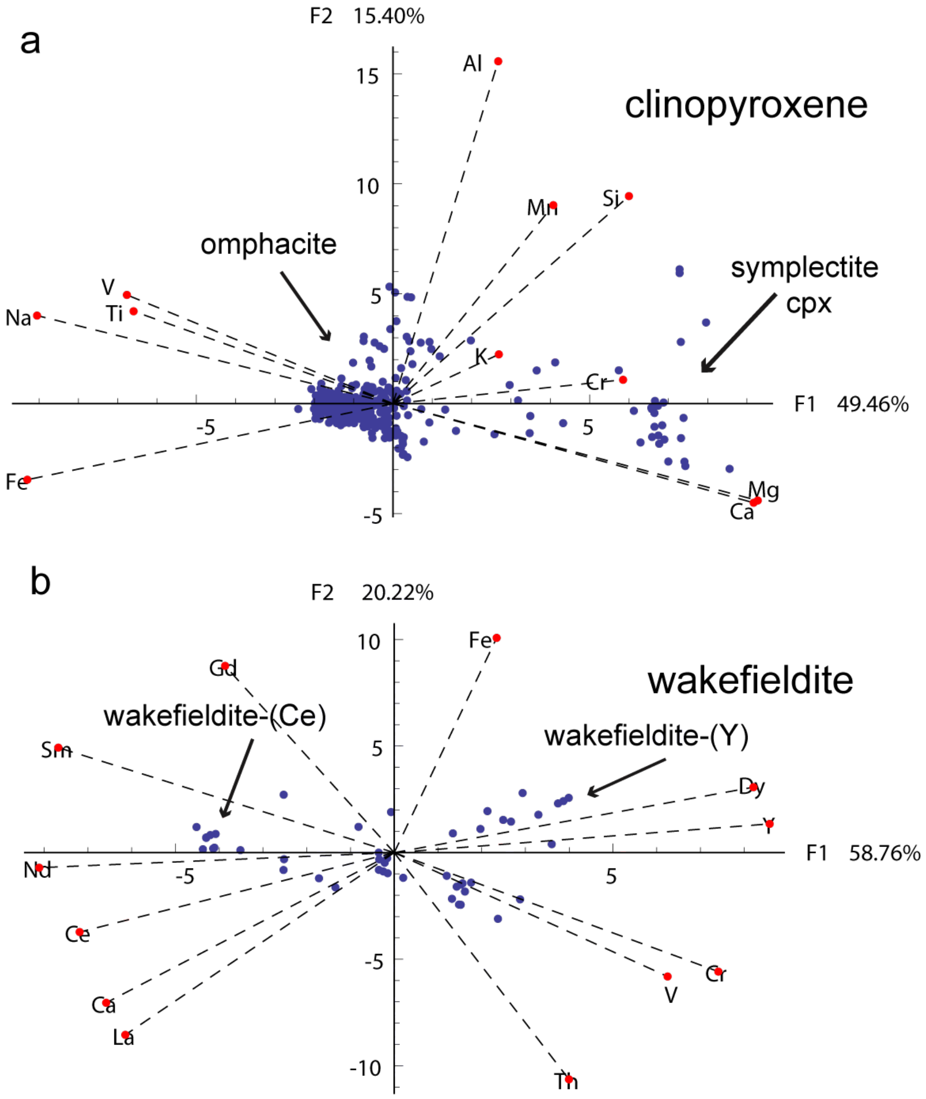
Supplementary Table 1: Vanadium-bearing minerals reported in the unmetamorphosed radiolarites (cherts) belonging to the Jurassic Ligurian ophiolites [mines of Gambatesa and Molinello - Val Graveglia (Genova, Italy); mine of Cerchiara, Rocchetta di Vara (La Spezia, Italy]; www.mindat.org, accessed in June 2019]. TL = type locality.

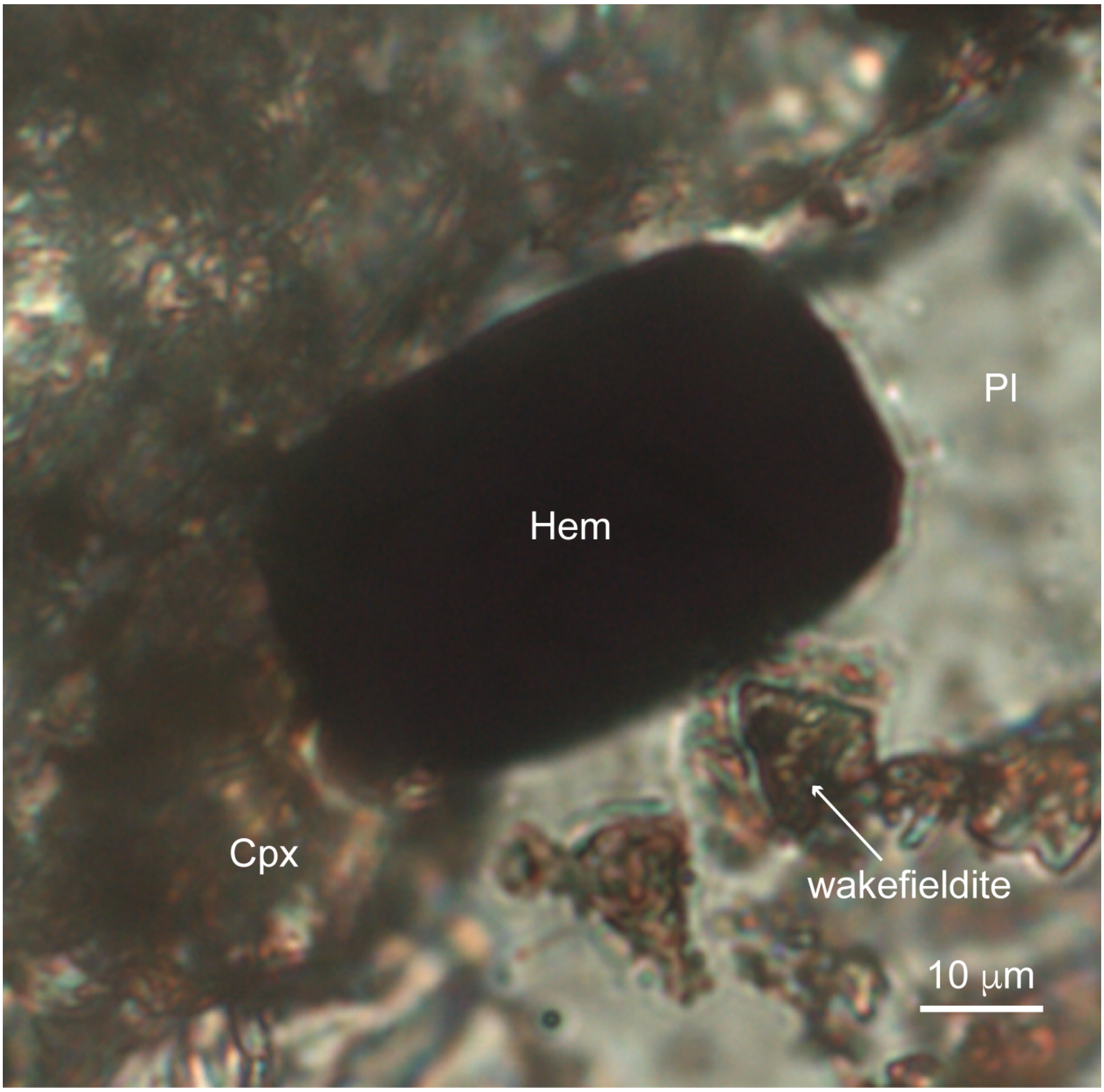
Vanadium phase	Formula	Vanadium oxid. state
Ansermetite	$MnV_2O_6 \cdot 4H_2O$	+5
Argandite	$Mn_7(VO_4)_2(OH)_8$	+5
Balestraite	$KLi_2VSi_4O_{12}$	+5
Barnesite	$Na_2V_6O_{16} \cdot 3H_2O$	+5
Bassoite (TL)	$SrV_3O_7 \cdot 4H_2O$	+4
Cavoite (TL)	CaV_3O_7	+4
Cortesognoite (TL)	$CaV_2(Si_2O_7)(OH)_2{\cdot}H_2O$	+3
Duttonite	$V^{4+}O(OH)_2$	+4
Franciscanite	$Mn^{2+}{}_6(V^{5+}\square)(SiO_4)_2O_3(OH)_3$	+5
Gamagarite	$Ba_2Fe^{3+}(VO_4)_2(OH)$	+5
Goldmanite	$Ca_3V^{3+}{}_2(SiO_4)_3$	+3
Häggite	$V^{3+}V^{4+}O_2(OH)_3$	+3, +4
Haradaite	$SrVSi_2O_7$	+4
Hummerite	$KMgV^{5+}{}_5O_{14} \cdot 8H_2O$	+5
Lenoblite	$V^{4+}{}_2O_4 \cdot 2H_2O$	+4
Medaite (TL)	$Mn^{2+}{}_6V^{5+}Si_5O_{18}(OH)$	+5
Metatyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 3H_2O$	
Molinelloite (TL)	$Cu(H_2O)(OH)V^{4+}O(V^{5+}O_4)$	+4, +5
Nabiasite	$BaMn_9(VO_4)_6(OH)_2$	+5
Oxyvanite	$V^{3+}{}_2V^{4+}O_5$	+3, +4
Palenzonaite (TL)	$(NaCa_2)Mn^{2+}{}_2(VO_4)_3$	+5
Pascoite	$Ca_3(V_{10}O_{28}) \cdot 17H_2O$	+5
Paseroite (TL)	$PbMn^{2+}(Mn^{2+},Fe^{3+})_2(V^{5+},Ti,\square)_{18}O_{38}$	+5
Poppiite (TL)	$Ca_2(V^{3+},Fe^{3+},Mg)(V^{3+},Al)_2(Si_2O_7)(SiO_4)(OH,O)_2 \cdot H_2O$	+3
Reppiaite (TL)	$Mn^{2+}{}_5(VO_4)_2(OH)_4$	+5
Pyrobelonite	$PbMn^{2+}(VO_4)(OH)$	+5
Roscoelite	$K(V^{3+},Al)_2(AlSi_3O_{10})(OH)_2$	+3
Saneroite (TL)	$NaMn^{2+}{}_5[Si_5O_{14}(OH)](VO_3)(OH)$	
Santafeite	$(Na,Ca,Sr)_{12}(Mn^{2+},Fe^{3+},Al,Mg)_8Mn^{4+}{}_8(VO_4)_{16}(OH,O)_{20}{\cdot}\ 8H_2O$	
Scheuchzerite	$Na(Mn,Mg,Zn)_9[VSi_9O_{28}(OH)](OH)_3$	
Senaite	$Pb(Mn,Y,U)(Fe,Zn)_2(Ti,Fe,Cr,V)_{18}(O,OH)_{38}$	
Sengierite	$Cu_2(UO_2)_2(VO_4)_2(OH)_2 \cdot 6H_2O$	
Tangeite	$CaCu(VO_4)(OH)$	
Tokyoite	$Ba_2Mn^{3+}(VO_4)_2(OH)$	
Vanadiocarpholite (TL)	$Mn^{2+}V^{3+}Al(Si_2O_6)(OH)_4$	+3
Vanadomalayaite (TL)	$CaV^{4+}(SiO_4)O$	+4
Volborthite	$Cu_3(V_2O_7)(OH)_2 \cdot 2H_2O$	
Wakefieldite-(La)	$La(VO_4)$	+5

```
V2O3      EoS = 2 |
VO(2)O2(0.5)
G0 = -1140065.64 S0 = 98.724744 V0 = 2.987
c1 = 122.883 c2 = 0.0199292 c3 = -2.26925E+06 c5 = 0.244677E-4
b1 = .599E-4 b5 = -.599E-3 b6 = 1996000. b7 = -299.4 b8 = 4
end

VO     EoS = 2 |
VO(1)
G0 = -404444.88 S0 = 38.93724 V0 = 1.162
c1 = 47.3946 c2 = 0.00674075 c3 = -527537.0 c5 = -4.51551E-6
b1 = .599E-4 b5 = -.599E-3 b6 = 1996000. b7 = -299.4 b8 = 4
end

VO2      EoS = 2 |
VO(1)O2(0.5)
G0 = -659630.34 S0 = 51.581376 V0 = 1.815
c1 = 74.7344 c2 = 0.00711756 c3 = -1.6496E+06 c5 = 1.07875E-6
b1 = .599E-4 b5 = -.599E-3 b6 = 1996000. b7 = -299.4 b8 = 4
end

V2O5      EoS = 2 |
VO(2)O2(1.5)
G0 = -1420581.24 S0 = 131.04684 V0 = 5.413
c1 = 194.854 c2 = -0.0163285 c3 = -5.53495E+06 c5 = -5.98864E-6
b1 = .599E-4 b5 = -.599E-3 b6 = 1996000. b7 = -299.4 b8 = 4
end

Mn3O4      EoS = 2 |
MNO(3)O2(0.5)
G0 = -1282434 S0 = 164.10 V0 = 4.695  |G0 = -1282434.0 S0 = 166.6 V0 = 4.695
c1 = -7.4 c2 = 9.49E-2 c3 = -6712000  c5 = 3396.0
b1 = 4.45E-5 b5 = -4.45E-4 b6 = 1370000 b7 = -205.5 b8 = 4
transition = 1 type = 4 t1  = 1443 t2  = 14.53
end

Mn2O3      EoS = 2 |
MNO(2)O2(0.5)
G0 = -882042 S0 = 113.7 V0 = 3.137
c1 = 1.624E+02 c2 = 1.211E-02 c3 = 1.046E+06 c4 = 3.462E-06 c5 = -1.317E+03
b1 = 4.38E-5 b5 = -4.38E-4 b6 = 1691000 b7 = -271.65 b8 = 7.35
end

braunite      EoS = 2 |
MNO(7)SIO2(1)O2(1.5)
G0 = -3944653.0 S0 = 416.4 V0 = 12.508
c1 = 430.1 c2 = 1.11E-1 c3 = -7325000
b1 = 4.9E-5 b5 = -4.9E-4 b6 = 1807000 b7 = -271.05 b8 = 6.5
end

piemontite      EoS = 2 |
AL2O3(1)SIO2(3)CAO(2)MNO(1)O2(.25)H2O(.5)
G0 = -6143680 S0 = 328 V0 = 13.87
c1 = 610 c2 = .24781E-1 c3 = -11230000 c5 = -1192.1
b1 = .505E-4 b5 = -.505E-3 b6 = 1233000. b7 = -184.95 b8 = 4
end
```

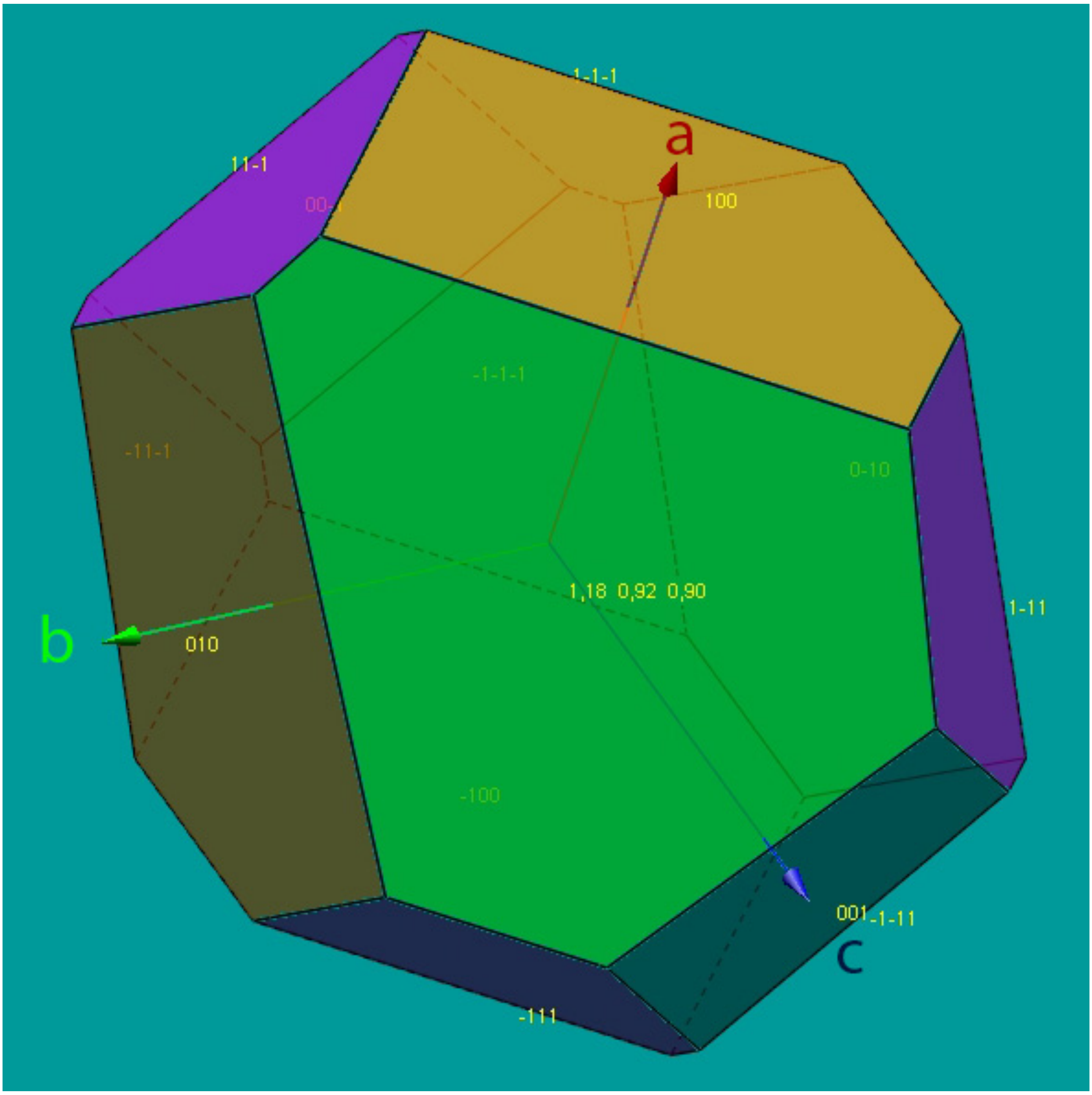
Supplementary Table 2: thermodynamic data used for vanadium oxides, manganese oxides and piemontite, formatted for the Perple_X package (http://www.perplex.ethz.ch). See text for details.



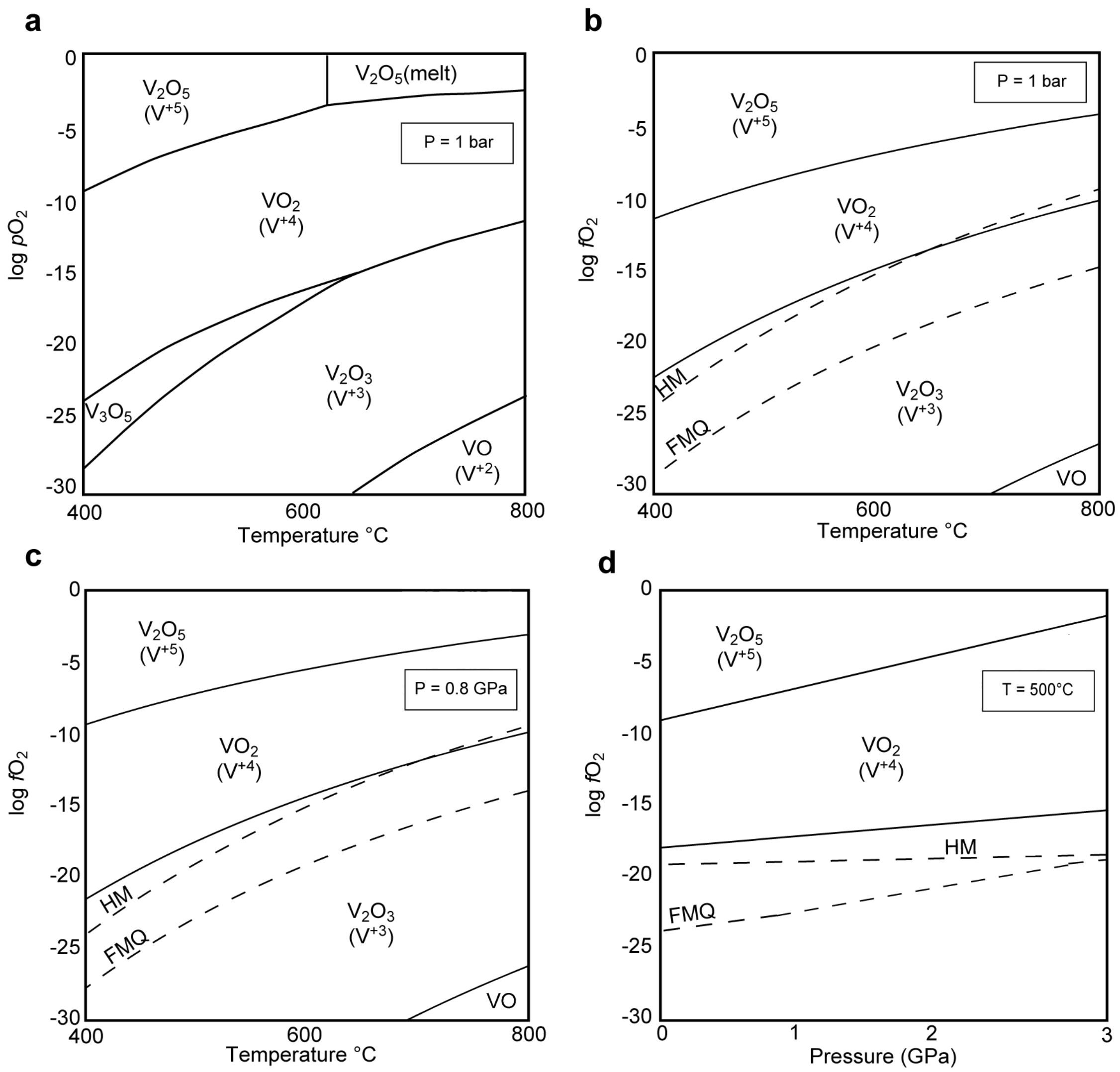
Supplementary Figure 1: Principal component analysis (PCA) performed on the correlation matrix of electron microprobe analyses of clinopyroxene (a: sample 26/03) and wakefieldite (b: sample SM96-2). The biplots show the first (F1) and the second (F2) principal components, accounting for 58.76% and 20.22% of the eigenvalues. The red and blue dots are the projection in the biplot of the basis vectors and composition vectors, respectively.



Supplementary Figure 2: Transmitted light photomicrograph of the studied wakefieldite. Same field of view as in the backscattered electron (BSE) image of Figure 4.



Supplementary Figure 3: Ideal shape of the studied crystal, modeled with ©StereoNet and ©KrystalShaper, considering {111} faces. The contours of the section (1.18 0.92 0.90) (green plane) are similar to those observed in thin section (Fig. 4 Y–La–Ce; Supplementary Figure 2).



Supplementary Figure 4: (a–b) log (pO_2/1 bar)–T diagram at ambient pressure showing the stability of vanadium oxides, calculated using (a) the FactSage package (http://www.factsage.com; Kim et al. 2012) and (b) the Perple_X package (Connolly, 2005; http://www.perplex.ethz.ch) considering the thermodynamic parameters reported in Weast (1984); (c–d) log (fO_2/1 bar)–T and (log fO_2/1 bar)–P diagrams calculated with Perple_X at high pressure conditions, borrowing the bulk modulus parameters from hematite. FMQ: equilibrium fayalite + O_2 = magnetite + quartz (ferrosilite + O_2 = magnetite + quartz at P > 1 GPa); HM: equilibrium magnetite + O_2 = hematite.