Supporting Information

Paper Title: *Pressure-Induced Cation Migration and Volume Expansion in the Defect Pyrochlores ANbWO_6 ($A=\text{NH}_4^+$, Rb^+ , H^+ , K^+).*

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Figure S1. Thermogravimetric analysis of ANbWO₆. Data were collected using a Perkin Elmer TG 7 over a temperature range of ~30 to ~900°C with a heating rate of 10°C/min.

Figure S2. Infrared spectra for ANbWO_6 . Data was collected on all compounds using a Mattson Cygnus 100 FTIR. (a) NH_4NbWO_6 . Peaks at 1414 cm^{-1} and $\sim 3400\text{ cm}^{-1}$ are indicative of N-H stretches. The peak at 1414 cm^{-1} is characteristic of the presence of NH_4^+ in the compound. The peak at 3400 cm^{-1} can be attributed to both N-H and O-H (from H_2O) bond stretches. The three peaks between $\sim 2850\text{ cm}^{-1}$ and 3030 cm^{-1} , seen in the spectra for all compounds, are characteristic of organic materials. The source of the organic material is small plastic pieces that broke off of the containers that the KBr and the pyrochlores were mixed in. (b) RbNbWO_6 . (c) $\text{HNbWO}_6 \cdot \text{H}_2\text{O}$. (d) $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$.

Figure S3. Observed, calculated, and difference patterns from the Rietveld refinement of NH_4NbWO_6 at ambient pressure. The tick marks represent the observed reflections fit. Note that the data fit includes reflections given by λ and $\lambda/2$ radiation.

Figure S4. Observed, calculated, and difference patterns from the Rietveld refinement of $\text{HNbWO}_6 \cdot \text{H}_2\text{O}$ at ambient pressure. The tick marks represent the observed reflections fit. Note that the data fit includes reflections given by λ and $\lambda/2$ radiation.

Figure S5. Observed, calculated, and difference patterns from the Rietveld refinement of RbNbWO₆ at ambient pressure. The tick marks represent the observed reflections fit. Note that the data fit includes reflections given by λ and $\lambda/2$ radiation. Table S2 and its discussion accompany this figure to better understand the refinement strategy.

Figure S6. Observed, calculated, and difference patterns from the Rietveld refinement of KNbWO₆•H₂O at ambient pressure. The tick marks represent the observed reflections fit. Note that the data fit includes reflections given by λ and $\lambda/2$ radiation. See the discussion accompanying table S2 for a possible explanation on the non-ideal fit of the intensities.

Figure S7. Complete x-ray diffraction patterns of RbNbWO₆ collected at (a) 0.62 GPa, (b) 0.99 GPa, and (c) 5.15 GPa (3-37.5° 2θ; λ~0.68329 Å). Arrows (↑ or ↓) adjacent to the labeled pressure denotes whether hydrostatic pressure was increased or released. Numbers accompanying the *hkl* indices in (c) denote reflections belonging to (1) the high pressure hydrated phase, (2) the ambient pressure compressed phase, or (3) a third, unknown phase. Asterisks denote the strongest λ/2 peaks. Intensity of the λ/2 reflections were about 2% of their corresponding λ reflection. The symbol ‡ marks peaks due to the stainless steel gasket used to retain the sample and hydrostatic fluid inside the DAC. Comparison of the 0.62 GPa (↑) and 0.99 GPa (↓) diffraction patterns show that RbNbWO₆ returns to its original structure with very little hysteresis observed upon pressure release.

Figure S8. (a) Examination of the (111) reflection for x-ray data collected on RbNbWO_6 at 4.67 GPa. (b) Examination of the (311) and (222) reflections for x-ray data collected on RbNbWO_6 at 4.67 GPa. The green lines denote where the (111), (311), and (222) reflections would be for a cubic phase with $a=10.131(1)$ Å. This “third phase” was seen in both the 4.67 GPa and 5.15 GPa data, and was modeled as a cubic phase with a stoichiometry and structure similar to RbNbWO_6 at ambient pressure. Only lattice and profile parameters were refined for this phase. The origin of this phase is currently unknown. The peak positions of the third phase were calculated using the EditCell function in CMPR (<http://www.ncnr.nist.gov/programs/crystallography/software/-cmp/cmpr.html>).

Figure S9. X-ray powder pattern simulation of RbNbWO_6 with Rb^+ on the (a) $8b$ ($a=10.37$ Å) and (b) $16d$ ($a=10.50$ Å) in space group $Fd\bar{3}m$ using the program Powdercell for Windows Version 2.3 (Kraus, W.; Nolze, G. *Powder Diffraction*, **1998**, 13(4), 256-259). Note the significant change in the diffraction pattern upon moving Rb^+ from $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$ to $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This is the model that was used to determine the position of Rb^+ at high pressure (see figure 2c of the article).

Figure S10. X-ray diffraction patterns of NH_4NbWO_6 taken as a function of pressure (4-28° 2θ ; $\lambda \sim 0.7\text{\AA}$). Asterisks are used to mark data that was collected upon partial pressure release. The background does not change significantly as pressure increases, suggesting pressure-induced amorphization did not occur to the sample during the experiment.

Figure S11. X-ray diffraction patterns of $\text{HNbWO}_6 \cdot \text{H}_2\text{O}$ taken as a function of pressure (4–28° 2θ ; $\lambda \sim 0.7\text{\AA}$). The background does not change significantly as pressure increases, suggesting pressure-induced amorphization did not occur to the sample during the experiment. High angle tailing of the reflections that occurs as pressure was increased can be easily seen in the 3.43 and 4.36 GPa patterns. The high angle asymmetry exhibited at higher pressures can not be easily modeled, so LeBail fits were performed on these patterns in order to determine the lattice parameter at that particular pressure.

Figure S12. X-ray diffraction patterns of RbNbWO₆ taken as a function of pressure (3-37.5° 2θ ; $\lambda \sim 0.7\text{\AA}$). The background does not change significantly as pressure increases, suggesting pressure-induced amorphization did not occur to the sample during the experiment.

Figure S13. X-ray diffraction patterns of KNbWO₆·H₂O taken as a function of pressure (4-28° 2θ ; $\lambda \sim 0.7\text{\AA}$). The background does not change significantly as pressure increases, suggesting pressure-induced amorphization did not occur to the sample during the experiment. High angle tailing of the reflections that occurs as pressure was increased can be easily seen in higher pressure patterns. The high angle asymmetry exhibited at higher pressures cannot be easily modeled, so LeBail fits were performed on these patterns to determine the lattice parameter at that particular pressure.

Table S1. Rietveld refinement details for ANbWO₆(•H₂O) data collected at ambient pressure.

	NH ₄ NbWO ₆	HNbWO ₆ •H ₂ O	RbNbWO ₆	KNbWO ₆ •H ₂ O
<i>R-factors:</i>				
R _p (%)	3.60	3.11	4.59	5.46
R _{wp} (%)	4.70	4.89	6.49	7.22
χ^2	3.97	25.88 ^a	7.42	5.62
R(F ²)	18.24	23.55	32.09	17.14
2 θ range (°)	6.10-47.61	5.80-47.50	4.37-49.00	4.47-47.43
Background	Fixed points	Fixed points	Fixed points	Fixed points
Sample displacement (°)	-0.000769(9)	0.00195(7)	0.00128(2)	0.000364 (6)
Number of reflections	146	130	138	129
Number of variables	16	13	13	13
Number of excluded regions	2	2	2	2
I ($\lambda/2$)/I (λ) ^b	0.0200	0.0120	0.0200	0.0175
<i>Profile parameters:</i> ^c				
GU	28(1)	4.1(5)	46(3)	—
GP	1.57(3)	1.24(2)	1.59(8)	1.65(2)
LX	0.94(3)	0.46(2)	0.63(9)	0.22(3)
LY	3.9(3)	2.0(2)	5.3(7)	2.9(3)
<i>Asymmetry parameters:</i> ^d				
S/L	—	0.0027(1)	0.0055(2)	0.0030(2)

^a-The high χ^2 reported for HNbWO₆•H₂O is due to the data having a flat, low noise background, so the fit of the data was not as good as the program expected. ^b- I ($\lambda/2$)/I (λ) is the ratio of the intensity of the reflections due to $\lambda/2$ radiation divided by the intensity of the reflections that arise from λ radiation. In EXP-GUI (GSAS), this was given as the ratio of wavelengths for the diffractometer constants. ^c-The profile function used in all refinements was the Thompson-Cox-Hastings pseudo-voigt function. ^d-H/L was set at 0.0121 and not refined.

Table S2. Rietveld comparison details for RbNbWO₆ data collected at ambient pressure.

<i>Model:</i> ^a	1	2	3	4	5
<i>Space Group:</i>	$Fd\bar{3}m$	$Fd\bar{3}m$	$Fd\bar{3}m$	$Fd\bar{3}m$	$F\bar{4}3m$
<i>Lattice Parameters:</i>	10.3736(1)	10.3736(1)	10.3736(1)	10.3736(1)	10.3736(1)
<i>Atom:</i>					
Rb(1) postion	$8b; x=\frac{3}{8}$	$8b; x=\frac{3}{8}$	$32e; x=0.3966(3)$	$32e; x=0.3972(3)$	$16e; x=0.5360(3)$
U _{iso}	0.070(2)	0.065(2)	0.007(2)	0.0003(213)	-0.015(1)
occupancy	1	0.993(7)	0.25	0.245(2)	0.25
Rb(2) postion	—	—	—	—	$16e; x=0.7652(4)$
U _{iso}	—	—	—	—	-0.015(1)
occupancy	—	—	—	—	0.25
Nb/W postion	$16c; x=0$	$16c; x=0$	$16c; x=0$	$16c; x=0$	$16e; x=0.1241(3)$
U _{iso}	0.0238(4)	0.0198(3)	0.0202(4)	0.0193(3)	0.0239(4)
occupancy	1	1	1	1	1
O(1) postion	$48f; x=0.3116(6)$	$48f; x=0.3123(6)$	$48f; x=0.3123(6)$	$48f; x=0.3118(6)$	$24f; x=0.180(2)$
U _{iso}	0.009(2)	0.007(2)	0.012(2)	0.012(2)	0.015(2)
occupancy	1	1	1	1	1
O(2) postion	—	—	—	—	$24g; x=0.443(3)$
U _{iso}	—	—	—	—	0.015(2)
occupancy	—	—	—	—	1
<i>R-factors:</i>					
R _p (%)	4.59	4.54	4.44	4.49	4.15
R _{wp} (%)	6.49	6.41	6.23	6.34	5.72
χ^2	7.42	7.20	6.82	7.03	5.74
R(F ²)	32.09	30.97	30.11	32.37	23.15
2 θ range (°)	4.37-49.00	4.37-49.00	4.37-49.00	4.37-49.00	4.37-49.00
Background	Fixed points	Fixed points	Fixed points	Fixed points	Fixed points
Sample displacement (°)	0.00128(2)	0.00129(2)	0.00129(2)	0.00129(2)	0.00131(7)
Number of reflections	160	160	160	160	180
Number of variables	13	13	13	14	28
Number of excluded regions	2	2	2	2	2
I ($\lambda/2$)/I (λ)	0.0200	0.0200	0.0200	0.0200	0.0200
<i>Profile parameters:</i>					
GU	46(3)	50(3)	50(3)	47(3)	52(3)
GP	1.59(8)	1.55(8)	1.61(8)	1.58(8)	1.56(7)
LX	0.63(9)	0.72(9)	0.76(9)	0.69(9)	0.86(8)
LY	5.3(7)	4.6(6)	3.7(7)	4.8(6)	3.1(6)
<i>Asymmetry parameters:</i>					
S/L	0.0055(2)	0.0055(2)	0.0054(2)	0.0055(2)	0.0053(2)

^a-(1) Rb⁺ fixed on $8b$ site ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$) with its occupancy=1. (2) Rb⁺ fixed on $8b$ site ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$) while allowing the site occupancy to refine. (3) Rb⁺ position allowed to refine ($32e$ site) with occupancy=0.25 (equivalent to 1 Rb/formula unit). (4) Both Rb⁺ postion ($32e$ site) and site occupancy are allowed to refine. (5) All metal atoms on $16e$ site; positions allowed to refine.

Discussion of the refinement of RbNbWO₆:

The model used to refine RbNbWO₆ data collected at ambient pressure corresponds to Rb⁺ residing on the $8b$ site with a fixed occupancy=1. This is the same model as used for the following single crystal neutron diffraction studies: Bydanov, N. N.; Chernaya, T. S.; Muradyan, L. A.; Sarin, V. A.; Rider, E. E.; Yanovskii, V. K.; Bosenko, A. A. *Kristallografiya*. **1987**, 32, 623-630; Chernaya, T. S.; Bydanov, N. N.;

Muradyan, L. A.; Savan, V. A.; Simonov, V. I. *Kristallografiya*. **1988**, 33, 75-81. The less than ideal fit of the calculated pattern (as shown in figure S5) may be attributed to the diffractometer setup. The beam was focused to $\sim 200\ \mu\text{m}$ using a bent Si (220) monochromator (that also produces the undesired $\lambda/2$ radiation) and the sample was placed in a 0.3-mm diameter capillary. The capillary was not rotated, but was rocked back and forth slightly ($<5^\circ$). The limited rotation of the capillary and the use of a focused beam enhance the likelihood that texture effects will be problematic. These would affect the intensities of the reflections observed in the diffraction pattern, especially if the sample is highly crystalline. These effects also appear to be present in other pyrochlores, especially $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$.

Significant improvement in the calculated fit of the diffraction pattern was not observed by allowing Rb^+ to move off of the $8b$ site, allowing its occupancy to deviate, or a combination of both. Changing the space group from the centrosymmetric $Fd\bar{3}m$ to the noncentrosymmetric $F\bar{4}3m$ (similar to the model used for NH_4NbWO_6) does improve the fit somewhat, but the same fitting problems are observed with this model. There is no evidence of extra reflections, such as the (200) peak, that violate the extinction conditions of the $8b$ site in $Fd\bar{3}m$ [$h=2n+1$ OR $h+k+l=4n$]. If such reflections were observed, this would suggest that the non-centrosymmetric space group should be used. Furthermore, no peak splitting indicative of lower symmetry such as the tetragonal distortion reported in Sleight, A. W.; Zumsteg, F. C.; Barkley, J. R.; Gulley, J. E. *Mat. Res. Bull.* **1978**, 13, 1247-1250, is observed. For these reasons, we opted to use the model reported in this work. Regardless of the model used to refine the pattern, Rb^+ resides at or near the $8b$ site and clearly migrates from this site to a crystallographic site near the $16d$ site at ~ 4 GPa.

Table S3. Bond valence sums (BVS) for ANbWO_6 at ambient pressure.^a

	NH_4NbWO_6	$\text{HNbWO}_6 \cdot \text{H}_2\text{O}$	$\text{KNbWO}_6 \cdot \text{H}_2\text{O}$	RbNbWO_6
A^+	—	—	1.87	0.41
Nb^{5+}	5.22	5.62	5.40	5.53
W^{6+}	5.31	5.71	5.49	5.62

^a- Nb^{5+} and W^{6+} are distributed randomly throughout the pyrochlore framework, so the expected valence for each of these ions should be about 5.5. K^+ is highly overbonded in its eight-coordination, and a large contribution to its valence comes from the short $\text{Rb}-\text{H}_2\text{O}$ bond (length=2.29 Å). Rb^+ is underbonded, suggesting that it is weakly bound to the NbWO_6 framework. BVS for NH_4^+-O (lattice) and $\text{H}_2\text{O}-\text{O}$ (lattice) are essentially zero (the shortest A-O interaction is ~ 3.05 Å for these ions). BVS were calculated using SPuDS, version 2.0 (Lufaso, M.W.; Woodward, P.M.; *Acta Cryst.* **2001**, B57, 725-738).

Table S4. Bond valence sums for K^+ and Rb^+ for low-pressure, high-pressure, and hypothetical phases.

	A-site	a (Å)	BVS
$ANbWO_6$ (A: CN=6) ^a	K^+ : 32e (x=0.4068)	10.3628(2)	0.46
	Rb^+ : 8b (x= $\frac{3}{8}$)	10.3736(1)	0.41
$ANbWO_6$ (A: CN=6) ^b	K^+ : 32e (x=0.4838)	10.5073(1)	1.33
	Rb^+ : 32e (x=0.481)	10.4676(1)	1.95
$ANbWO_6 \cdot H_2O$ (A: CN=8)	K^+ : 32e (x=0.4838)	10.5073(1)	1.87
	Rb^+ : 32e (x=0.481)	10.4676(1)	2.68

All BVS were calculated using SPuDS, version 2.0 (Lufaso, M.W.; Woodward, P.M.; *Acta Cryst.* **2001**, B57, 725-738). ^a- $KNbWO_6$ (dehydrated) structural data was taken from Murphy, D. W.; Cava, R. J.; Rhyne, K.; Roth, R. S.; Santoro, A.; Zahurak, S. M.; Dye, J. L. *Solid State Ionics*, **1986**, 18-19, 799-801. ^b-Theoretical model where A^+ is on the 32e site where it would reside if the compound was hydrated. Waters of hydration were not included in this calculation. BVS for Rb^+ in $RbNbWO_6 \cdot H_2O$ was calculated from the high pressure structure at 5.15 GPa. BVS for K^+ in $KNbWO_6 \cdot H_2O$ was calculated from the ambient pressure hydrated structure.

Discussion of the application of bond valence sums to the defect pyrochlores at high pressures:

The large BVS for Rb^+ in $RbNbWO_6$ (Rb: 32e, x=0.481) and $RbNbWO_6 \cdot H_2O$ suggests that rubidium is overbonded on that site. Typical Rb-O (framework) bond lengths with Rb^+ on a six-coordinate site are 2.89 Å ($\times 6$) (Shannon and Prewitt; *Acta Cryst.* **1969**, B25, 925; Shannon and Prewitt; *Acta Cryst.* **1970**, B25, 1046). Without water incorporated into the high pressure (5.15 GPa) structure, Rb-O (framework) bond lengths are 2.744(9) Å ($\times 3$) and 2.672(5) Å ($\times 3$). Whereas the bonds are significantly shorter at high pressure than at ambient pressure, we expect a significant contraction of Rb-O bonds with increasing pressure. Therefore, it may be difficult to apply bond valence theory to the high pressure $RbNbWO_6 \cdot H_2O$.