ^e	0.5654	0.3317	0.3969	0.062	0.138 (3)	36 <i>i 1</i>
H4ab ^e	0.5125	0.3377	0.3561	0.062	0.069 (2)	36 <i>i 1</i>
H4ac ^e	0.5100	0.2852	0.3896	0.062	0.069 (2)	36 <i>i 1</i>
W5 ^f	0.66667	0.33333	0.4203	0.107	0.83	6 <i>c 3m</i>
W5m ^f	0.6776 (5)	0.3224 (5)	0.4199 (5)	0.063 (7)	0.276 (7)	18 <i>h m</i>
H5ma ^e	0.6559	0.2879	0.4448	0.094	0.276 (7)	36 <i>i 1</i>
(b) Synthetic andersonite, <i>SYNAI</i>						
Atom ^a	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}} [\text{\AA}^2]$	s.o.f. (<1)	<i>MCMA-SYNAI</i> ^c
Na1	0.51735 (4)	0.48265 (4)	0.82952 (5)	0.0217 (3)		0.003
Na2	0.54023 (6)	0.45977 (6)	0.44279 (6)	0.0315 (3)		0.012
Ca1	0.45586 (2)	0.54414 (2)	0.94391 (2)	0.01177 (10)		0.002
U1	0.55706 (2)	0.44294 (2)	0.67833 (2)	0.01253 (4)		0.003
C1	0.59039 (10)	0.40961 (10)	0.56586 (13)	0.0171 (6)		0.007
C2	0.68339 (13)	0.59758 (13)	0.73465 (8)	0.0142 (4)		0.006
O1	0.59582 (8)	0.40418 (8)	0.51395 (10)	0.0237 (5)		0.017
O2	0.52616 (11)	0.35334 (11)	0.59574 (7)	0.0249 (4)		0.005
O3	0.60451 (10)	0.55222 (11)	0.75197 (7)	0.0202 (3)		0.004
O4	0.69934 (10)	0.57372 (10)	0.68687 (6)	0.0202 (3)		0.003
O5	0.74040 (10)	0.65995 (10)	0.76215 (6)	0.0180 (3)		0.004
O6	0.60732 (8)	0.39268 (8)	0.71409 (10)	0.0237 (5)		0.004
O7	0.50634 (8)	0.49366 (8)	0.64322 (10)	0.0263 (5)		0.005
W1	0.44026 (7)	0.55974 (7)	0.83849 (11)	0.0213 (5)		0.007
H1a ^d	0.46054 (11)	0.61096 (10)	0.8377 (16)	0.052 (11)		0.017
W2	0.58985 (9)	0.41015 (9)	0.86166 (11)	0.0284 (5)		0.001
H2a ^d	0.5994 (10)	0.4006 (10)	0.8929 (5)	0.039 (14)		0.015
H2b ^d	0.5641 (5)	0.3643 (5)	0.8463 (5)	0.013 (13)	0.5	0.010
W3	0.59335 (15)	0.59335 (15)	0.50000	0.0312 (6)		0.001

Table 2 (continued)(b) Synthetic andersonite, *SYNAI*

Atom ^a	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}} [\text{\AA}^2]$	s.o.f. (<1)	<i>MCMA-SYNAI</i> ^c
H3a ^d	0.6099 (8)	0.6304 (8)	0.4767 (6)	0.067 (14)		0.047
W4 ^f	0.4720 (2)	0.32250 (18)	0.39340 (11)	0.0404 (6)	0.856 (3)	0.006
H4a ^d	0.4214 (6)	0.305 (3)	0.396 (2)	0.061	0.856 (3)	0.153
H4b ^e	0.4755	0.3284	0.3597	0.061	0.4279 (17)	0.008
H4c ^e	0.4724	0.2774	0.3931	0.061	0.4279 (17)	0.008
W4a ^f	0.5222 (11)	0.3341 (10)	0.3894 (7)	0.037 (4)	0.144 (3)	0.041
H4aa ^e	0.5674	0.3329	0.3973	0.056	0.144 (3)	0.033
H4ab ^e	0.5144	0.3390	0.3572	0.056	0.0721 (17)	0.038
H4ac ^e	0.5116	0.2868	0.3904	0.056	0.0721 (17)	0.035
W5 ^f	0.66667	0.33333	0.4188	0.109	0.87	0.036
W5m ^f	0.6776 (4)	0.3224 (4)	0.4179 (6)	0.062 (6)	0.288 (7)	0.048
H5ma ^e	0.6562	0.2882	0.4435	0.093	0.288 (7)	0.032
XU ^g	0.7291 (7)	0.2709 (7)	0.4580 (9)	0.022 (7)	0.0061 (7)	—

^aW denote H₂O oxygen atoms^bSite symmetry information (s.s.i.): site multiplicity, Wyckoff notation, and point symmetry^cPositional differences (Å) between corresponding atoms in *MCMA* and *SYNAI*^dH atoms refined in *x,y,z,U_{iso}* applying the restraints O–H=0.80 Å and H–O–H=106°^eH atoms in calculated unrefined positions at O–H=0.80 Å on the hydrogen bond lines with $U_{\text{iso}} = 1.5 \times U_{\text{eq}}(\text{carrier})$ ^fW4 and W4a are alternative positions with ~86 and ~14% occupancy. W5 and W5m are alternative exclusive positions to describe the oxygen atom of the interstitial water; only W5m has been used for the final refinement and all geometric data^gXU corresponds to an electron density peak *X* of 1.84 e[−]/Å³ interpreted as arising from an unresolved lattice defect. A uranium atom was placed at site *X* (denoted *XU*) solely to account for the contribution of peak *X* to the structure factors; see text for further explanation. Occurs in *SYNAI* but not in *MCMA*.

shared with the $\text{NaIO}_4(\text{H}_2\text{O})_2$ octahedron. The $\text{CaIO}_6(\text{H}_2\text{O})$ polyhedron links four UTC groups: two UTC groups via equatorial edge-sharing with the $(\text{UO}_2)\text{O}_6$ bipyramid and two further UTC groups via corner-sharing with two terminal carbonate O5 atoms. These two O5 atoms and one W1 define a shared triangular face between $\text{CaIO}_6(\text{H}_2\text{O})$ polyhedron and $\text{NaIO}_4(\text{H}_2\text{O})_2$ octahedron. The coordination environment of Na1 is completed by a second water molecule (W2) located trans to W1, as well as by two O3 atoms that constitute the shared edge with the $(\text{UO}_2)\text{O}_6$ bipyramid. The Na2 polyhedra form edge-linked double octahedra with six coordinated water molecules (2 W3 and 4 W4) arranged in a plane. Each Na2 polyhedron further links to the uranyl oxygen O7 of one UTC group and the terminal carbonate oxygen O1 of another UTC group. Together, these constituents form a complex three-dimensional framework with the composition $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\text{H}_2\text{O}$. Because of the structural complexity, the framework is difficult to illustrate as a whole and is therefore described in segmented form below.

An important fundamental feature of the andersonite framework is the $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layer parallel to (001) depicted in Fig. 2. This layer is constructed from infinite, undulating ribbons of UTC groups linked by pairs of inversion-related Ca^{2+} cations. The ribbons extend along [100], [010], and [110], and intersect at angles of 60°. Their nodes are defined by the Ca1 pairs and the

Ca-coordinating H₂O molecule W1. In this way, they form the unique $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layer, characterized by a combination of 6-membered and 3-membered rings of UTC groups, a topology so far known only from andersonite. Based on this ring arrangement and the number of rings, the layer may be described as 6–3–3 grid.

When UTC–Ca ribbons intersect at 90°, tetragonal or pseudotetragonal layers are formed, consisting of 4-membered rings of UTC groups and $\text{CaO}_6(\text{H}_2\text{O})$ polyhedra, with the same overall composition as the andersonite layers (Fig. 3). Such layers, termed *square-grid layers* by Plášil et al. (2017), constitute the structural basis of a larger family of calcium uranyl tricarbonates, for which the crystal structures of linekite, $\text{K}_2\text{Ca}_3[(\text{UO}_2)(\text{CO}_3)_3]_2 \cdot 8\text{H}_2\text{O}$ (Plášil et al. 2017) and synthetic $\text{Na}_2\text{Ca}_3[(\text{UO}_2)(\text{CO}_3)_3]_2 \cdot 10\text{H}_2\text{O}$ (Vochten et al. 1994; Mereiter et al. 2026) are prototypes, recently supplemented by minerals of the markeyite family (Kampf et al. 2018, 2020, 2022). These layers may also be described as 4–4 grids, as they contain two distinct types of 4-membered rings.

A key structural feature common to all these layers is the *paddle-wheel motif*, in which four UTC groups act as paddles linked by two Ca atoms forming the wheel (Figs. 2 and 3). These Ca atoms are coordinated in a trigonal prismatic manner by UTC oxygen atoms and face each other at relatively short, repulsive Ca···Ca distances imposed by the four bridging CO₃ groups. In *MCMA* this

Table 3 Atomic displacement parameters ($\text{\AA}^2$) for *MCMA* and *SYNAI*(a) Andersonite from Monte Cristo mine, *MCMA*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0259 (4)	0.0259 (4)	0.0171 (5)	0.0131 (5)	0.0020 (2)	-0.0020 (2)
Na2	0.0342 (5)	0.0342 (5)	0.0271 (7)	0.0150 (6)	-0.0026 (3)	0.0026 (3)
Ca1	0.01471 (16)	0.01471 (16)	0.0137 (2)	0.00785 (19)	0.00020 (9)	-0.00020 (9)
U1	0.01398 (4)	0.01398 (4)	0.01383 (5)	0.00459 (4)	0.00072 (2)	-0.00072 (2)
C1	0.0178 (9)	0.0178 (9)	0.0176 (12)	0.0061 (10)	0.0014 (5)	-0.0014 (5)
C2	0.0170 (8)	0.0163 (8)	0.0156 (8)	0.0074 (7)	0.0009 (6)	0.0005 (6)
O1	0.0287 (8)	0.0287 (8)	0.0150 (9)	0.0104 (9)	0.0010 (4)	-0.0010 (4)
O2	0.0244 (7)	0.0205 (7)	0.0196 (7)	-0.0006 (6)	0.0059 (6)	-0.0046 (6)
O3	0.0164 (7)	0.0214 (7)	0.0207 (7)	0.0026 (6)	0.0038 (5)	-0.0048 (6)
O4	0.0200 (7)	0.0210 (7)	0.0188 (6)	0.0050 (6)	0.0056 (5)	-0.0036 (5)
O5	0.0168 (6)	0.0187 (7)	0.0191 (6)	0.0045 (5)	-0.0014 (5)	-0.0027 (5)
O6	0.0266 (8)	0.0266 (8)	0.0289 (11)	0.0162 (9)	-0.0014 (4)	0.0014 (4)
O7	0.0317 (9)	0.0317 (9)	0.0268 (11)	0.0194 (10)	-0.0032 (4)	0.0032 (4)
W1	0.0221 (8)	0.0221 (8)	0.0224 (10)	0.0109 (8)	0.0001 (4)	-0.0001 (4)
W2	0.0306 (9)	0.0306 (9)	0.0298 (12)	0.0152 (11)	-0.0005 (5)	0.0005 (5)
W3	0.0299 (9)	0.0299 (9)	0.0332 (13)	0.0097 (10)	-0.0037 (5)	0.0037 (5)
W4	0.0455 (15)	0.0393 (13)	0.0361 (11)	0.0168 (12)	-0.0048 (12)	0.0011 (10)
W4a	0.0455 (15)	0.0393 (13)	0.0361 (11)	0.0168 (12)	-0.0048 (12)	0.0011 (10)
W5m	0.063 (9)	0.063 (9)	0.066 (7)	0.032 (6)	-0.005 (3)	0.005 (3)

(b) Synthetic andersonite, *SYNAI*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na1	0.0243 (5)	0.0243 (5)	0.0164 (6)	0.0121 (6)	0.0017 (2)	-0.0017 (2)
Na2	0.0325 (6)	0.0325 (6)	0.0257 (7)	0.0133 (7)	-0.0023 (3)	0.0023 (3)
Ca1	0.01183 (17)	0.01183 (17)	0.0125 (2)	0.0066 (2)	0.00011 (9)	-0.00011 (9)
U1	0.01112 (5)	0.01112 (5)	0.01191 (6)	0.00298 (4)	0.00069 (2)	-0.00069 (2)
C1	0.0142 (9)	0.0142 (9)	0.0175 (14)	0.0030 (11)	0.0013 (6)	-0.0013 (6)
C2	0.0148 (9)	0.0128 (9)	0.0134 (9)	0.0058 (7)	0.0014 (7)	0.0010 (7)
O1	0.0257 (8)	0.0257 (8)	0.0147 (10)	0.0091 (10)	0.0012 (5)	-0.0012 (5)
O2	0.0216 (8)	0.0165 (8)	0.0196 (8)	-0.0032 (6)	0.0076 (6)	-0.0038 (6)
O3	0.0141 (7)	0.0189 (8)	0.0184 (7)	0.0013 (6)	0.0042 (6)	-0.0045 (6)
O4	0.0175 (7)	0.0187 (7)	0.0170 (7)	0.0035 (6)	0.0054 (6)	-0.0034 (6)
O5	0.0135 (7)	0.0159 (7)	0.0174 (7)	0.0021 (6)	-0.0006 (6)	-0.0026 (6)
O6	0.0237 (9)	0.0237 (9)	0.0261 (12)	0.0138 (10)	-0.0015 (5)	0.0015 (5)
O7	0.0293 (10)	0.0293 (10)	0.0252 (12)	0.0183 (11)	-0.0028 (5)	0.0028 (5)
W1	0.0221 (9)	0.0221 (9)	0.0211 (11)	0.0120 (10)	-0.0002 (5)	0.0002 (5)
W2	0.0276 (10)	0.0276 (10)	0.0294 (14)	0.0132 (11)	-0.0009 (5)	0.0009 (5)
W3	0.0271 (9)	0.0271 (9)	0.0312 (14)	0.0074 (11)	-0.0030 (6)	0.0030 (6)
W4	0.0453 (16)	0.0396 (14)	0.0344 (13)	0.0199 (13)	-0.0026 (12)	0.0029 (11)
W5m	0.052 (8)	0.052 (8)	0.088 (8)	0.031 (5)	-0.009 (3)	0.009 (3)

Ca...Ca distance is 3.825 Å, which is notably shorter than in línekite (4.048 Å) and minerals of the markeyite family (4.01–4.18 Å). In all these compounds, the Ca atoms of the paddle-wheel motif are seven-coordinated by an additional H₂O molecule, expanding the trigonal prism to a monocapped trigonal prism. This H₂O molecule donates usually one internal hydrogen bond to a neighboring terminal carbonate oxygen atom; in andersonite, it donates two. The Ca sites within the paddle-wheel motif appear to be highly selective for Ca²⁺, and significant substitution by competing cations such as Na⁺, K⁺, or Sr²⁺ has not been observed (Mereiter et al. 2026).

In andersonite, the trigonal {Ca(H₂O)[(UO₂)(CO₃)₃]}²⁻ layers are stacked along the *c* axis according to the *R*-lattice translations $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ (Fig. 2). As a result, each 6-membered UTC ring is under- and overlaid by a 3-membered ring, whereas each 3-membered ring neighbors both a 6-membered and another 3-membered ring. Consequently, the ring sequence along [001] is periodic as -6-3-3-. Structural coherence between adjacent {Ca(H₂O)[(UO₂)(CO₃)₃]}²⁻ layers along [001] is achieved primarily through NaIO₄(H₂O)₂ octahedra. These octahedra share edges with the (UO₂)O₆ polyhedron of one layer (O3, O3ⁱ; Table 4) and bond to two terminal carbonate oxygen atoms

Table 4 Comparison of selected structural data for the andersonites *MCMA*, *SYNA1*, *SYNA2*, *SYNA3*, *CSCA* (Gurzhiy et al. 2018), and *JACA* (Plášil and Čejka 2015)

Structure		<i>MCMA</i>	<i>SYNA1</i>	<i>SYNA2</i> ^a	<i>SYNA3</i> ^a	<i>CSCA</i> ^b	<i>JACA</i> ^c
Source		natural	synthetic	synthetic	synthetic	natural	natural
Temperature [K]		297	297	200	100	100	293
Unit cell <i>a</i> , <i>c</i> [Å]		17.9012(6), 23.7978(12)	17.9015(6), 23.7752(12)	17.8834(13) 23.6713(17)	17.8498(3), 23.6250(4)	17.8448(4), 23.6688(6)	17.8589(6), 23.6935(8)
<i>R</i> 1 (>4σ(<i>F</i>)) / reflections		0.0139/2283	0.0144/2190	0.0134/2169	0.0122/2303	0.0185/1697	0.0300/1729
Bond lengths [Å]							
Na1–O3 ^{n, i}	×2	2.331(2)	2.333(2)	2.326(2)	2.320(2)	2.323(3)	2.330(5)
Na1–O5 ^{ii, iii}	×2	2.434(2)	2.437(2)	2.427(2)	2.417(2)	2.416(3)	2.429(5)
Na1–W1		2.402(2)	2.400(3)	2.392(3)	2.382(2)	2.379(4)	2.405(7)
Na1–W2		2.378(3)	2.374(3)	2.369(3)	2.368(2)	2.375(4)	2.371(7)
<Na1–O>		2.385	2.386	2.378	2.371	2.372	2.382
Na2–O1		2.415(3)	2.415(3)	2.401(3)	2.391(2)	2.390(4)	2.424(7)
Na2–O7 ^{iv}		2.501(3)	2.503(3)	2.478(3)	2.459(2)	2.464(4)	2.489(7)
Na2–W3 ^{n, iv}	×2	2.500(2)	2.490(2)	2.483(2)	2.479(2)	2.479(3)	2.494(5)
Na2–W4 ^{n, i}	×2	2.429(3)	2.431(3)	2.428(3)	2.425(2)	2.427(3)	2.425(6)
<Na2–O>		2.462	2.460	2.450	2.443	2.440	2.458
Na2–W4a ^{n, i}	(×2)	2.459(16)	2.459(16)	2.468(15)	2.480(14)	2.52(2)	no W4a
W4–W4a		0.85(2)	0.82(2)	0.85(2)	0.88(2)	0.88(2)	no W4a
Ca1–O2 ^{v, vi}	×2	2.314(2)	2.316(2)	2.310(2)	2.303(2)	2.304(2)	2.305(4)
Ca1–O4 ^{vii, viii}	×2	2.398(2)	2.398(2)	2.396(2)	2.394(2)	2.396(2)	2.392(4)
Ca1–O5 ^{ii, iii}	×2	2.372(2)	2.370(2)	2.367(2)	2.366(2)	2.368(2)	2.363(4)
Ca1–W1		2.552(2)	2.553(2)	2.543(3)	2.537(2)	2.542(3)	2.531(6)
<Ca1–O>		2.389	2.389	2.384	2.380	2.383	2.379
U1–O6		1.776(2)	1.775(2)	1.784(2)	1.789(2)	1.784(3)	1.767(6)
U1–O7		1.784(2)	1.780(2)	1.785(2)	1.790(2)	1.792(3)	1.775(6)
<U1–O _{ur} >		1.780	1.778	1.784	1.789	1.788	1.771
U1–O2 ^{n, i}	×2	2.418(2)	2.418(2)	2.417(2)	2.416(2)	2.416(2)	2.419(4)
U1–O3 ^{n, i}	×2	2.438(2)	2.440(2)	2.438(2)	2.436(2)	2.435(2)	2.428(4)
U1–O4 ^{n, i}	×2	2.462(2)	2.459(2)	2.459(2)	2.457(2)	2.458(2)	2.453(5)
<U1–O _{eq} >		2.439	2.439	2.438	2.436	2.436	2.433
C1–O1		1.237(3)	1.246(4)	1.244(4)	1.249(3)	1.247(5)	1.232(10)
C1–O2 ^{n, i}	×2	1.298(2)	1.297(2)	1.303(2)	1.303(2)	1.301(3)	1.294(6)
C2–O3		1.299(2)	1.295(3)	1.300(3)	1.300(2)	1.302(4)	1.299(6)
C2–O4		1.299(2)	1.295(3)	1.299(3)	1.300(2)	1.299(4)	1.287(7)
C2–O5		1.254(2)	1.255(3)	1.256(3)	1.260(2)	1.255(4)	1.251(7)
<C–O>		1.282	1.281	1.285	1.286	1.284	1.277
<C–O1,5>		1.249	1.252	1.252	1.256	1.251	1.245
<C–O2,3,4>		1.299	1.296	1.301	1.301	1.301	1.293
Hydrogen bonds [Å]							
W1(H1a)···O1 ^{vii}	×2	2.927(2)	2.929(2)	2.917(2)	2.910(2)	2.914(3)	2.915(6)
W2(H2a)···O6 ⁱⁱⁱ		3.057(3)	3.058(3)	3.050(3)	3.035(2)	3.038(4)	3.045(6)
W2(H2b)···W2 ^{ix}	×2	2.736(3)	2.736(4)	2.733(3)	2.730(3)	2.726(4)	2.723(7)
W3(H3a)···O5 ^x	×2	2.924(2)	2.924(2)	2.907(2)	2.893(2)	2.899(3)	2.906(6)
W4(H4a)···O3 ^{xi}		3.026(3)	3.025(4)	3.004(3)	2.990(3)	2.993(4)	3.046(8)
W4(H4b)···W4 ^{xii}		2.873(5)	2.876(5)	2.856(4)	2.844(4)	2.846(6)	2.850(11)
W4(H4c)···W4 ^{xiii}		3.086(5)	3.096(6)	3.071(5)	3.056(4)	3.052(6)	3.059(12)
<Donor···Acceptor>		2.947	2.949	2.934	2.923	2.924	2.935
W4a(H4aa)···W5m		2.96(2)	2.97(2)	2.93(2)	2.93(2)	on-axis W5	no W4a
W5m(H5ma)···O1 ^{xiv}		3.052(10)	3.068(11)	3.033(10)	3.009(9)	on-axis W5	on-axis W5
Bond angles [°]							
W1–Na1–W2		156.0(1)	156.1(1)	156.6(1)	156.6(1)	156.5(1)	156.0(2)
O6–U1–O7		179.3(1)	179.3(1)	179.4(1)	179.4(1)	179.3(2)	179.1(2)
O2–U1–O2 ⁱ		53.03(5)	52.98(7)	53.19(7)	53.30(7)	53.25(11)	53.0(2)
O3–U1–O4	×2	53.07(5)	52.96(5)	53.08(5)	53.22(4)	53.15(7)	53.0(2)

Table 4 (continued)

Structure		<i>MCMA</i>	<i>SYNA1</i>	<i>SYNA2</i> ^a	<i>SYNA3</i> ^a	<i>CSCA</i> ^b	<i>JACA</i> ^c
O6–U1–O2 ^{n, i}	×2	93.36(9)	93.47(8)	93.50(8)	93.68(7)	93.76(11)	93.3(2)
O6–U1–O3 ^{n, i}	×2	90.07(8)	89.95(7)	90.14(7)	90.07(6)	90.03(10)	90.0(2)
O6–U1–O4 ^{n, i}	×2	84.08(5)	84.04(5)	84.02(4)	83.92(4)	83.88(5)	84.0(2)
O1–C1–O2	×2	123.7(1)	123.7(1)	123.9(1)	123.7(1)	123.7(2)	123.5(3)
O2–C1–O2 ⁱ		112.5(3)	112.5(3)	112.2(3)	112.5(2)	112.6(4)	112.9(6)
O3–C2–O4	×2	114.9(2)	115.1(2)	114.7(2)	114.9(2)	114.6(3)	114.7(4)
O3–C2–O5	×2	122.9(2)	122.6(2)	122.9(2)	122.7(2)	122.8(3)	122.7(4)
O4–C2–O5	×2	122.3(2)	122.4(2)	122.5(2)	122.4(2)	122.6(3)	122.6(4)
Na1–W1–Ca1		84.23(8)	84.18(8)	83.82(8)	83.74(7)	83.90(12)	84.2(2)
Na2–W3–Na2 ^{iv}		96.03(10)	95.68(10)	96.19(9)	96.43(8)	96.59(14)	95.0(2)
Peak heights and occupancies							
peak height of W5/W5m		4.66 e [−] /Å ³	4.45 e [−] /Å ³	4.90 e [−] /Å ³	4.80 e [−] /Å ³	4.69 e [−] /Å ³	4.87 e [−] /Å ³
Interstitial H ₂ O per formula unit		0.276(7)	0.288(7)	0.275(8)	0.280(9)	0.278(8) (O _w 5+O _w 5a)	fixed at 1/3
H ₂ O in W4a per formula unit		0.276(7)	0.288(7)	0.264(14)	0.256(12)	0.238(12)	no W4a
height of peak <i>X</i>		—	1.84 e [−] /Å ³	2.81 e [−] /Å ³	2.72 e [−] /Å ³	2.51 e [−] /Å ³	—
<i>X</i> –W1		—	1.78(2) Å	1.84(2) Å	1.83(2) Å	1.82(2) Å	—
<i>X</i> –W5m		—	1.86(2)	1.78(2)	1.75(2)	2.04(2) W5	—
<i>X</i> –O1	×2	—	2.468(13)	2.473(9)	2.465(9)	2.43(1)	—
<i>X</i> –W4	×2	—	2.434(16)	2.402(11)	2.396(11)	2.46(2)	—

^aFor crystallographic data of *SYNA2* and *SYNA3* see supplementary material

^bStructural data of Gurzhiy et al. (2018), except that their atom O_w5b is now interpreted as peak *X*. For an improved structure model giving 0.30(1) W5 + W5a, see supplementary material

^cStructural data of Plášil and Čejka (2015) without W4/W4a splitting and H-atoms. For an improved structure model giving 0.30(3) W4a and 0.29(1) W5, see supplementary material

Symmetry codes: nil or (n) *x*, *y*, *z*; (i) $-y+1, -x+1, z$; (ii) $-x+4/3, -x+y+2/3, -z+5/3$; (iii) $x-y+1/3, x-1/3, -z+5/3$; (iv) $-x+1, -y+1, -z+1$; (v) $-y+2/3, x-y+1/3, z+1/3$; (vi) $-x+y+2/3, y+1/3, z+1/3$; (vii) $-x+y+2/3, -x+4/3, z+1/3$; (viii) $x-1/3, x-y+1/3, z+1/3$; (ix) $x-y+1/3, -y+2/3, -z+5/3$; (x) $-y+4/3, x-y+2/3, z-1/3$; (xi) $-x+y+1/3, y-1/3, z-1/3$; (xii) $x-y+1/3, -y+2/3, -z+2/3$; (xiii) $x, x-y, z$; (xiv) $-y+1, x-y, z$

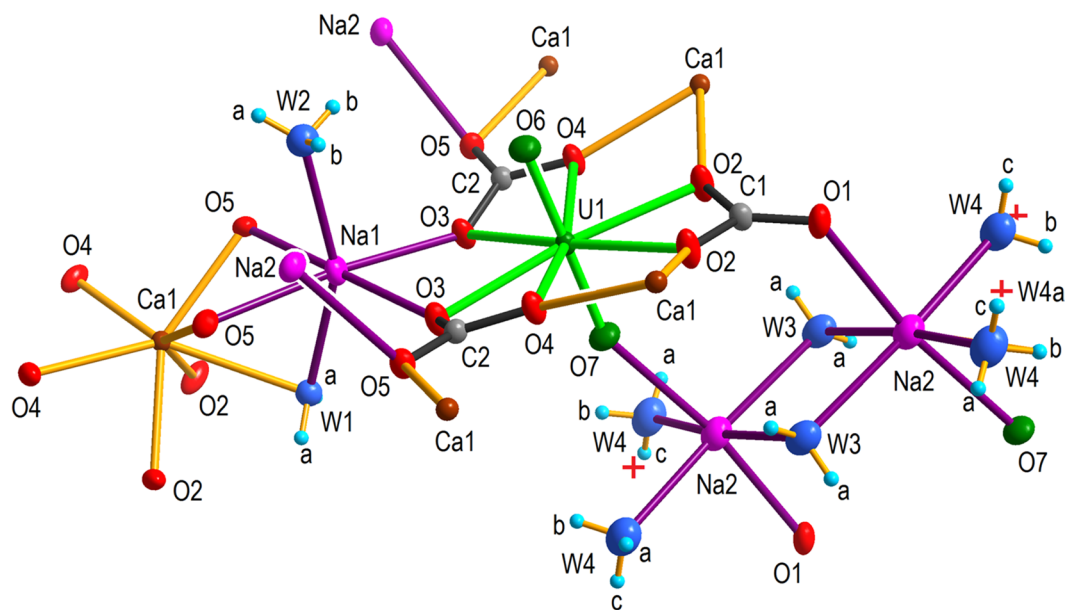


Fig. 1 Andersonite from the Monte Cristo mine (*MCMA*), showing an extended asymmetric unit with 50% displacement ellipsoids. A mirror plane passes through Na1, Na2, Ca1, U1, C1, O1, O6, O7, W1,

and W2, where W denotes H₂O oxygen atoms. Satellite sites W4a are marked by red crosses, and the interstitial H₂O at W5m is omitted. H atoms are labeled by their trailing letters

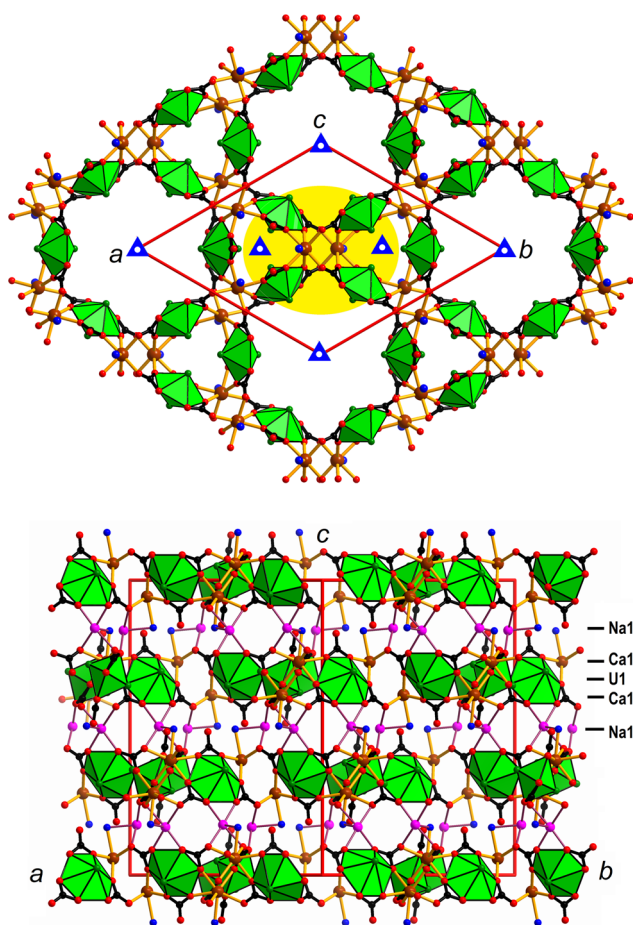


Fig. 2 *Top*: $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layer in andersonite at $z \approx 0$ showing the 6- and 3-membered UTC rings formed by intersecting undulating ribbons. $(\text{UO}_2)\text{O}_6$ polyhedra green, Ca brown, CO_3 black and red, H_2O blue. Blue triangles mark $\bar{3}$ axes. The yellow background highlights the paddle-wheel motif. *Bottom*: Stacking of layers viewed along $[110]$, with Na1 atoms (violet) added to illustrate the principal interlayer linkages. The ring sequence along $[001]$ is $-6-3-3-$ periodic

of the adjacent layer (O5^{ii} , O5^{iii} , Table 4). This linkage operates between two UTC 3-rings and produces a barrel-like, ellipsoidal cage (Fig. 4). The $\text{Na}_2\text{O}_2(\text{H}_2\text{O})_4$ octahedra contribute less significantly to interlayer coherence, linking a terminal carbonate oxygen atom (O1) of one $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layer with a uranyl oxygen atom (O7) of the next. The large UTC 6-rings shown in Fig. 2, are occupied by six O7-bonded Na2 atoms and twelve Na2-bonded H_2O molecules (W4), except for the ring centers, which host interstitial H_2O molecules (Fig. 5).

The interlayer cross-linking in andersonite is sufficiently strong that crystals typically exhibit a blocky habit and lack a pronounced cleavage parallel to the layers. Nevertheless, thermal expansion data indicate a layered character: between 25 and 90 °C, expansion along the c axis is several times greater than along the a axis (Gurzhiy et al. 2018).

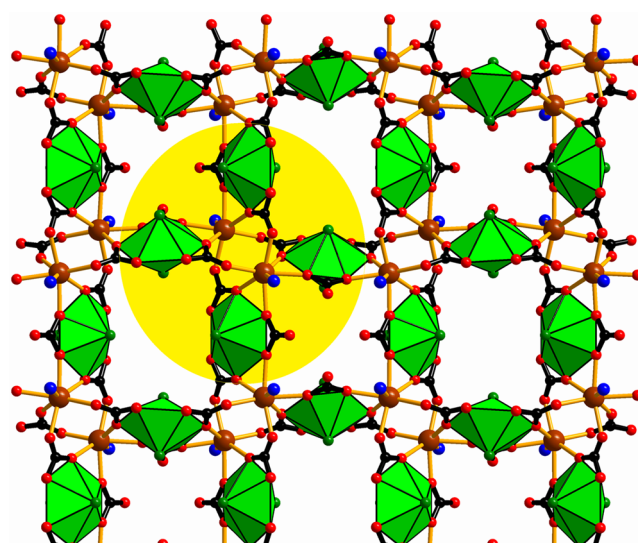


Fig. 3 The $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ square-grid layer in linekite, $\text{K}_2\text{Ca}_3[(\text{UO}_2)_2(\text{CO}_3)_3]_2 \cdot 8\text{H}_2\text{O}$ (Plášil et al. 2017), $\text{Na}_2\text{Ca}_3[(\text{UO}_2)_2(\text{CO}_3)_3]_2 \cdot 10\text{H}_2\text{O}$ (Mereiter et al. 2026), and related minerals (4-4 grids), to be compared with the isochemical trigonal layer in andersonite (6-3-3 grid) shown in Fig. 2. The yellow background highlights the paddle-wheel motif

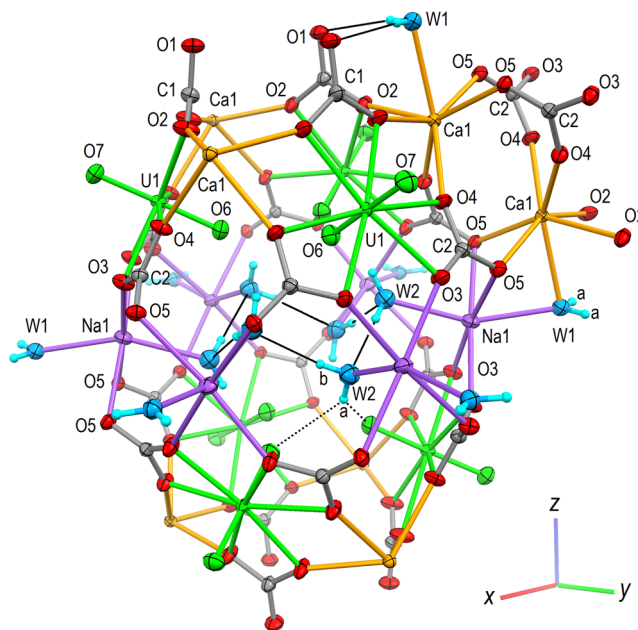


Fig. 4 Barrel-like segment of two 3-membered Ca-UTC rings linked by six $\text{Na1O}_4(\text{H}_2\text{O})_2$ octahedra in andersonite. The barrel has $3m$ symmetry and is centered at $x,y,z=0,0,\frac{1}{2}$; $\frac{2}{3},\frac{1}{3},\frac{5}{6}$; and $\frac{1}{3},\frac{2}{3},\frac{1}{6}$. Ca1 coordination is incomplete for clarity, except in the upper right. The center contains a six-membered ring of $\text{W2} \cdots \text{W2}$ hydrogen bonds (black lines) and one example of a bifurcated hydrogen bond from H2a to two O6 atoms (dotted lines). A one-third segment of the six-membered hydrogen-bond ring between W1 and O1 is shown at the top. This ring is also part of the interstitial H_2O cavity shown in Fig. 6

Bond lengths and bond angles for the Monte Cristo mine andersonite *MCMA* (Table 4) largely fall within expected

ranges for NaO and CaO coordination polyhedra. The mean Na–O bond length in the $\text{NaIO}_4(\text{H}_2\text{O})_2$ octahedron (2.385 Å) is shorter than that in the more regular $\text{Na}_2\text{O}_2(\text{H}_2\text{O})_4$ octahedron (2.462 Å), reflecting the larger number of Na–O bonds involving carbonate oxygen atoms in the former. The mean Ca–O bond length in the $\text{CaIO}_6(\text{H}_2\text{O})$ polyhedron is 2.389 Å, comparable to those reported for linekite (Plášil et al. 2017) and other structures with square-grid layer architectures. For comparison, Gagné and Hawthorne (2016) reported mean values of 2.441(56) Å for $^{[6]}\text{Na}$ –O and 2.447(38) Å for $^{[7]}\text{Ca}$ –O in a large dataset of inorganic compounds. Mixed occupancy of the Na1, Na2, and Ca1 sites by Na and Ca was excluded by various test refinements.

For UTC groups, Lussier et al. (2016) reported mean bond lengths of 1.783(30) Å for $^{[8]}\text{U}^{6+}\text{--O}_{\text{yl}}$ and 2.460(107) Å for $^{[8]}\text{U}^{6+}\text{--O}_{\text{eq}}$, values that agree well with values found in andersonite (Table 4). A notable feature of andersonite is the pronounced saddle-like deformation of the UTC group. The CO_3 group of C1 is strongly bent toward Na2, whereas the two CO_3 groups of C2 are bent in the opposite direction toward Na1 (Fig. 1). Consequently, the six oxygen atoms chelating U1 deviate substantially from a common least-squares plane (r.m.s. deviation = 0.151 Å). The terminal carbonate oxygen atoms deviate by $-0.705(4)$ Å (O1) and $+0.385(2)$ Å (O5) from this plane, corresponding to tilt angles between the UO_6 plane and the CO_3 planes of $18.1(1)^\circ$ for C1 and $13.2(1)^\circ$ for C2. This distortion is largely attributed to the restricted size of the UTC 3-rings in the andersonite layer and is absent in square-grid $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layers.

Water molecules, hydrogen-bonding and the H_2O cavity

Andersonite from the Monte Cristo mine contains five crystallographically distinct H_2O groups in the $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3]\cdot 5\text{H}_2\text{O}$ framework, in addition to an interstitial H_2O molecule. Framework water molecules are represented by oxygen atoms W1, W2, W3, W4, and W4a and their associated hydrogen atoms.

W1, located on a mirror plane, bridges Ca1 and Na1 and donates two symmetry-equivalent hydrogen bonds to terminal carbonate oxygen O1 ($\text{W1}\cdots\text{O1}=2.927(2)$ Å). Its coordination by Na1, Ca1, and two O1 atoms is distorted tetrahedral, with angles ranging from $81.6(1)^\circ$ (O1–W1–O1) to $139.2(1)^\circ$ (Na1–W1–O1). The hydrogen bond $\text{W1--H1a}\cdots\text{O1}$ forms a nearly planar six-membered ring of $\text{R}^3_3(12)$ topology (Etter 1990) around a threefold axis (Figs. 4 and 6).

The second water coordinating Na1, W2, also lies on a mirror plane. Six W2 molecules are arranged around a center of $\bar{3}m$ symmetry at $(0, 0, \frac{1}{2})$ within the barrel-like

assembly formed by two Ca1–UTC three-rings linked by six Na1 atoms (Fig. 4). These W2 molecules form a puckered six-membered hydrogen-bond ring in chair conformation with $\text{W2}\cdots\text{W2}$ distances of 2.736(3) Å, corresponding to $\text{R}^6_6(12)$ topology. The hydrogen bonds are symmetry-disordered, with half-occupied H2b positions; clockwise and counterclockwise orientations may occur randomly. The second hydrogen atom, H2a, lies on the mirror plane and shows a symmetrically bifurcated interaction with two uranyl oxygen atoms O6 ($\text{W2}\cdots\text{O6}=3.057(3)$ Å; $\text{W2--H2a}\cdots\text{O6}=135(1)^\circ$).

W3 lies on a twofold axis and bridges two symmetry-equivalent Na2 atoms. It donates two equivalent hydrogen bonds to carbonate oxygen O5 ($\text{W3}\cdots\text{O5}=2.924(2)$ Å) and contributes to linking adjacent $\{\text{Ca}(\text{H}_2\text{O})[(\text{UO}_2)(\text{CO}_3)_3]\}^{2-}$ layers. W3 does not participate in hydrogen-bond ring formation. Tetrahedral angles around W3 range from $88.6(1)^\circ$ (O5–W3–O5) to $126.8(1)^\circ$ (Na2–W3–O5).

The Na-bonded water of W4/W4a and the interstitial water W5/W5m form a unique integrated system, a water-in-water capsule, that is outlined in Figs. 5 and 6. W4 occupies a general position and is terminally coordinated to Na2 atoms on mirror planes. Six Na2 atoms form an octahedral arrangement around a center of $\bar{3}m$ symmetry at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$. The twelve associated W4 molecules form two stacked six-membered rings, defining a hexagonal prism $(\text{W4})_{12}$ (Fig. 6). This assembly is centered within the six-membered UTC rings shown in Fig. 2. Within this prism, the twelve W4 molecules form a conjugated twelve-membered hydrogen-bond ring with crown-like geometry and $\text{R}^1_1{}^2_2(24)$ topology. Hydrogen bond $\text{W4}\cdots\text{W4}$ distances are 2.873(5) Å parallel to [001] and 3.086(5) Å perpendicular to it, while W4--W4 distances of 3.682(5) Å are edges of the Na2 octahedron. The hydrogen bonds within the ring are symmetry-disordered, with half-occupied H4b and H4c positions, but individual rings may adopt a uniform clockwise or counterclockwise orientation. In addition, W4 donates an ordered exo-oriented hydrogen bond via H4a to carbonate oxygen O3 ($\text{W4}\cdots\text{O3}=3.026(3)$ Å). The coordination environment of W4 is distorted tetrahedral, with angles ranging from $87.3(1)^\circ$ to $139.4(1)^\circ$.

Approximately 14% of the W4 molecules occupy the nearby alternative position W4a, displaced by 0.85(2) Å. W4a retains coordination to Na2 and its two hydrogen bonds within the twelve-membered ring, but replaces the exo-oriented hydrogen bond (H4a) with an endo-oriented bond (H4aa) directed toward the axis of the $(\text{W4})_{12}$ prism. This orientation enables hydrogen bonding to the interstitial water molecule W5m, which is located within the $(\text{W4}/\text{W4a})_{12}$ prism. The distance from the prism axis to W4 is 3.39 Å, decreasing to 2.57 Å for W4a.

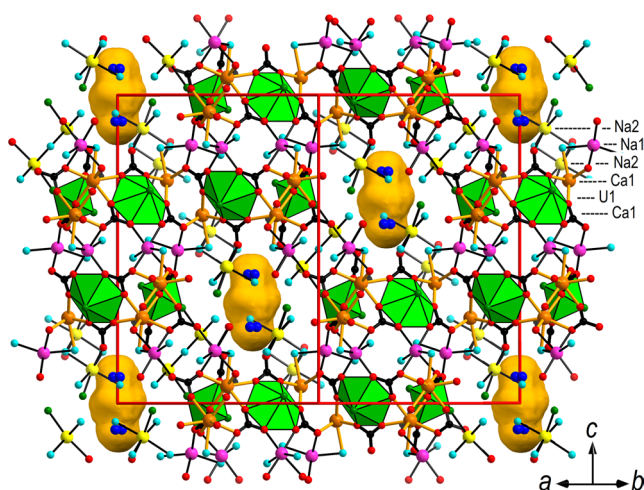


Fig. 5 Interstitial water in andersonite. Projection of a (110) slab of the structure showing solvent-accessible cavity surfaces hosting the interstitial H_2O at W5m (dark blue). The cavities have point symmetry $\bar{3}m$ and occur at $x,y,z=0,0,0$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; and $\frac{1}{3},\frac{2}{3},\frac{2}{3}$. Each cavity is closed, has a solvent-accessible volume of $\sim 60 \text{ \AA}^3$, and can incorporate two H_2O molecules, corresponding to $\frac{1}{3} \text{H}_2\text{O}$ per formula unit. $(\text{UO}_2)_6$ polyhedra are shown in green, CO_3 in black and red, and Na/Ca-bonded H_2O in light blue

The $(\text{W4}/\text{W4a})_{12}$ prism is capped above and below by two six-membered $\text{W1} \cdots \text{O1}$ hydrogen-bond rings ($\text{W1} \cdots \text{O1} = 2.928(2) \text{ \AA}$), with O1 atoms located only $2.21 \text{ \AA}$ from the prism axis. Beyond these caps are three uranyl oxygen atoms O6, only $1.84 \text{ \AA}$ from the axis, forming nearly close-packed triangular arrangements ($\text{O6} \cdots \text{O6} = 3.19 \text{ \AA}$, Fig. 4). Together, these features define a tightly enclosed cavity that can accommodate two interstitial H_2O molecules per cavity, corresponding to $\frac{1}{3} \text{H}_2\text{O}$ per formula unit (Fig. 5). Due to O1 and O6, there is no infinite channel along $[001]$.

Void-volume analysis using standard van der Waals radii for oxygen ($1.52 \text{ \AA}$) and a probe radius of $1.2 \text{ \AA}$ (PLATON; Spek 2015, 2021) yields a cavity volume of $78 \text{ \AA}^3$, which decreases to $64 \text{ \AA}^3$ when two W4 positions are replaced by W4a. This void volume is about twice the space requirement for an average interstitial water molecule ($\sim 40 \text{ \AA}^3$ per molecule according to Spek 2021; H_2O in ice *1h* occupies a volume of $\sim 32 \text{ \AA}^3$). Hence, this volume is consistent with the accommodation of two interstitial H_2O molecules and excludes a third. No other voids exceeding $15 \text{ \AA}^3$ are present in the structure (Fig. 5).

The interstitial water oxygen appears as a distinct triangular electron-density peak about the threefold axis. It may be modeled either as an average on-axis position (W5) with a large oblate displacement ellipsoid or as an off-axis position W5m, displaced by $0.34(2) \text{ \AA}$ onto a mirror plane. Both models yield comparable *R* values; the W5m model was adopted as more representative of an angular H_2O molecule and the shape of its electron-density peak.

Two clusters of W5m positions occur at opposite ends of the $(\text{W4}/\text{W4a})_{12}(\text{O1})_6$ cavity near the terminal carbonate oxygen

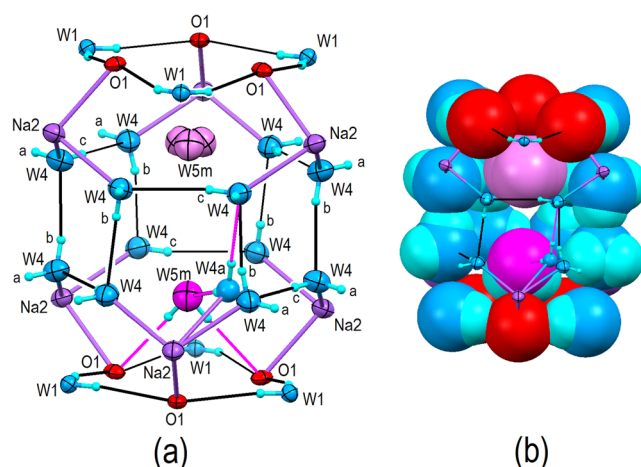


Fig. 6 The water-in-water capsule in andersonite: a cavity formed by a hexagonal prism of 12 hydrogen-bonded W4 molecules coordinated to six Na2 atoms ($\text{W4} \cdots \text{W4} = 2.873 \text{ \AA}$ vertical, $3.086 \text{ \AA}$ horizontal; *MCMA*) encloses two interstitial H_2O molecules (W5m). Two hydrogen-bond rings ($\text{W1} \cdots \text{O1} = 2.927 \text{ \AA}$) confine the cavity. **a** Structure with 50% displacement ellipsoids; **b** van der Waals spheres, Na omitted. *Upper side*: Three symmetry-equivalent W5m sites are slightly displaced from the threefold axis. *Lower side*: A single W5m is hydrogen-bonded to two O1 atoms ($3.05 \text{ \AA}$) and one W4a site ($\sim 14\%$ occupancy), which forms an endo-oriented bond to W5m instead of the exo-oriented $\text{W4} \cdots \text{O3}$ bond

atoms O1. They are mutually separated by $4.14 \text{ \AA}$ leaving a gap of $\sim 1.2 \text{ \AA}$ when the van der Waals radius of oxygen is taken into account. The surrounding W4 molecules (shortest $\text{W5m} \cdots \text{W4} = 3.16 \text{ \AA}$) are poor hydrogen-bond acceptors for W5m due to their involvement in the cavity-wall hydrogen-bond network, whereas W4a is favorably oriented to donate a hydrogen bond to W5m ($\text{W4a}(\text{H4aa}) \cdots \text{W5m} = 2.96 \text{ \AA}$). In turn, W5m appears to donate two hydrogen bonds to adjacent O1 atoms ($\text{W5m}(\text{H5ma}) \cdots \text{O1} = 3.05 \text{ \AA}$), which are the only suitable acceptors for W5m.

Refinement of W5m without hydrogen atoms yields an oxygen occupancy of $94(3)\%$ for *MCMA*; inclusion of hydrogen atoms reduces this value by $\sim 10\%$, reflecting the diffuse electron density of the oxygen hydrogen atom system spread out about the threefold axis. Because the occupancies of W4a and W5m are closely correlated, they were refined using a single variable. The final refinement indicates that the cavity is statistically occupied to $83(2)\%$ of its maximum capacity of two H_2O molecules, corresponding to a total water content of $5 + 0.28 \text{H}_2\text{O}$ per formula unit, in close agreement with the ideal value of $5\frac{1}{3} \text{H}_2\text{O}$ for a 100% occupancy of W5m.

Synthetic andersonite (SYNA)

We report here the crystal structures of three synthetic andersonites (acronyms *SYNA1*, *SYNA2*, *SYNA3*), which were investigated at temperatures of 297 K , 200 K , and

100 K in order to study the thermal response of the structures and to find out how they agree with the natural andersonite *MCMA*.

Synthesis and chemical analysis

Samples of synthetic andersonite, sample designations *SYNA1* and *SYNA2*, were prepared following the method of Meyrowitz and Ross (1961) using analytical grade Na_2CO_3 , $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in molar 3:1:1 proportion. The reaction scheme can be summarized as $3\text{Na}_2\text{CO}_3 + \text{UO}_2(\text{NO}_3)_2 \rightarrow \text{Na}_4\text{UO}_2(\text{CO}_3)_3$ and $\text{Na}_4\text{UO}_2(\text{CO}_3)_3 + \text{Ca}(\text{NO}_3)_2 \rightarrow \text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \downarrow + 4\text{NaNO}_3$. Crystallization was achieved by fractional crystallization from aqueous solution (80 ml H_2O per 0.01 mol U) at ambient temperature through slow partial evaporation. Sample *SYNA3* was obtained by recrystallization of pure *SYNA2* from an aqueous solution saturated at about 50 °C under vigorous stirring followed by filtration to remove excess material; for *SYNA3* this means that the crystallization solution was free of NaNO_3 , unlike for *SYNA1* and *SYNA2*.

In all syntheses, polycrystalline incrustations formed on the entire contact surface of the glassware, accompanied by smaller amounts of floating aggregates. The products consisted mainly of intimately intergrown crystals of approximately 0.1 mm size and yielded X-ray powder diffraction patterns of pure andersonite. Only a few clear, flawless euhedral rhombohedra {101} of cube-like shape, occasionally with small triangular {001} truncations, were observed; these were selected for single-crystal X-ray diffraction studies.

In contrast to Meyrowitz and Ross (1961), who reported crystals up to 0.5–1 mm, our crystals reached a maximum size of only ~0.2 mm, in agreement with a side-note of Coda et al. (1981). These size characteristics are noteworthy because many natural andersonites form similar small and intimately intergrown crystals, comparable to our synthetic material (Mindat.org 2025b). Notable exceptions include localities such as the Monte Cristo and Repete mines, Utah, USA, where well-formed euhedral crystals exceeding 3 mm have been reported (Mindat.org 2025c; see also Fronzel 1958; Mereiter 1986). The natural andersonite sample *MCMA* belongs to this latter category. Unlike the cuboid-like habit of the synthetic crystals, the *MCMA* specimen contained crystals with thick tabular habit and some faces of the forms {401}, {502}, {20–1}, {10–2} in addition to dominant forms {101} and {001} (Mereiter 1986).

Another distinction between *MCMA* and the synthetic material concerns optical properties. *MCMA* is optically uniaxial, whereas the synthetic crystals exhibit weak optical anomalies such as sector zoning or weak biaxial character, in agreement with earlier observations (Mereiter 1986).

It is unclear how this feature relates to the lattice defect described below.

Chemical analyses of two *SYNA2* samples were performed at the Mikroanalytisches Laboratorium, Faculty of Chemistry, University of Vienna. C/H/N analyses were carried out using an Eurovector EA 3000 elemental analyzer employing flash combustion in pure oxygen at ~1200 °C. Milligram quantities of sample were digested in tin cups, with vanadium pentoxide added to prevent the formation of metastable carbonates during thermal decomposition. Carbon (as CO_2) and hydrogen (as H_2O) were quantified by gas chromatography using a thermal conductivity detector with high-purity helium as the carrier gas.

Measured carbon contents from triplicate analyses were 5.74(5) and 5.61(14) wt%, and hydrogen contents were 1.67(3) and 1.72(4) wt%. These values compare well with the theoretical values of 5.70 wt% C and 1.70 wt% H for $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\frac{1}{2}\text{H}_2\text{O}$. The corresponding analytical water contents are 5.24(9) and 5.40(13) H_2O per formula unit. These values are lower than those previously reported (Plášil and Čejka 2015), but fall within the range supported by the present crystal structure analyses.

Structure determination

Single-crystal X-ray diffraction studies were conducted on three synthetic andersonite samples: *SYNA1* at 297 K, *SYNA2* at 200 K, and *SYNA3* (recrystallized andersonite) at 100 K. Data for *SYNA1* were collected on the same instrument used for *MCMA*. *SYNA2* was measured using a Bruker Kappa APEX2 system, and *SYNA3* was studied using a STOE StadiVari diffractometer equipped with a MoK α microsource and a Dectris EIGER CdTe hybrid photon-counting detector. Reflection intensities were extracted and corrected for absorption using a multi-scan procedure. Structure refinements were performed using SHELXL (Sheldrick 2015b), starting from the *MCMA* structure model in space group $R\bar{3}m$. Hydrogen atoms were treated using the same constraints or fixed-position models as applied for *MCMA*.

As in *MCMA*, the Na2-coordinating H_2O molecule W4 is split into a main site (W4) and a satellite site (W4a), with refined occupancies of approximately 86/14% in all three synthetic samples. This ratio is essentially temperature-independent. The electron density associated with the interstitial water molecule W5m exhibits a triangular distribution that becomes sharper with decreasing temperature, further supporting the off-axis position model previously introduced for *MCMA*.

In *SYNA2* (200 K) and *SYNA3* (100 K), but not in *SYNA1* or *MCMA*, an additional weak difference-Fourier peak was observed within the interstitial water cavity at approximately $x, y, z \approx \frac{2}{3}, \frac{1}{3}, \frac{1}{3} \pm 0.03$, with peak heights of

$0.8\text{--}0.9\text{ e}^-/\text{\AA}^3$. This peak lies close to the inversion center at $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ and midway between two opposing W5m sites. It was interpreted as an alternative position for the incompletely occupied W5m molecule, with an occupancy of $\sim 10\%$, and was included in the refinement as site W5a.

In all synthetic samples, a pronounced residual electron-density peak *X* was observed at $x,y,z=0.73, 1-x, 0.46$ (site symmetry *m*), with peak heights of $1.84\text{ e}^-/\text{\AA}^3$ (*SYNA1*), $2.81\text{ e}^-/\text{\AA}^3$ (*SYNA2*), and $2.72\text{ e}^-/\text{\AA}^3$ (*SYNA3*). The magnitude of this peak exceeds that associated with the low-occupancy W4a site and is consistently reproduced in three independent datasets. This peak was entirely absent in *MCMA*.

All datasets were carefully re-examined for evidence of symmetry lowering, superstructure reflections, stacking faults, or twinning. No systematic indications of such effects were detected. Apart from a few very weak, randomly distributed reflections in *SYNA3*, attributed to a minor adhering crystal fragment, no signs of long-range crystallographic disorder were observed.

Geometrically, peak *X* lies near the center of a quadrilateral defined by two O1 and two W4 atoms, corresponding to the O1–W4 edges of two adjacent, mirror-related $\text{Na}_2\text{O}_2(\text{H}_2\text{O})_4$ octahedra. The *X*–O1 and *X*–W4 distances are $\sim 2.45\text{ \AA}$. Perpendicular to this plane, W1 and W5m occur in trans positions, with *X*–W distances of $\sim 1.8\text{ \AA}$ to W1 and to one of three symmetry-equivalent W5m sites, and $\sim 2.3\text{ \AA}$ to the remaining two W5m sites, together defining a compressed octahedral coordination environment around *X*.

Assignment of *X* as an additional interstitial H_2O molecule can be excluded because all *X*–O distances are far too short. Refinements modeling *X* as Na, Ca, or U yield low occupancies. For *SYNA3*, occupancies of 6.7(6)% (Na), 4.1(4)% (Ca), and 0.8(1)% (U) were obtained, with corresponding isotropic displacement parameters of 0.002(5), 0.012(4), and 0.017(4) $\text{\AA}^2$. Comparable results were obtained for *SYNA1* and *SYNA2*. Although these parameters are formally reasonable for Ca and U, but not for Na, none of the models with *X*=U, Ca, or Na provide a satisfactory chemical or structural interpretation. In particular, incorporation of an UO_2^{2+} group is incompatible with the known bond-valence requirements for 2+4-coordinated U(VI) of $\sim 0.7\text{ v.u.}$ per equatorial bond (Burns 2005). Ca^{2+} would also impose an unfavorable bond-valence load on the surrounding O1 and W4 atoms, while Na^+ might be acceptable in this regard (Gagné and Hawthorne 2015). Both Ca and Na at site *X*, however, face an insurmountable issue with water molecule W1, which is fully occupied and located in a region of insufficient space to increase the *X*–W1 distance from $\sim 1.8\text{ \AA}$ to at least $2.2\text{ \AA}$ without clashing with neighboring atoms. Although a local Na-disorder mechanism involving a small relocation of Na from site Na1 to site *X* could be envisaged, such a model does not quantitatively

account for the magnitude of peak *X*. In view of these observations, peak *X* is interpreted as arising from an unresolved lattice defect that is not adequately described by the average $R\bar{3}m$ structure model. This defect is likely local or short-range in nature and below the sensitivity of conventional single-crystal diffraction methods.

For the final refinements of the synthetic andersonite structures, a uranium atom was placed at site *X* (denoted *XU*) solely to account for the contribution of peak *X* to the structure factors. This treatment is not intended to imply a physically meaningful atomic site. Inclusion of *XU* results in modest improvements in *R* values, e.g. from 0.0141 to 0.0122 for *SYNA3*, while all bond lengths and angles in the main structural framework remain unchanged within one estimated standard deviation.

Comparisons of present and previously refined andersonite structures

The crystal structure refinements of the Monte Cristo mine andersonite (*MCMA*) and the synthetic andersonites (*SYNA1*, *SYNA2*, *SYNA3*) have converged to lower *R*-values with larger data sets compared to all previous refinements. Atomic positions and all bond lengths are very similar for *MCMA* and *SYNA1* as shown in Tables 2 and 4. Differences between the atomic positions of *MCMA* and *SYNA1* ($T=297\text{ K}$ for both) are, for non-hydrogen atoms, on the average only $0.005\text{ \AA}$, excluding W4a and W5m (0.041 and $0.048\text{ \AA}$, respectively). Small differences to *SYNA2* and *SYNA3* are attributable to the lower temperatures ($T=200$ and 100 K) and show no abnormal features (Table 4).

Between 297 K and 100 K , bonds to Na and Ca decrease by $\sim 0.5\%$, equatorial U–O bonds by $\sim 0.1\%$ and hydrogen bonds by $\sim 0.8\%$, whereas C–O bonds increase by $\sim 0.25\%$. The W4/W4a disorder ratio is not materially affected by temperature and corresponds approximately to the content of interstitial H_2O . This observation supports the interpretation that the disorder arises from hydrogen-bond donation of W4a to the interstitial H_2O located at W5m positions. The triangular shape of the W5m electron-density peak becomes better defined at $T=100\text{ K}$, as does the off-axis position of W5m. The small electron density peak W5a near W5m in *SYNA2* ($T=200\text{ K}$) and *SYNA3* ($T=100\text{ K}$) was also observed by Gurzhiy et al. (2018) at $T=100\text{ K}$. It may be explained as a low-temperature effect combined with incomplete filling of the interstitial H_2O cavity, that is, when a cavity is not filled by two H_2O molecules in opposing W5m positions, a single H_2O molecule appears to adopt one of two W5a positions closer to the center of the centrosymmetric cavity. For *MCMA* and *SYNA1* (both $T=297\text{ K}$), this feature was not detected. The structure-based water content

of the synthetic andersonites ranges between 5.27 and 5.29 H₂O per formula unit, similar to *MCMA*.

The most important difference between *MCMA* and all *SYNA* samples is the electron density peak *X* discussed in the previous section. This peak was not observed in the high-quality *MCMA* crystal. A symmetry-equivalent peak was previously reported as unexplained for another synthetic andersonite (Mereiter 1986; *X* at $x \sim 0.61$, $y = -x$, $z \sim 0.21$, $\rho_{\text{peak}} = 2.2 \text{ e}^-/\text{\AA}^3$).

Peak *X* was observed again in a natural andersonite sample from Cane Springs Canyon, Utah, USA (acronym *CSCA*), investigated by single crystal X-ray diffraction at $T = 100 \text{ K}$ by Gurzhiy et al. (2018) and refined to $R1 = 0.0182$ for 1697 reflections. Those authors interpreted this peak as an interstitial water $\text{O}_{\text{w}5\text{b}}$ ($x, y, z = 0.7265, 1-x, 0.4583$; $\rho_{\text{peak}} = 2.5 \text{ e}^-/\text{\AA}^3$). They modelled this peak by removing a part of the Na1–Ca1-bridging H₂O molecule of $\text{O}_{\text{w}1}$ (W1 in *MCMA* and *SYNA*) and shifting it into the adjacent $\text{O}_{\text{w}5\text{b}}$ position (site *X*). At this site, $\text{O}_{\text{w}5\text{b}}$ is surrounded by four oxygen atoms at distances of $\sim 2.44 \text{ \AA}$ that are far too short for an interstitial H₂O molecule. In this model, restraints on the displacement parameters of $\text{O}_{\text{w}1}$ and $\text{O}_{\text{w}5\text{b}}$ were required to prevent non-positive definite values. We conclude that $\text{O}_{\text{w}5\text{b}}$, equivalent to peak *X* in our structures, must be explained by the same unidentified lattice defect proposed for the synthetic andersonites. Apart from this feature, the *CSCA* structure agrees closely with *SYNA3*, except that $\text{O}_{\text{w}5}$ (equivalent to W5m) was retained in an on-axis position, resulting in a disk-like displacement ellipsoid. Disregarding $\text{O}_{\text{w}5\text{b}}$, the content of interstitial water (sites $\text{O}_{\text{w}5}$ and $\text{O}_{\text{w}5\text{a}}$) amounts to 0.28 H₂O per formula unit, similar to that in our andersonite samples. If the structure model of *SYNA3* is applied to *CSCA*, this value increases to 0.30(1) H₂O (see supplementary material).

The crystal structure of a natural andersonite from Jachymov, Czech Republic (acronym *JACA*) was reported Plášil and Čejka (2015). This structure was refined to $R1 = 0.0336$ for 1879 unique reflections using program JANA2006 (Petříček et al. 2014). Hydrogen atoms were not located, and all non-hydrogen atoms were refined with non-split sites of full occupancy. A difference electron density peak of $\rho_{\text{peak}} = 1.13 \text{ e}^-/\text{\AA}^3$, located $\sim 0.50 \text{ \AA}$ from peak *X* in *SYNA*, was reported and tentatively attributed to disordered H₂O of zeolitic character. Recalculation using program SHELXL and the deposited diffraction data of *JACA* showed that this peak is diffuse and represents only the fifth-largest difference-Fourier peak; the four larger peaks ($\rho_{\text{peak}} = 1.4\text{--}1.8 \text{ e}^-/\text{\AA}^3$) are located near U1. Consequently, peak *X*—always very sharp in the *SYNA* structures and apparently also in *CSCA*—was considered absent within the limits of the *JACA* diffraction data. A subsequent least-squares refinement of *JACA* using the starting parameters of *MCMA* demonstrated that

W4/W4a splitting is also present in this structure, whereas W5 exhibits anomalous displacement parameters with $U_{11} < U_{33}$ (i.e. an ellipsoid elongated along *c*, in contrast to all other andersonite structures). With hydrogen atoms in *MCMA* positions, the re-refinement of *JACA* converged to $R1 = 0.0317$ for all 1879 reflections. The refined site occupancies of W4/W4a are 85(2)/15(2)%, and that of W5 is 88(4)%. This result corresponds to the chemical formula $\text{Na}_2\text{Ca}[\text{UO}_2(\text{CO}_3)_3] \cdot 5.29\text{H}_2\text{O}$ (see supplementary material).

Conclusions

The present structural reinvestigation of andersonite shows that the site splitting of the water W4 into a W4 main site and a W4a satellite site is not a low-temperature phenomenon found for *CSCA* at $T = 100 \text{ K}$ (Gurzhiy et al. 2018) but persists also at ambient temperature without significant changes in W4/W4a proportions. The site occupancy of W4a remains fairly constant at $\sim 14\%$ and appears to correlate with the number of interstitial water molecules in the structural cavity of andersonite. This behavior can be explained by hydrogen-bond donation from one W4a molecule among the six W4/W4a molecules surrounding each interstitial H₂O located at W5/W5m.

Crystal structure refinements of six different andersonite samples (this work; Gurzhiy et al. 2018; Plášil and Čejka 2015) yield between 1.6 and 1.8 interstitial H₂O molecules per cavity, corresponding to approximately 5.27–5.30 total H₂O per formula unit $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3]$. If hydrogen atoms for the interstitial H₂O are omitted in the refinements, these values would approach the upper limit of 2 H₂O per cavity, or 5.33 H₂O per formula unit, but do not exceed it. The H₂O-bearing cavity of andersonite, which has been described in some earlier studies as a zeolitic channel parallel to the *c* axis, is in fact a closed water-in-water cavity. It is surrounded by a belt of 12 Na-bonded H₂O molecules and is delimited at both ends by 6-membered hydrogen-bond rings formed by terminal carbonate oxygen atoms O1 and the Na1–Ca1-bridging H₂O molecule of W1 (Fig. 6). Any interstitial H₂O molecule attempting to escape along the *c* axis through this hydrogen-bonded rings would encounter an insurmountable barrier formed by three closely converging uranyl oxygen atoms O6 (see supplementary material, Fig. S5).

The only conceivable pathway for an interstitial H₂O molecule to leave the cavity is diffusion via H₂O defects within the hydration spheres of Na. Such a defect-jumping mechanism is expected to be slow and requires sufficient thermal activation. Multi-temperature X-ray powder diffraction data reported by Gurzhiy et al. (2018) show that andersonite

remains X-ray stable up to about 95 °C, accompanied by an increase in the c -axis length and unit-cell volume. Above 95 °C, both the c axis and unit-cell volume contract within a temperature interval of ~ 15 °C, followed by breakdown of the lattice and formation of an X-ray amorphous product. These observations suggest that the total water content of andersonite is stable up to approximately 75 °C, corresponding to the upper limit of an essentially linear increase in unit-cell volume (Gurzhiy et al. 2018).

Analyses, particularly those reported by Čejka and coworkers (for references and discussions see Plášil and Čejka 2015), have yielded water contents for natural and synthetic andersonite that are consistently below 6 H_2O per formula unit, ranging between 5.4 and 5.8 H_2O , with a mean value of ~ 5.6 H_2O that entered crystallographic literature following the work of Coda et al. (1981). Whether reported values of 5.4 H_2O or higher are due to impurities, H_2O inclusions, or analytical uncertainties cannot be resolved based on the published evidence. However, robust evidence from six crystal-structure refinements of sufficient accuracy demonstrates that the $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\text{H}_2\text{O}$ framework accommodates at most two interstitial H_2O molecules per cavity, or slightly fewer.

Void-volume analysis of the cavity defined by ten W4 and two W4a molecules yields a solvent-accessible volume of ~ 64 Å³, which is sufficient to host two H_2O molecules per cavity, but not more. No additional cavities exist in the crystal structure of andersonite that could accommodate further interstitial water molecules. Accordingly, the idealized chemical formula of andersonite should be expressed as $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5\frac{1}{2}\text{H}_2\text{O}$, or, to account for incomplete filling of the H_2O cavity, as $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3] \cdot 5(\frac{1}{2}-x)\text{H}_2\text{O}$, where x varies only slightly (0.04–0.06) based on six crystal-structure refinements. Independent H_2O determinations for two synthetic andersonites by CHN elemental analysis, yielding 5.24(9) and 5.40(13) H_2O per formula unit (5.34 H_2O from the H: C ratio), are consistent with this interpretation.

The puzzling electron-density peak X observed in *SYNA1*, *SYNA2*, *SYNA3*, *CSCA*, and the synthetic andersonite studied by Mereiter (1986), and interpreted as arising from an unidentified lattice defect, remains an open question for future investigation. The high-quality crystal from the Monte Cristo mine (*MCMA*) is distinctive in that it does not exhibit this defect. Finally, the close structural relationships between andersonite, with its 6–3–3 grid, and the square-grid layer minerals characterized by 4–4 grids represent an intriguing aspect of their paragenetic coexistence. Based on current knowledge, andersonite occurrences are distinctly more frequent than those of the square-grid layer minerals. This indicates that the 6–3–3 grid architecture of andersonite is no disadvantage compared with the more relaxed isochemical 4–4 grids.

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Declarations

Competing interests The authors declare no competing interests.

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