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Atomic-scale environment of niobium in ore minerals as revealed by XANES and EXAFS at the Nb K-edge

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1) Crystallographic and chemical analysis of Nb minerals

Table S1. Representative chemical composition of the pyrochlore samples

Representative compositions of pyrochlore

wt%	Fluorcalciopyrochlore	Hydropyrochlore	Ba-rich kenopyrochlore	U-rich oxynatropyrochlore
F	7.407	0.181	0.094	1.5
Na_2O	8.324	0.055	0.046	2.14
MgO	0.041	0.005	0.057	-
Al_2O_3	0.028	1.260	0.648	0.07
SiO_2	0.077	0.919	1.349	-
K_2O	0.004	0.212	0.038	0.05
CaO	13.971	0.268	0.198	12.3
TiO_2	0.957	4.162	1.236	12.3
MnO	-	0.011	0.152	0.32
FeO	0.030	0.362	7.978	1.91
SrO	1.695	2.865	0.113	0.17
Y_2O_3	-	-	0.016	0.32
ZrO_2	-	0.008	2.571	-
Nb_2O_5	68.824	76.409	64.497	34.5
BaO	-	-	8.043	0.17
Ta_2O_5	0.146	0.063	0.159	9.5
PbO	-	-	0.00	1.76
La_2O_3	0.163	0.040	0.026	
CeO_2	0.443	0.069	1.246	0.49 (Ln_2O_3)
Nd_2O_3	-	-	0.00	
ThO_2	0.237	0.085	3.067	1.13
UO_2	-	0.025	0.197	19.7
Total	102.207	87.000	91.732	97.85
O=F	3.119	0.076	0.038	0.53
Total	99.008	86.924	91.694	97.32

Table S2. Representative chemical composition of the other natural samples studied.

Representative compositions of Nb minerals							
wt%	Columbite-(Mn)	Nb perovskite	Niocalite	Lueshite	Wöhlerite	Fergusonite-(Y)	Aeschynite-(Y)
F	0.013	0.019	3.291	-	5.394	-	-
Na_2O	0.017	1.499	0.788	17.701	8.796	-	-
MgO	0.006	0.250	0.334	0.015	0.169	-	-
Al_2O_3	-	0.208	0.112	0.001	0.015	-	-
SiO_2	-	-	29.076	0.009	29.841	-	-
P_2O_5	-	-	-	-	-	0.275	0.189
K_2O	-	-	-	0.009	0.015	-	-
CaO	0.011	33.485	43.692	1.061	25.609	1.567	2.144
TiO_2	0.719	36.799	0.120	2.552	1.256	1.273	30.242
MnO	12.011	0.052	0.806	0.005	0.965	-	-
FeO	7.804	4.696	0.260	0.093	1.273	-	0.713
SrO	-	0.232	0.246	0.054	0.000	-	-
Y_2O_3	-	-	0.051	-	0.401	24.364	15.792
ZrO_2	-	0.974	0.404	0.012	13.233	-	-
Nb_2O_5	69.201	16.392	15.368	74.644	12.034	46.842	14.218
BaO	-	-	-	-	0.000	-	-
Ta_2O_5	7.179	0.728	0.848	0.528	0.212	1.273	3.481
PbO	-			-	0.000	-	-
La_2O_3	-	0.765	0.180	0.456	0.047	0.029	-
Ce_2O_3	-	2.343	0.639	1.144	0.200	0.402	0.781
Pr_2O_3	-	-	-	-	-	0.128	0.173
Nd_2O_3	-	0.124	0.035	0.036	0.012	0.814	1.573
Sm_2O_3	-	-	-	-	-	0.511	1.691
Eu_2O_3	-	-	-	-	-	0.109	0.561
Gd_2O_3	-	-	-	-	-	1.117	3.365
Tb_2O_3	-	-	-	-	-	0.148	0.457
Dy_2O_3	-	-	-	-	-	1.232	3.547
Ho_2O_3	-	-	-	-	-	0.509	0.878
Er_2O_3	-	-	-	-	-	2.165	2.681
Tm_2O_3	-	-	-	-	-	3.624	2.513
Yb_2O_3	-	-	-	-	-	-	-
Lu_2O_3	-	-	-	-	-	0.603	0.408
ThO_2	-	-	-	0.906	0.000	7.562	7.388
UO_2	-	-	-	-	0.000	4.888	3.412
Total	97.057	98.570	96.249	99.251	99.470	99.435	96.221
O=F	0.005	0.008	1.386		2,27		
Total	97.052	98.562	94.863	99.251	97.200	99.435	96.221

Table S3. Representative chemical composition of the other natural samples studied.

Nb mineral reference	Crystal system	Space group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å³)	Reflection indexed	Θ (°)
Columbite-(Mn)	Orthorombic	Pbcn	4	14.244(2)	5.7361(14)	5.1216(10)	90.0	90.0	90.0	418.40(12)	402	3.8180–28.4390
Lueshite	Cubic	Pn-3m	8	7.8103(5)	7.8103(5)	7.8103(5)	90.0	90.0	90.0	476.43(6)	214	5.2270-27.6040
Nb perovskite	Tetragonal	Pbnm	4	5.429(4)	5.4860(3)	7.718(4)	90.0	90.0	90.0	229.8(2)	294	5.2810–28.5230
Niocalite	Monoclinic	P1c1	2	10.8741(15)	10.4515(8)	7.3997(13)	90.0	109.89(2)	90.0	790.78(19)	942	3.5880–28.8090
Wöhlerite	Monoclinic	P1211	4	10.8227(9)	10.2312(5)	7.2901(5)	90.0	109.156(9)	90.0	762.52(3)		
Pyrochlore samples												
Fluorcalciopyrochlore	Cubic	Fd-3m	8	10.450(3)	10.450(3)	10.450(3)	90.0	90.0	90.0	1141.2(5)	111	6.3470–25.4270
Ba-rich kenopyrochlore	Cubic	Fd-3m	8	10.5852(9)	10.5852(9)	10.5852(9)	90.0	90.0	90.0	1186.04(17)	128	6.3470–26.6960
Hydropyrochlore	Cubic	Fd-3m	8	10.6054(14)	10.6054(14)	10.6054(14)	90.0	90.0	90.0	1192.8(3)	229	6.3600–26.3740

3) XRD pattern of synthetic Nb-substituted oxides

The diffraction patterns of Nb-substituted anatase reveal variations in the Bragg reflections, as depicted in Fig. S1b and c. Specifically, in the diffraction pattern of anatase containing 5 wt% Nb, only reflections (103) and (112) are prominent. Additionally, the reflections (211), (116), and (220) appear less pronounced in the diffraction pattern of anatase with 1 wt% Nb. The variations in the width of the reflections can be attributed to disparities in crystallinity. Using the Scherrer equation with the (101) reflection, we determined that the nanocrystal sizes are 92 nm, 108 nm, and 107 nm for anatase samples containing 1 wt% Nb, 5 wt% Nb, and 10 wt% Nb, respectively.

Moreover, there are discernible shifts in 2θ between these diffraction patterns (Fig. S1c). As shown for the (101) reflection, the diffraction peak of Nb-doped anatase with 1 wt % Nb and 5 wt% Nb are aligned at 29.5° while that of 10 wt% Nb is located at 29.3°. This shift involves modifications in the unit-cell parameters due to the incorporation of Nb^{5+} in the crystal lattice of anatase. Rietveld refinement of the diffraction patterns reveals that the unit-cell parameters of Nb-doped anatase are larger than pure anatase (a = b = 3.78 Å, c = 9.51 Å). More specifically, an increase in the *c* parameter with Nb doping, resulting in *c* values of 9.51 Å, 9.55 Å, and 9.58 Å for

Nb-anatase with 1 wt%, 5 wt%, and 10 wt% Nb, respectively. Conversely, the impact of Nb doping on the *a* parameter is less straightforward. It is slightly larger in anatase with 1 wt% Nb than in the case of 5 wt% Nb. However, the a parameter reaches its maximum value in anatase with 10 wt% Nb (a = 3.85 Å) .

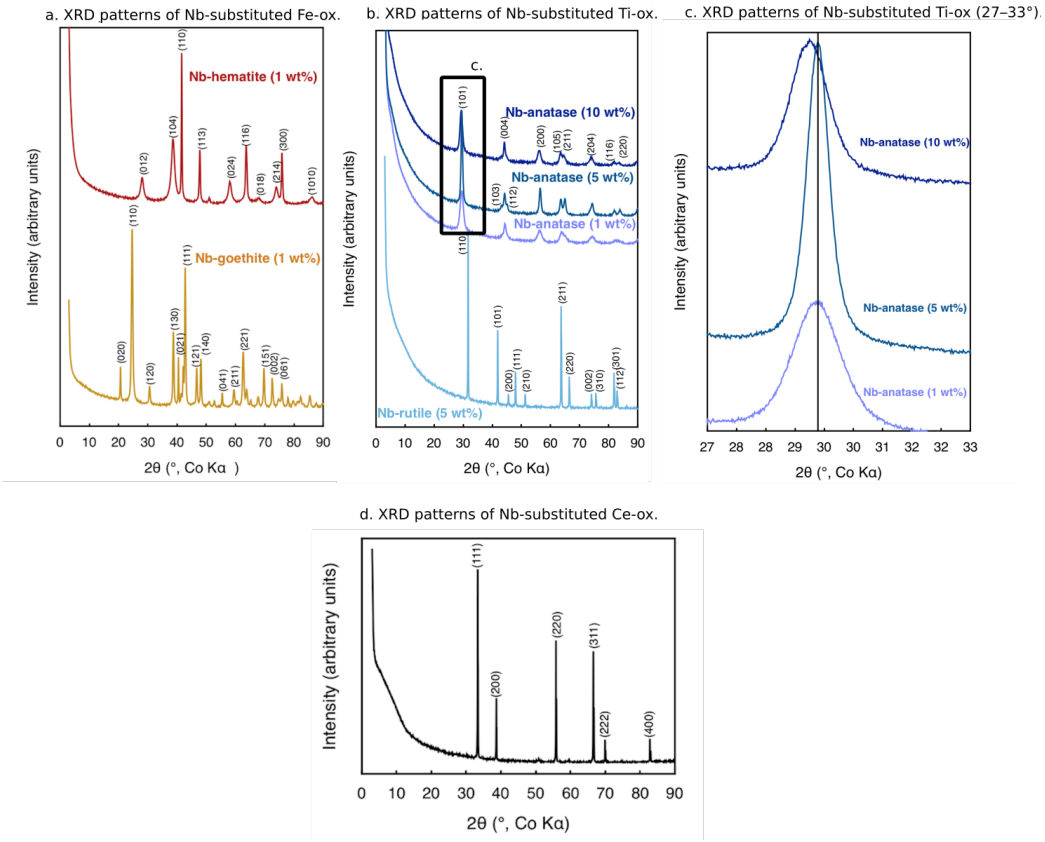

Figure S1. XRD patterns of (a) Nb-substituted hematite and goethite; (b) Nb-substituted rutile and anatase; (c) Close-up on the (101) peak. (d) Nb-substituted cerianite.

4) Refinement details of hydropyrochlore sample

Table S4. Crystallographic data and structure refinement of hydropyrochlore sample.

Empirical formula	$Nb_{1.9}O_{8.75}Sr_{0.07}Ti_{0.1}$
Formula weight	327.45
Temperature/K	293
Crystal system	cubic
Space group	Fd-3m
a/Å	10.5690(10)
b/Å	10.5690(10)
c/Å	10.5690(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1180.6(3)
Z	8
ρ_{calc}g/cm^3	3.685
μ/mm^1	4.460
F(000)	1222.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.678 to 56.162
Index ranges	-8 ≤ h ≤ 14, -12 ≤ k ≤ 14, -9 ≤ l ≤ 11
Reflections collected	615
Independent reflections	89 [R_{int} = 0.0342, R_{sigma} = 0.0164]
Data/restraints/parameters	89/0/10
Goodness-of-fit on F^2	1.309
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0831
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.0881
Largest diff. peak/hole / e Å^{-3}	0.38/-1.34

Table S5. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3). U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Nb	2500	5000	7500	40.8(6)
Ti	2500	5000	7500	40.8(6)
O3	3750	5623(5)	8750	30.9(10)
O2	5000	7500	7500	37(2)
O1	6250	6250	6250	199(16)
Sr	6250	6250	6250	199(16)

Table S6. Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb	40.8(6)	40.8(6)	40.8(6)	6.0(3)	-6.0(3)	6.0(3)
Ti	40.8(6)	40.8(6)	40.8(6)	6.0(3)	-6.0(3)	6.0(3)
O3	30.7(15)	31(3)	30.7(15)	0	-2.8(18)	0
O2	37(2)	37(2)	37(2)	6(2)	-6(2)	-6(2)
O1	199(16)	199(16)	199(16)	0	0	0
Sr	199(16)	199(16)	199(16)	0	0	0

Table S7. Bond lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Nb01	$O3^1$	1.9811(16)	Nb01	$O3^5$	1.9811(16)
Nb01	$O3^2$	1.9811(17)	O3	$Nb01^6$	1.9811(16)
Nb01	$O3^3$	1.9811(16)	O3	$Sr1^7$	3.304(5)
Nb01	$O3^4$	1.9811(16)	O2	$Sr1^7$	2.2883(2)

Table S8. Bond angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$O3^1$	Nb01	O3	180.0	$O3^2$	Nb01	$O3^5$	90.06(19)
O3	Nb01	$O3^2$	89.94(19)	$O3^4$	Nb01	$O3^5$	89.94(19)
O3	Nb01	$O3^3$	89.94(19)	$O3^1$	Nb01	$O3^2$	90.06(19)
$O3^2$	Nb01	$O3^3$	89.94(19)	$O3^3$	Nb01	$O3^5$	180.0
O3	Nb01	$O3^4$	90.06(19)	Nb01	O3	$Nb01^6$	141.1(3)
$O3^1$	Nb01	$O3^3$	90.06(19)	Nb01	O3	$Ti01^6$	141.1
$O3^1$	Nb01	$O3^4$	89.94(19)	Nb01	O3	$Sr1^7$	109.43(13)
$O3^4$	Nb01	$O3^3$	90.06(19)	$Nb01^6$	O3	$Sr1^7$	109.43(13)
O3	Nb01	$O3^5$	90.06(19)	$Ti01^6$	O3	$Nb01^6$	0.0
$O3^4$	Nb01	$O3^2$	180.0	$Ti01^6$	O3	$Sr1^7$	109.43(13)
$O3^1$	Nb01	$O3^5$	89.94(19)				

5) Fit of the hydropyrochlore EXAFS data considering one oxygen shell only

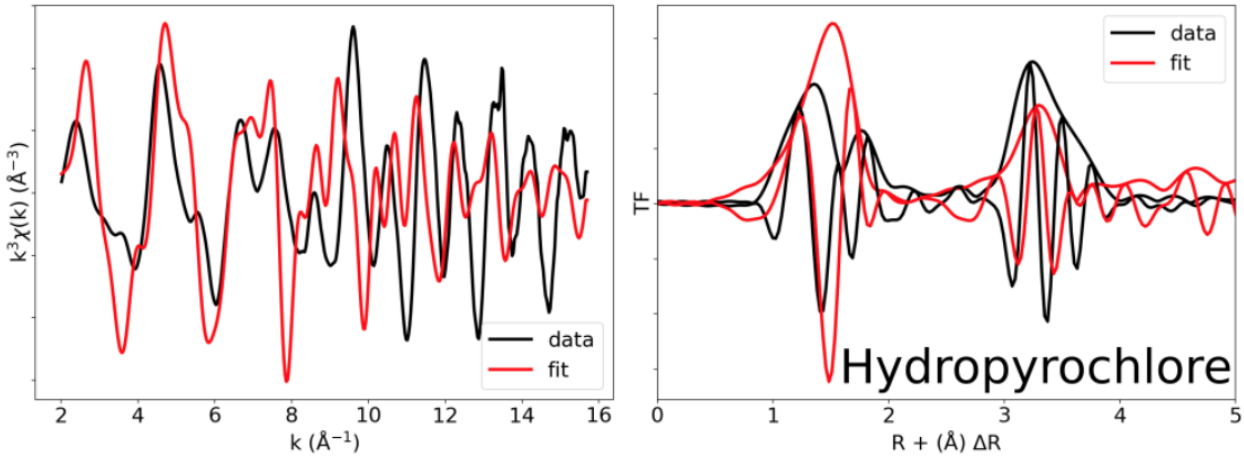

Figure S2. Discrepancy between the fit and the experimental EXAFS and FFT spectra of hydropyrochlore considering a single oxygen shell as determined by XRD refinement.