Crystal structure determination of orthorhombic variscite*2O*

and its derivative AlPO₄ structure at high temperature

Matteo Ardit [a], Brian L. Phillips [b] and David L. Bish [c]

[a] Department of Physics and Earth Sciences, University of Ferrara, via Saragat 1, I-44122 Ferrara, Italy

[b] Department of Geosciences, Stony Brook University, Stony Brook, New York, NY 11794-2100, USA

[c] Department of Chemistry, Indiana University Molecular Structure Center, 800 E. Kirkwood Ave.,

Bloomington IN 47405-7102, USA

Authors e-mail: [a] rdtmtt@unife.it

[b] brian.phillips@stonybrook.edu

[c] bish@indiana.edu

SUPPLEMENTAL DATA

Chemical analysis

Chemical analysis of an aliquot of the sample placed on a Mylar film was performed in air by means of a Shimadzu EDX 7000 energy dispersive X-ray fluorescence spectrometer (elemental measuring range $_{11}$Na–$_{92}$U). The spectrometer was equipped with a Rh target X-ray tube and an electronically cooled silicon drift detector (SSD). Semiquantitave analysis (as reported in Table S1) was obtained through the fundamental parameter (FP) method by the software PCEDX Navi 2.05 (2006-2018 Shimadzu Corporation).

Table S1. Semiquantitative XRF chemical analysis of the variscite specimen from Tooele County (Utah, USA).

Oxide	wt%	3-sigma	Line
Al_2O_3	49.668	0.669	Al$K\alpha$
P_2O_5	47.991	0.172	P$K\alpha$
SiO_2	1.089	0.065	Si$K\alpha$
CaO	0.838	0.006	Ca$K\alpha$
Cr_2O_3	0.152	0.002	Cr$K\alpha$
SO_3	0.092	0.012	S$K\alpha$
V_2O_5	0.069	0.001	V$K\alpha$
Fe_2O_3	0.043	0.001	Fe$K\alpha$
K_2O	0.015	0.002	K$K\alpha$
ZnO	0.015	0.000	Zn$K\alpha$
TiO_2	0.011	0.002	Ti$K\alpha$
SrO	0.007	0.000	Sr$K\alpha$
Ga_2O_3	0.005	0.000	Ga$K\alpha$
CuO	0.004	0.000	Cu$K\alpha$
ZrO_2	0.001	0.000	Zr$K\alpha$

Figure S1. Room temperature X-ray powder diffraction data collection for the variscite specimen before (*a*) and after (*b*) heating.

a

b

3
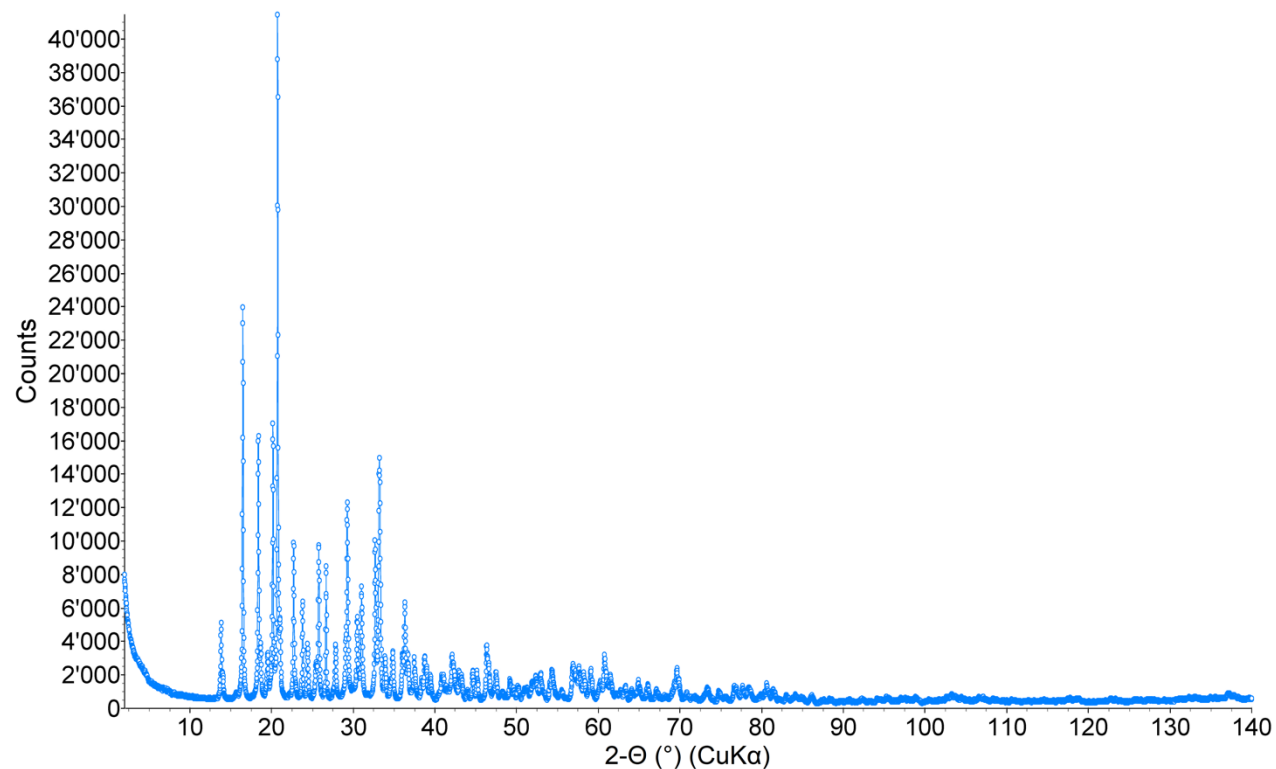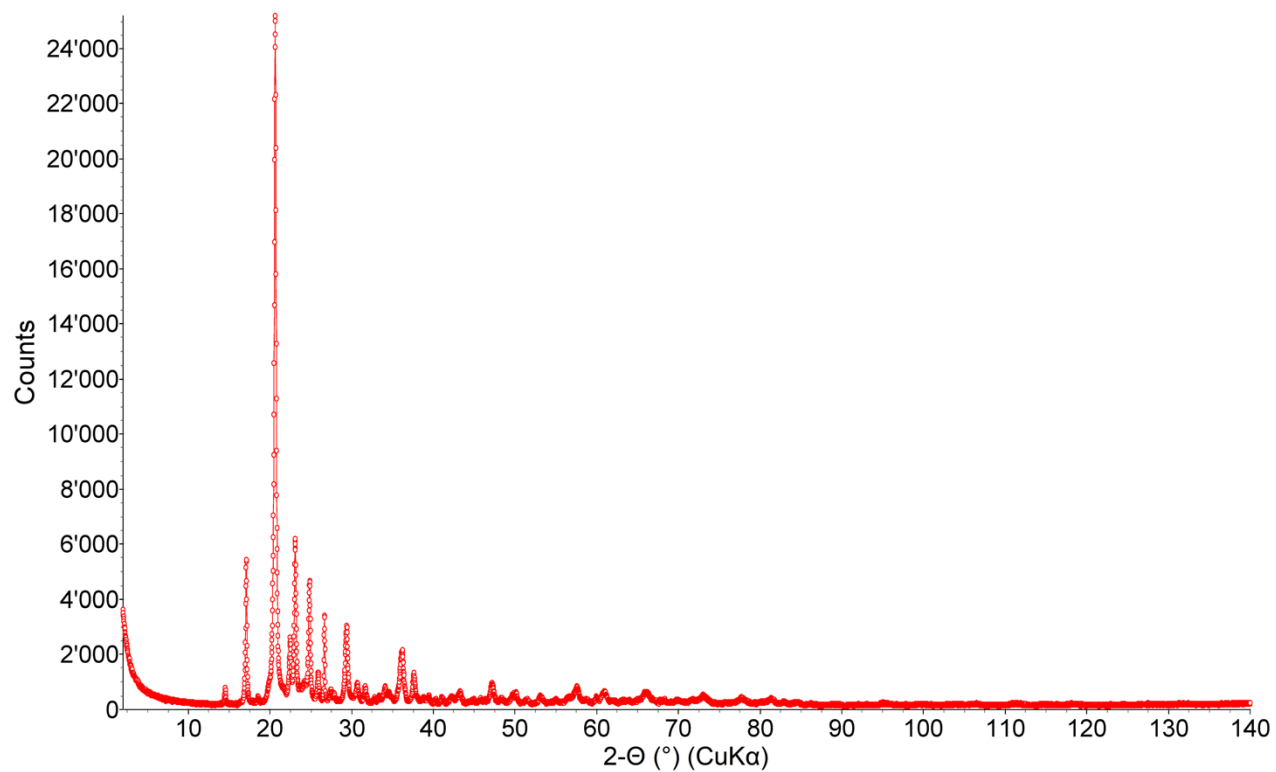
Table S2. Final atomic coordinates and isotropic ADPs (B_{iso}) with their standard deviations for the variscite*2O* crystal structure at RT. Sites labeled O_w represent oxygen atoms associated with H_2O molecules.

		$AlPO_4 \cdot 2H_2O$ (s.g. *Pbca* (61); Z = 8)			
Site label	*Atom type*	*x*	*y*	*z*	B_{iso}
Al1	Al	0.2301(3)	0.4525(2)	0.6701(3)	0.66(7)
Al2	Al	0.5045(3)	0.7033(2)	0.6644(3)	0.66(7)
P1	P	0.2146(3)	0.1084(2)	0.8547(3)	0.38(5)
P2	P	0.0053(3)	0.3545(2)	0.8486(3)	0.38(5)
O11	O	0.7975(4)	0.8854(3)	0.9873(3)	0.81(7)
O12	O	0.8179(4)	0.1654(2)	0.7069(5)	0.81(7)
O13	O	0.9215(4)	0.6283(3)	0.7153(5)	0.81(7)
O14	O	0.2543(5)	0.0248(2)	0.8189(5)	0.81(7)
O21	O	0.9745(5)	0.2314(2)	0.3214(5)	0.81(7)
O22	O	0.6104(4)	0.8987(3)	0.7785(5)	0.81(7)
O23	O	0.9885(4)	0.6378(3)	0.9937(3)	0.81(7)
O24	O	0.8574(4)	0.6195(3)	0.2101(4)	0.81(7)
O_W11	O	0.9407(4)	0.0011(3)	0.8701(5)	0.95(12)
O_W12	O	0.1847(5)	0.0286(3)	0.5534(5)	0.95(12)
O_W21	O	0.3284(4)	0.7415(3)	0.6127(5)	0.95(12)
O_W22	O	0.9203(5)	0.2890(2)	0.5581(5)	0.95(12)

Table S3. Final atomic coordinates and isotropic ADPs (B_{iso}) with standard deviations for the AlPO$_4$-var2O crystal structure.

AlPO$_4$-var2O (s.g. _Pbca_ (61); Z = 8)					
Site label	_Atom type_	_x_	_y_	_z_	_B$_{iso}$_
Al1	Al	0.2534(4)	0.3959(3)	0.7157(4)	1.24(9)
Al2	Al	0.5247(4)	0.6466(3)	0.7268(6)	1.24(9)
P1	P	0.2088(4)	0.0562(2)	0.8706(4)	1.11(6)
P2	P	0.0189(4)	0.3101(3)	0.8728(5)	1.11(6)
O11	O	0.8045(7)	0.9276(4)	0.9557(5)	2.18(15)
O12	O	0.8140(6)	0.1126(4)	0.6950(7)	2.18(15)
O13	O	0.9247(5)	0.5730(4)	0.7099(7)	2.18(15)
O14	O	0.2560(7)	-0.0296(3)	0.8482(8)	2.18(15)
O21	O	0.9681(5)	0.2745(3)	0.3467(9)	2.18(15)
O22	O	0.5885(5)	0.8570(4)	0.7832(8)	2.18(15)
O23	O	0.9702(5)	0.6736(5)	0.9521(6)	2.18(15)
O24	O	0.8499(5)	0.6750(4)	0.2149(8)	2.18(15)

Table S4. Rietveld refinement agreement factors, quantitative phase analysis, and unit-cell parameters for the variscite sample measured at RT after heating at 723 K.

Refinement agreement factors				
R_{exp} = 0.049	R_{wp} = 0.102	R_p = 0.075		G.O.F. = 0.021

Quantitative phase analysis & unit-cell parameters						
Phase	Wt %	s.g.	a(Å)	b(Å)	c(Å)	V(Å^3)
AlPO$_4$-var2O	94.4(2)	*Pbca*	9.9703(9)	17.1523(15)	8.6314(7)	1476.1(2)
crandallite	1.8(2)	*R-3m*	6.942(5)	–	15.920(23)	664.6(1.4)
quartz	3.8(1)	*P3$_1$21*	4.9163(5)	–	5.4049(9)	113.13(3)

Table S5. Selected metal-oxygen bond distances and bond angles with standard deviations for the $AlPO_4$-var$2O$ crystal structure.

AlPO₄-var2O (s.g. *Pbca* (61); Z = 8)

Intrapolyhedral metal-oxygen bond distances (Å)

Al1–O11	1.679(7)	Al2–O12	1.733(8)	P1–O11	1.531(6)	P2–O21	1.553(8)
Al1–O14	1.717(8)	Al2–O13	1.699(8)	P1–O12	1.535(8)	P2–O22	1.547(8)
Al1–O22	1.712(7)	Al2–O21	1.705(9)	P1–O13	1.529(7)	P2–O23	1.541(7)
Al1–O24	1.702(8)	Al2–O23	1.701(8)	P1–O14	1.557(7)	P2–O24	1.533(7)
⟨Al1–O⟩	1.703(7)	⟨Al2–O⟩	1.710(8)	⟨P1–O⟩	1.538(7)	⟨P2–O⟩	1.543(7)
TQE (Al1O₄)	1.004	TQE (Al2O₄)	1.003	TQE (P1O₄)	1.001	TQE (P2O₄)	1.008

Intrapolyhedral bond angles (°)

O11–Al1–O14	109.1(5)	O12–Al2–O13	110.2(5)	O11–P1–O12	107.8(5)	O21–P2–O22	100.8(5)
O11–Al1–O22	116.6(4)	O12–Al2–O21	108.9(4)	O11–P1–O13	109.6(5)	O21–P2–O23	109.6(6)
O11–Al1–O24	109.5(4)	O12–Al2–O23	104.1(4)	O11–P1–O14	108.6(5)	O21–P2–O24	111.2(5)
O14–Al1–O22	109.7(4)	O13–Al2–O21	114.8(5)	O12–P1–O13	108.0(4)	O22–P2–O23	116.4(5)
O14–Al1–O24	105.3(4)	O13–Al2–O23	107.9(4)	O12–P1–O14	110.1(5)	O22–P2–O24	104.9(5)
O22–Al1–O24	106.1(4)	O21–Al2–O23	110.4(5)	O13–P1–O14	112.6(5)	O23–P2–O24	113.2(5)
⟨O–Al1–O⟩	109.4(4)	⟨O–Al2–O⟩	109.4(4)	⟨O–P1–O⟩	109.5(5)	⟨O–P2–O⟩	109.4(5)
TAV (Al1O₄)	15.99	TAV(Al2O₄)	12.19	TAV (P1O₄)	3.21	TAV(P2O₄)	32.23

Interpolyhedral bond angles (°)

Al1–O11–P1	153.2(6)	Al2–O12–P1	154.8(5)	Al1-O22-P2	146.9(5)	Al2-O21-P2	144.7(6)
Al1–O14–P1	140.3(5)	Al2–O13–P1	142.9(5)	Al1-O24-P2	144.0(6)	Al2-O23-P2	156.5(5)
⟨Al1–O–P1⟩	146.8(6)	⟨Al2–O–P1⟩	148.9(5)	⟨Al1–O–P2⟩	145.5(5)	⟨Al2–O–P2⟩	150.6(5)

TQE = Tetrahedral Quadratic Elongation; TAV = Tetrahedral Angle Variance ($^{\circ 2}$); (Robinson et al. 1971).