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Letter to editor

A note on the molecular water content in uranyl carbonate mineral andersonite

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The crystal structure of andersonite from Jáchymov (western Bohemia, Czech Republic) was refined from single-crystal X-ray diffraction data to an $R = 0.0286$ against 1657 unique observed reflections. Andersonite from Jáchymov is trigonal, $R\bar{3}2/m$, with $a = 17.8589(6)$, $c = 23.6935(8)$, $V = 6544.4(4)$ Å^3 and $Z = 18$. The structural formula derived from the refinement of X-ray data is $Na_2Ca[(UO_2)(CO_3)_3](H_2O)_{5.28}$. This formula confirms previous structure determination on synthetic material. The maximal H_2O content in andersonite is discussed also with regard to the published thermal analysis and vibration spectroscopy studies and disunities in chemical formula of andersonite in the literature.

Keywords: andersonite, uranyl carbonate, crystal structure, molecular water
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1. Introduction

Uranyl carbonates are important products of hydration–oxidation weathering of primary uranium minerals, mainly uraninite, in the presence of solutions with dissolved CO_2 (atmospheric or juvenile). These solutions can be also derived by dissolution of the gangue-carbonates on hydrothermal vein carrying U-ores (Plášil 2014). Due to the potentially high mobility of U in carbonate-bearing groundwaters (Langmuir 1978; Grenthe et al. 1984) and thus its environmental impact, the good knowledge of the crystal chemistry and behavior of uranyl carbonate minerals is of great importance.

Uranyl carbonate mineral andersonite was originally described in 1951 from the Hillside mine, Yavapai County, Arizona (Axelrod et al. 1951), with assigned chemical formula $Na_2Ca[(UO_2)(CO_3)_3](H_2O)_6$. The structure of synthetic analogue of this mineral was given by Coda et al. (1981), based on single-crystal X-ray diffraction data. According to them synthetic analogue of andersonite is trigonal, $R\bar{3}2/m$, with $a = 17.902$ (4), $c = 23.734$ (4) Å, Z = 18. The structure was refined to $wR = 0.049$ against 794 unique reflections (Coda et al. 1981). The formula of andersonite resulting from their structure refinement was $Na_2Ca[(UO_2)(CO_3)_3](H_2O)_5$; corresponding with four H_2O sites localized by the difference Fourier syntheses. In the same paper, based on the results of the thermal analysis study, they inferred the water content in synthetic andersonite to be 5.6 H_2O and concluded that the molecular water is statistically distributed within the channels in the structure besides the ones coordinated to the Na and Ca sites. They compared the observed H_2O content with the observations and conclusions of Čejka (1969) providing a similar figure.

Later, Mereiter (1986) revisited the structure of synthetic andersonite and presented some relations to the natural mineral, stating the overall similarities in the structure, however, without exact figures. The structure refinement ($R_1 = 0.028$ for 1860 observed unique reflections) of the synthetics presented in that paper provided a localization of additional O site within the channel that belongs to the molecular H_2O, leading to the structure formula $Na_2Ca[(UO_2)(CO_3)_3](H_2O)_{5.333}$. Thermal analysis of the natural specimen published by Čejka and Urbanec (1988) nevertheless confirmed the results of the previous thermal studies by Coda et al. (1981) and Čejka (1969).

There have been several articles focused on physical-chemical properties of synthetic andersonite (Alwan and Williams 1980; Amayri et al. 2004; Kubatko et al. 2005), or those describing finds of andersonite and assessing its environmental impact (e.g., Stefaniak et al. 2009). The common feature all of these papers is the fact that they are citing or assigning disunited chemical formulae of andersonite. As the structure of natural andersonite has never been published, we have decided to write this remark on the andersonite structure and discussion of its molecular water content.

2. Sample

The crystal of andersonite investigated by single-crystal X-ray diffraction was obtained from the specimen originating from the Geschieber vein, Svornost mine in

Fig. 1 Andersonite from Jáchymov in aggregate of rhombohedral green crystals growing with schröckingerite (yellowish) on altered matrix. The Svornost mine, Jáchymov. Width of photo 3.5 mm (photo P. Škácha).

Jáchymov, Czech Republic. On this specimen, andersonite forms abundant perfectly developed pseudocubic (rhombohedral) crystals up to 0.5 mm across (Fig. 1) in association with schröckingerite.

3. Single-crystal X-ray crystallography

A rhombohedral crystal of andersonite, with dimensions 0.24 × 0.18 × 0.10 mm, was selected for diffraction experiment on an Oxford Diffraction Gemini diffractometer equipped with Atlas CCD detector (crystal-to-detector distance of 80 mm) and graphite-monochromatized MoK$_\alpha$ radiation provided by the conventional X-ray tube (55 kV, 35 mA). A sphere of three-dimensional intensity data was collected using frame widths of 1.0° in ω, with 100 seconds spent on counting per each frame. The trigonal (rhombohedral) unit cell of natural andersonite, a = 17.8589(6) and c = 23.6935(8) Å, was refined from 11914 reflections by the least-squares techniques (Agilent Technologies 2014). Of the total of 28,237 collected reflections, 1879 were independent and 1657 were classified as uniquely observed, with [$I_{obs} > 3\sigma(I)$] (Tab. 1). The data were reduced and corrected for Lorentz and polarization effects and also background using the CrysAlis RED software. Absorption correction combining shape of the crystal (X-shape software; Stoe 2005) and empirical scaling of the frames was done in Jana2006 (Petříček et al. 2014) leading to the R_{int} = 0.165 for all reflections. Worth noting is that the high R_{int} is most probably due to presence of the weak twin domain (–1 0 0.03, –1 1 –0.01, 0 –0.01 –1) and less adequately fitted absorption effects. The structure was solved independently from the previous structure solutions utilizing the charge-flipping algorithm implemented in the Superflip program (Palatinus and Chapuis 2007). We prefer this approach, rather than simply refine the structure using known models, since it may lead to sometimes otherwise elusive differences.

The structure was subsequently refined by the full-matrix least-squares algorithm of the Jana2006 program (Petříček et al. 2006, 2014) based on F^2. Superflip program confirmed the chosen space-group, $R\bar{3}2/m$, based on the symmetry operators of the flipped electron density (Palatinus and van der Lee 2008). All atoms were found by the solution, except the single O site localized within the channel of the structure (see below) that was found by the difference-Fourier syntheses. All atoms were refined with harmonic atomic displacement parameters (ADP). Interestingly, hydrogen atoms still could not be reliably localized and refined from the current X-ray data, despite of their good quality and convincing results of the structure refinement. The final cycles converged to R = 0.0286 and wR = 0.0837 for 1657 observed reflections with GOF

Tab. 1 Comparison of the reported unit-cell parameters for natural and synthetic andersonites

Locality	Reference	*a*	*c*	*V*	*n* H_2O
Jáchymov	this work	17.8589(6)	23.6935(8)	6544.4(4)	5.333
Synthetic	Coda et al. (1981)	17.902(4)	23.734(4)	6587	~5.6
Synthetic	Mereiter (1986)	17.904(2)	23.753(3)	6594	5.333
Monte Cristo Mine, Grand County, Utah, USA	RRUFF (Downs 2006)	18.04(4)	23.90(4)	6738(12)	–

= 1.18 (Tab. 2). The maximal positive difference-Fourier peak of the electron density, 1.19 e$Å^{-3}$, was located near O8 atom (H_2O) coordinated to the Ca site. Details of the data collection and miscellaneous crystallographic and structure refinement parameters are listed in Tab. 2. Final atom coordinates and their displacement parameters are given in Tab. 3, selected interatomic distances are in Tab. 4. The CIF file, containing also a block with the reflections, is deposited at the Journal's web page *www.jgeosci.org*.

4. Results and discussion

The structure of synthetic andersonite is well-known (Coda et al. 1981; Mereiter 1986) and we found no significant departure from it. The basic structural feature in andersonite is an isolated cluster of polyhedra of the composition $[(UO_2)(CO_3)_3]^{4-}$; the well-known uranyl tricarbonate cluster (UTC; Burns 2005). Each UTC is linked in the structure to the two (symmetrically related) Ca atoms and two (symmetrically distinct) Na atoms. The Ca atom is linked to uranyl hexagonal bipyramid (UHB) *via* equatorial O atoms shared between the UHB and a CO_3^{2-} group, chelating the UHB. The Na2 atom site is linked to the UHB *via* uranyl oxygen atom O2 and also *via* atom O3 to the C1 atom, which is chelating the UHB from the other side. Further, the Na1 atom is coordinated to the equatorial O atom (O5) of the UHB. The Ca site is coordinated by seven ligands at an average distance of 2.38 Å, one of them is a H_2O molecule (O8). Both of the two Na atoms are coordinated by six ligands; Na1 (at average distance 2.38 Å) by four O atoms and two H_2O molecules (O8, O9) and Na2 atom (at average distance 2.46 Å) by four H_2O molecules (O10 and O11).

The structure is a robust framework (Fig. 2) consisting of the oval, buckyball-like cages, formed by six Na, six Ca and six $[(UO_2)(CO_3)_3]$ clusters (Coda et al. 1981). Such compact linkage arises from the linking of the two Ca atoms *via* four bridging CO_3 groups of the four uranyl UTC, called the paddle-wheel structure, which is very characteristic also of other uranyl carbonates (Mereiter 2013, Hughes-Kubatko and Burns 2004). There are five O sites in the structure of natural andersonite, belonging to the H_2O molecules. Four of these H_2O molecules are coordinated to the Ca or Na cations and the remaining O site was found, in accordance to the structure of the synthetic analogue (Mereiter 1986) within the channels of the structure running parallel to the **c**. The channel is defined by a skeleton of the paddle-wheels and the Na-polyhedra. The inter-channel O site has a 6*c* Wyckoff symmetry (*0, 0, 0.85*), resulting in the content of 1/3 H_2O per unit-cell (with $Z = 18$). The total number of H_2O in the structure based on the current data is thus 5.333, as was previously stated based on the structure determination from the synthetic crystal (Mereiter 1986). In that paper the following difference maximum at $x \sim 0.61$, $y \sim -x$, $z \sim 0.21$ with $\rho = 2.2$ e$Å^{-3}$ (~1.95 Å from W5; corresponding to the O12 atom in our structure) is mentioned, however remaining unassigned and unrefined. In present case the

Tab. 2 Crystallographic data and refinement details for andersonite from Jáchymov

Crystal data	
Structure formula	$U_1Ca_1Na_2C_3O_{16.333}H_{10.666}$
Crystal system	trigonal
Space group	$R\bar{3}2/m$
Unit-cell parameters: *a*, *c* [Å]	17.8589(6), 23.6935(8)
Unit-cell volume [$Å^3$]	6544.4(4)
Z	18
Calculated density [g/cm^3]	2.887
Crystal size [mm]	0.24 × 0.18 × 0.10
F_{000}	5076
Data collection	
Diffractometer	Oxford Diffraction Gemini with Atlas detector
Temperature [K]	293
Radiation, wavelength [Å]	MoK_α, 0.71073 (50 kV, 30 mA)
θ range for data collection [º]	2.7727.98
Limiting Miller indices	$h = -23 \rightarrow 23$, $k = -22 \rightarrow 22$, $l = -29 \rightarrow 30$
Axis, frame width (º), time per frame (s)	ω, 1, 100
Total reflections collected	28237
Unique reflections	1879
Unique observed reflections, criterion	2657, $[I > 3\sigma(I)]$
Absorption coefficient [mm^{-1}], type	11.66; Gaussian
T_{min}/T_{max}	0.165/0.379
R_{int}	0.168
Structure refinement by Jana2006	Full-matrix least-squares on F^2
Number of refined parameters, restraints, constraints	124, 0, 0
R, *wR* (obs)	0.0286, 0.0837
R, *wR* (all)	0.0336, 0.0879
GOF obs/all	1.18, 1.16
Weighting scheme, weights	σ, $w = 1/(\sigma^2(I)+0.00284I^2)$
Largest diffraction peak and hole ($e^-/Å^3$)	1.19, –1.13

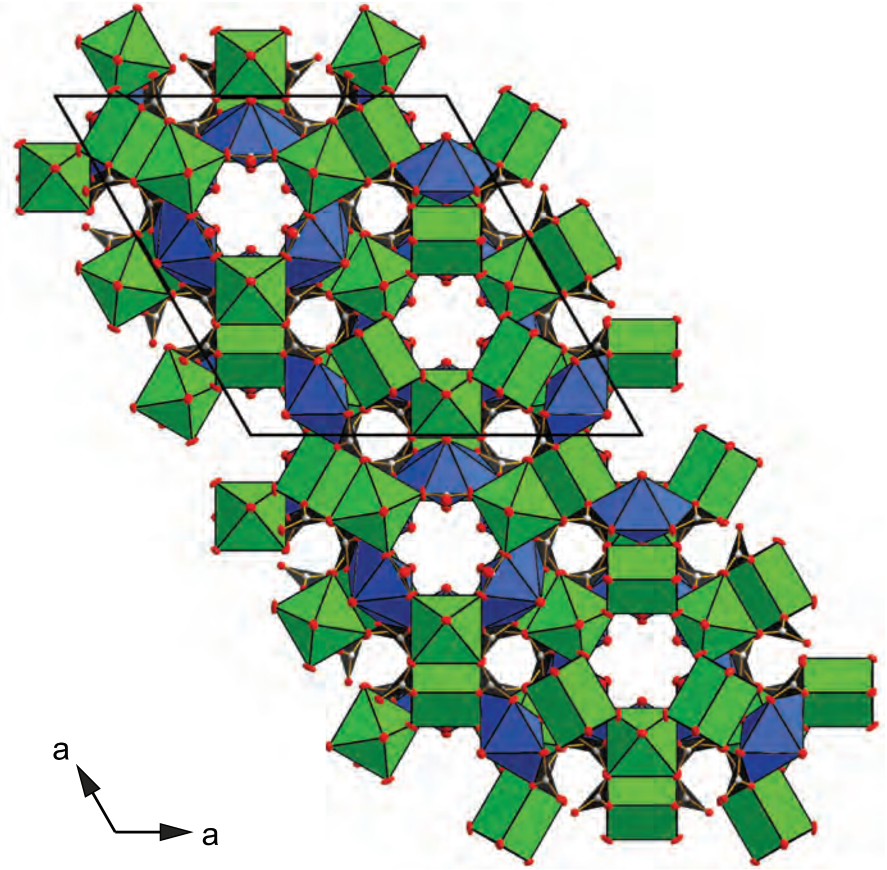

Fig. 2 The framework structure of andersonite viewed along **c**. Framework is built from uranyl tricarbonate cluster (UO_8 polyhedra are blue, CO_3 groups dark grey) and CaO_7 polyhedra (green). The channels, running parallel to **c**, are occupied by H_2O (omitted for clarity). Na atoms are not displayed.

highest peak of the positive difference Fourier density, of 1.13 eÅ^{-3} (charge of 0.57e^{-}), is located 1.29 Å from the O8 atom, 2.36 Å from O3 and 2.57 Å from inter-channel O12 atom; otherwise the difference Fourier map is relatively smooth (Fig. 3). It is possible that the positive maximum in the difference electron density localized by Mereiter (1986) within the channel is connected with some highly disordered electron density corresponding to disordered H_2O molecules having the zeolitic character.

To conclude, from X-ray diffraction data follows that the highest H_2O content that can be reached is 5.333 H_2O. This corresponds to five fully occupied O sites (coordinated to both Na and Ca sites) and one third of H_2O molecule localized within the channels. However it is possible that some additional H_2O can be accommodated within the channels in the structure having a disordered character. Thermogravimetric experiments, done

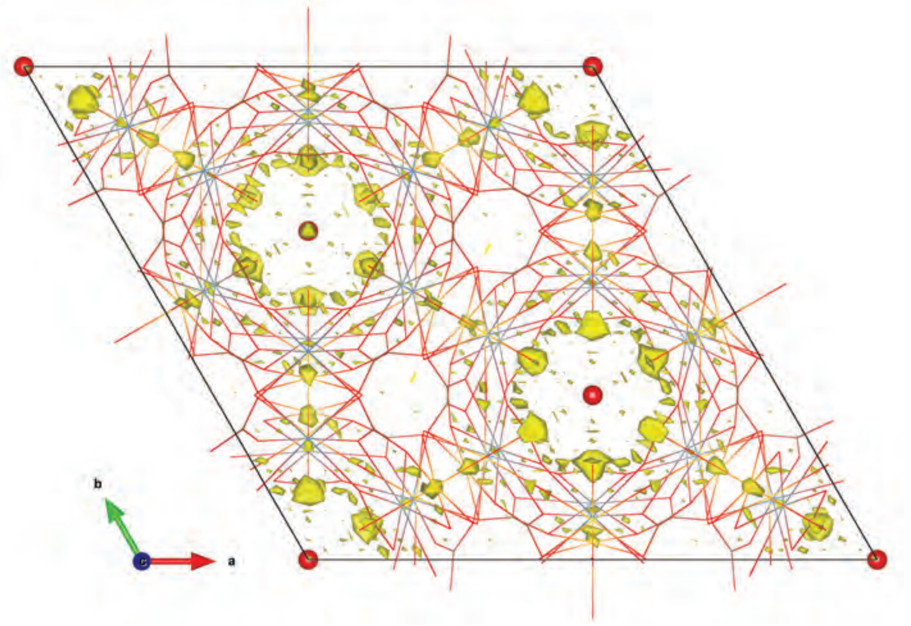

Fig. 3 The structure of andersonite (represented by wires and sticks) viewed along **c** with pronounced channels occupied by molecular H_2O (O12). The maxima of the difference-Fourier electron density are displayed and the framework structure is represented here as wireframe for clarity. The highest maximum is localized in between atoms O3, O8 and inter-channel O12.

on synthetic and natural andersonite, provided largely different H_2O contents in the structure, ranging from 5 (Kubatko et al. 2005), through 5.6 (Čejka and Urbanec 1988) and 5.4–5.8 (Coda et al. 1981) to 6 (Alwan and Williams 1980; Vochten et al. 1994; Kubatko et al. 2005). However, various methods of thermal analysis applied to well-defined synthetic and natural samples of andersonite proved that in every case the H_2O content was lower than six, varying from 5.4 to 5.8, or given as an average of ~ 5.6 H_2O (Urbanec and Čejka 1979; Čejka et al. 1987; Čejka and Urbanec 1988). The sharp bands in the infrared spectra of andersonite (Čejka et al. 1987; Čejka and Urbanec 1988), occurring at 3545–3565 cm^{-1}, may be connected with certain portion (~ 0.4–0.8 H_2O) of molecular H_2O, which is relatively weakly bonded in the channels of the structure. Likewise, such bands were also observed in the Raman spectra (Frost et al. 2004). The five H_2O molecules referred by Kubatko et al. (2005) correspond to the partially dehydrated andersonite, which already lost its "zeolitic" H_2O from the channels (giving 1/3 molecule of H_2O per unit-cell). According to our opinion the molecular water content in andersonite is faintly variable, depending on the distribution of the disordered H_2O in the channels and varies approximately in the range 5.333 to 5.6 H_2O. However, there is a question, how much were the thermodynamical properties derived e.g. by Alwan and Williams (1980) or Kubatko et al. (2005) affected by the variable H_2O content in the samples they studied. The inter-channel H_2O, even if weakly bonded, will most probably contribute to the overall value of the enthalpy of formation (ΔH) of the corresponding phases. This effect has been demonstrated e.g., in case of more firmly bonded H_2O in Mg-sulfate hydrate minerals (Grevel and Majzlan 2011). The relation between ΔH and H_2O content seems to be much more dependent on the total H_2O content (activity of the solid phase) than on the way how the H_2O is connected in the structure. From this point of view the thermodynamic re-examination of andersonite is necessary for development of thermodynamic models.

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Tab. 3 Atom coordinates and displacement parameters for the crystal structure of andersonite from Jáchymov

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.109630(8)	0.219260(16)	0.155110(10)	0.01512(12)	0.01242(14)	0.01746(17)	0.01716(18)	0.00873(8)	0.00077(4)	0.00153(9)
C1	0.0761(2)	0.1522(5)	0.2676(3)	0.021(2)	0.014(2)	0.022(4)	0.029(4)	0.0111(18)	0.0028(15)	0.006(3)
C2	−0.0170(3)	0.2472(3)	0.0988(2)	0.0165(18)	0.015(2)	0.016(2)	0.019(2)	0.0081(19)	0.0033(18)	0.0018(18)
Ca1	−0.12250(4)	0.12250(4)	0.22287(6)	0.0142(4)	0.0128(5)	0.0128(5)	0.0176(7)	0.0070(5)	−0.0001(3)	0.0001(3)
Na1	0.20680(12)	0.4136(2)	0.27605(15)	0.0368(13)	0.0362(14)	0.042(2)	0.0342(19)	0.0210(10)	−0.0020(8)	−0.0039(16)
Na2	0.14922(9)	0.29843(18)	0.00377(12)	0.0233(10)	0.0263(11)	0.0240(15)	0.0187(14)	0.0120(8)	0.0021(6)	0.0043(12)
O1	0.05961(16)	0.1192(3)	0.1191(2)	0.0249(18)	0.024(2)	0.020(3)	0.030(3)	0.0099(13)	0.0008(11)	0.002(2)
O2	0.16032(17)	0.3206(3)	0.1903(2)	0.0274(19)	0.025(2)	0.025(3)	0.032(3)	0.0125(14)	−0.0010(12)	−0.002(2)
O3	0.07052(18)	0.1410(4)	0.3191(2)	0.027(2)	0.031(2)	0.036(3)	0.016(3)	0.0179(16)	0.0016(11)	0.003(2)
O4	0.0195(2)	0.1598(3)	0.23784(16)	0.0271(17)	0.0170(18)	0.048(2)	0.023(2)	0.0216(18)	0.0047(15)	0.0119(17)
O5	0.0625(2)	0.2813(2)	0.08171(15)	0.0221(15)	0.0154(17)	0.029(2)	0.0234(19)	0.0126(16)	0.0035(14)	0.0090(15)
O6	−0.0327(2)	0.2076(2)	0.14646(14)	0.0222(15)	0.0200(18)	0.028(2)	0.0216(18)	0.0144(16)	0.0056(14)	0.0083(15)
O7	−0.0738(2)	0.2527(2)	0.07125(14)	0.0197(14)	0.0141(16)	0.0240(18)	0.0225(18)	0.0107(15)	−0.0003(14)	0.0023(14)
O8	−0.10672(16)	0.10672(16)	0.3277(2)	0.0229(19)	0.026(2)	0.026(2)	0.020(3)	0.016(2)	0.0000(10)	0.0000(10)
O9	0.07659(18)	0.1532(4)	−0.0283(2)	0.030(2)	0.029(2)	0.027(3)	0.035(3)	0.0133(15)	0.0010(12)	0.002(2)
O10	0.2610(3)	0.333333	0.333333	0.033(2)	0.028(2)	0.034(3)	0.039(3)	0.0172(16)	−0.0032(13)	−0.006(3)
O11	0.1409(4)	0.4848(4)	0.2264(2)	0.065(3)	0.092(4)	0.077(4)	0.049(3)	0.061(4)	−0.005(3)	−0.007(3)
O12	0	0	0.4118(10)	0.136(11)	0.119(11)	0.119(11)	0.17(2)	0.060(6)	0	0

Tab. 4 Selected interatomic distances in the structure of andersonite from Jáchymov

U1–O1	1.767(5)	C1–O3	1.234(9)
U1–O2	1.776(5)	C1–O4	1.293(8)
U1–O4	2.419(4)	C1–O4^{i}	1.293(8)
U1–O4^{i}	2.419(5)	<C1–O>	1.27
U1–O5	2.427(4)		
U1–O5^{i}	2.427(4)	C2–O5	1.298(6)
U1–O6	2.454(4)	C2–O6	1.287(6)
U1–O6^{i}	2.454(6)	C2–O7	1.250(7)
<U1–O$_{Uranyl}$>	1.77	<C2–O>	1.28
<U1–O$_{eq}$>	2.43		
Na1–O2	2.488(6)	Na2–O5	2.330(5)
Na1–O3^{vii}	2.423(6)	Na2–O5^{i}	2.330(5)
Na1–O10	2.494(6)	Na2–O7^{ix}	2.429(5)
Na1–O10^{viii}	2.494(4)	Na2–O7^{x}	2.429(4)
Na1–O11	2.43(1)	Na2–O8^{v}	2.404(5)
Na1–O11^{i}	2.425(9)	Na2–O9	2.372(6)
<Na1–O>	2.46	<Na2–O>	2.38
Ca1–O4	2.306(4)		
Ca1–O4ii	2.306(4)		
Ca1–O6	2.392(3)		
Ca1–O6ii	2.392(3)		
Ca1–O7iii	2.363(4)		
Ca1–O7iv	2.363(4)		
<Ca1–O>	2.354		
O1–O6	2.870(7)	O5–O5^{i}	2.791(7)
O2–O4	2.936(5)	O5–O6	2.177(5)
O2–O5	2.990(6)	O5–O7	2.237(6)
O3–O4	2.226(7)	O6–O7	2.226(6)
O3–O8	2.915(5)	O7–O8^{iv}	2.968(6)
O3–O8^{vi}	2.915(5)	O7–O10^{xii}	2.906(6)
O4–O4^{i}	2.155(8)	O7–O10^{xiii}	2.906(5)
O4–O6	2.662(6)	O9–O9^{xi}	2.723(9)
O4–O8	2.894(6)	O9–O9^{ix}	2.723(5)
O4–O8^{ii}	2.894(6)	O11–O11^{iii}	2.850(8)

Symmetry codes: (i) –*x*+*y*, *y*, *z*; (ii) –*y*, –*x*, *z*; (iii) *y*–1/3, *x*+1/3, –*z*+1/3; (iv) –*x*–1/3, –*y*+1/3, –*z*+1/3; (v) –*x*+*y*–1/3, –*x*+1/3, *z*+1/3; (vi) –*y*, *x*–*y*, *z*; (vii) *x*–*y*+1/3, –*y*+2/3, –*z*+2/3; (viii) –*x*+1/3, –*y*+2/3, –*z*+2/3; (ix) –*x*, –*x*+*y*, –*z*; (x) *y*, –*x*+*y*, –*z*; (xi) *y*, *x*, –*z*; (xii) *x*–*y*+2/3, *x*+1/3, –*z*+1/3; (xiii) –*y*+2/3, –*x*+1/3, *z*+1/3.

Electronic supplementary material. Supplementary crystallographic data for this paper are available online at the Journal web site (*http://dx.doi.org/10.3190/jgeosci.193*).

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