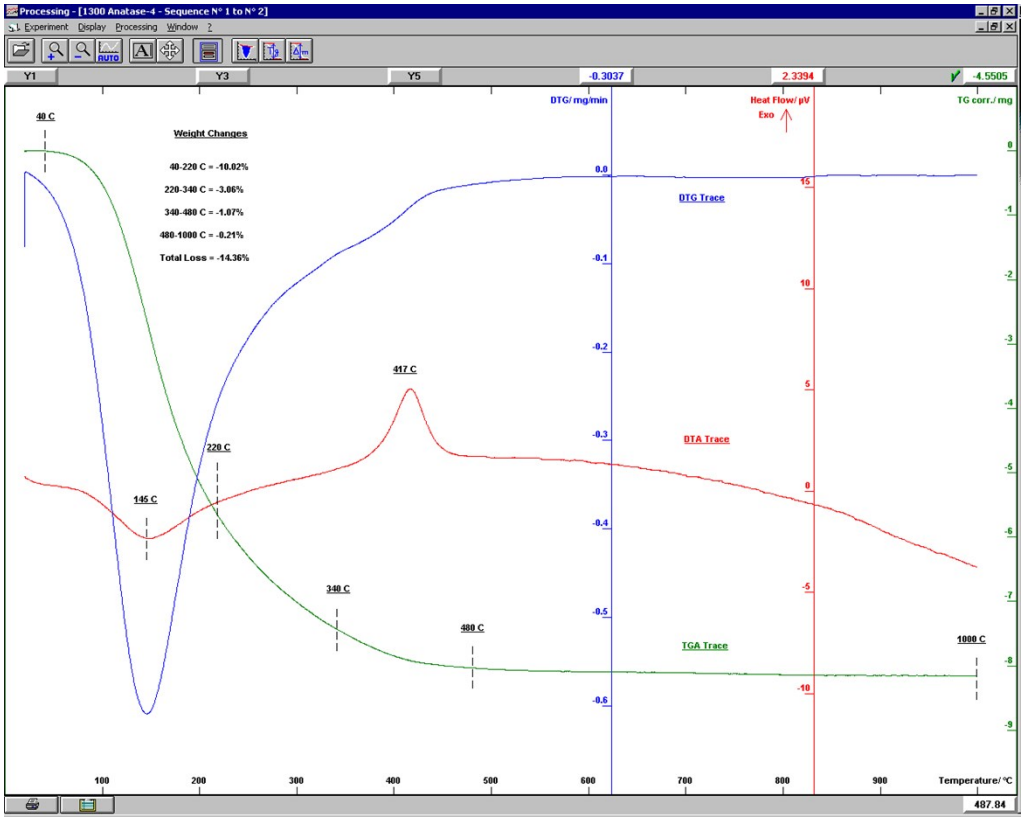

Figure S1a. TGA/DTG/DTA curves for amorphous titania heated in helium.

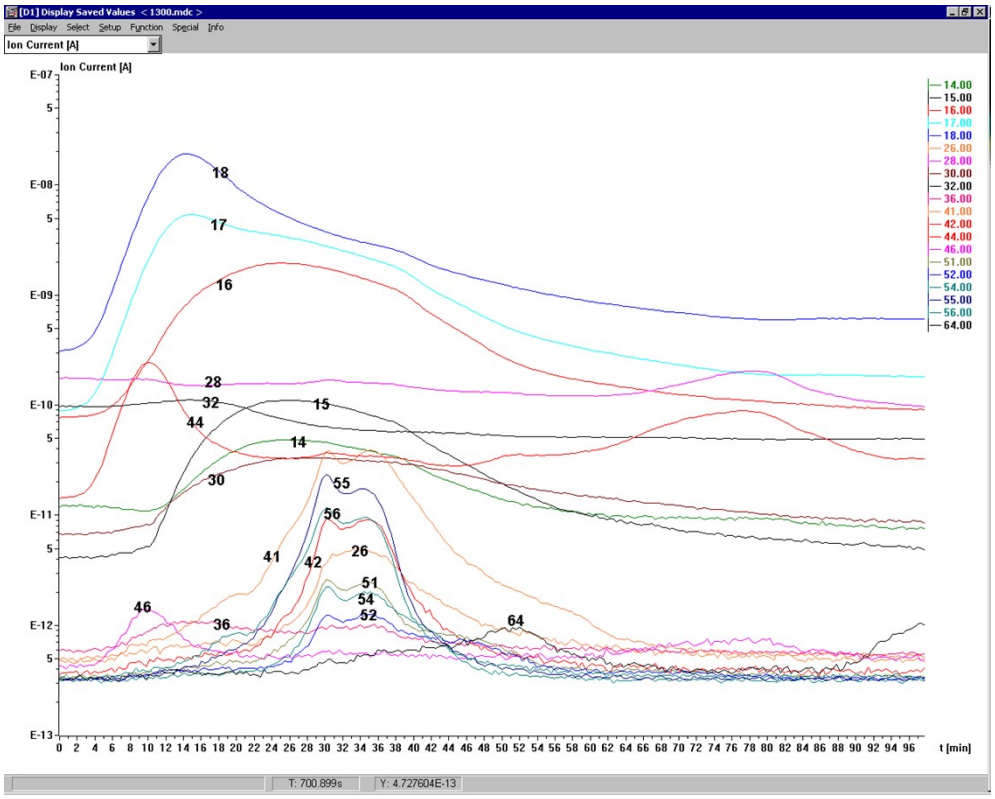

Figure S1b. MS gas evolution curves for amorphous titania heated in helium. Numbers correspond to mass numbers of evolved species, e.g. 15 = NH, 16 = NH_2, 17 = OH and NH_3, 18 = H_2O, 28 = CO, 30 = NO, 44 = CO_2.

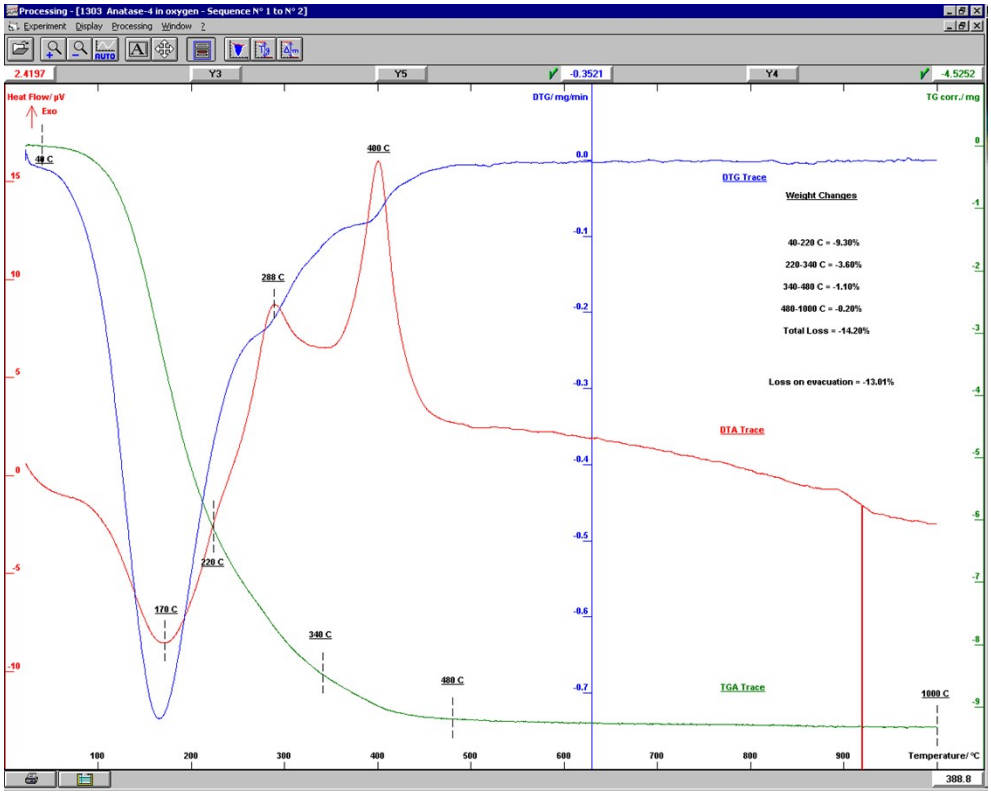

Figure S1c. TGA/DTG/DTA curves for amorphous titania heated in oxygen

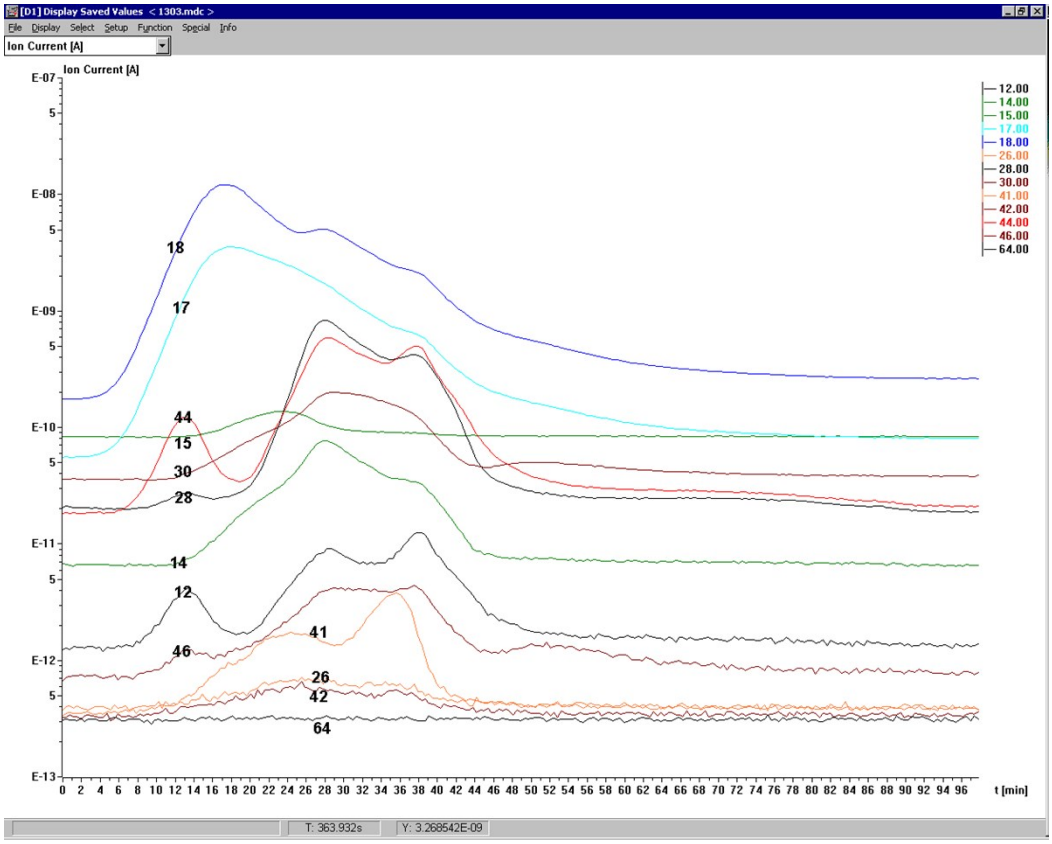

Figure S1d. MS gas evolution curves for amorphous titania heated in oxygen.

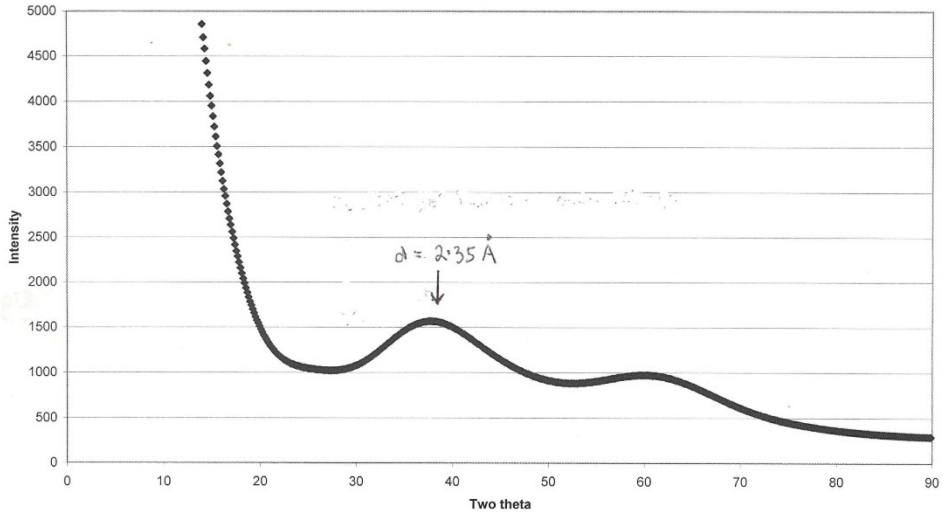

Figure S2(a). Debye function calculation for lepidocrocite segment, based on the $Cs_xTi_{2-x/4}O_4$ structure (reference 28) involving 1 x 1 x 3 multiples of the unit-cell. Arrow shows a peak at d = 2.35 Å due to diffraction from cubic-stacked layers.

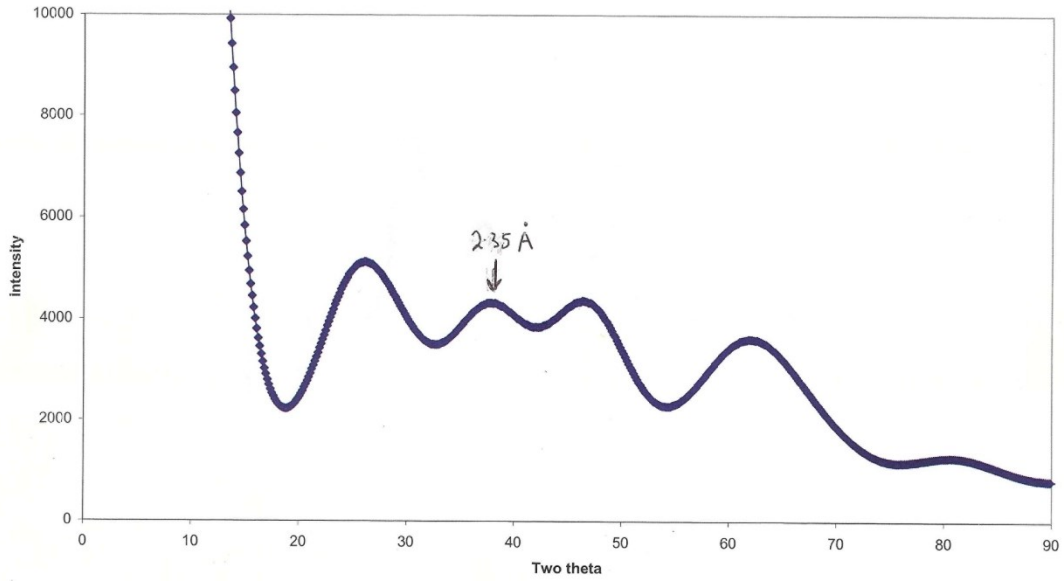

Figure S2(b). As in S2(a) for a lepidocrocite segment based on 3 x 1 x 3 multiples of the unit cell.

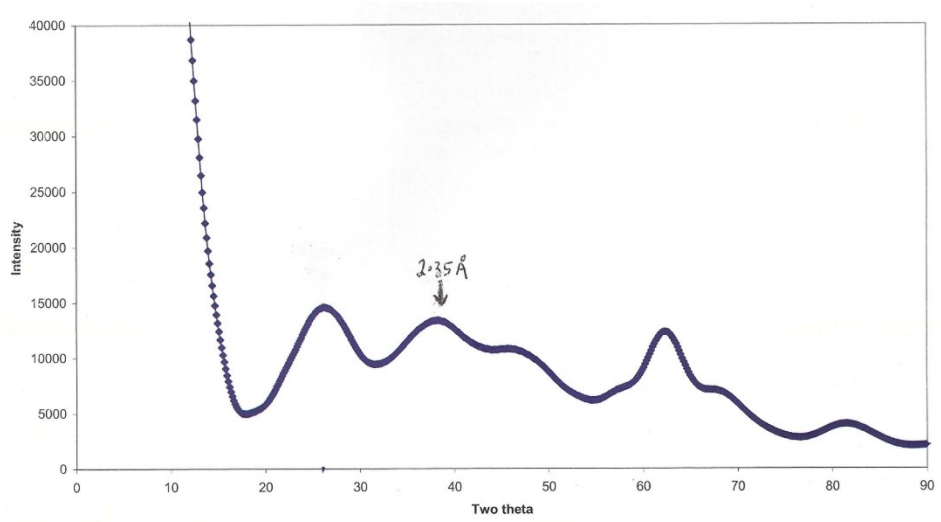

Figure 2(c). As for Figure 2(a), for a lepidocrocite segment based on 3 x 1 x 9 multiples of the unit cell.

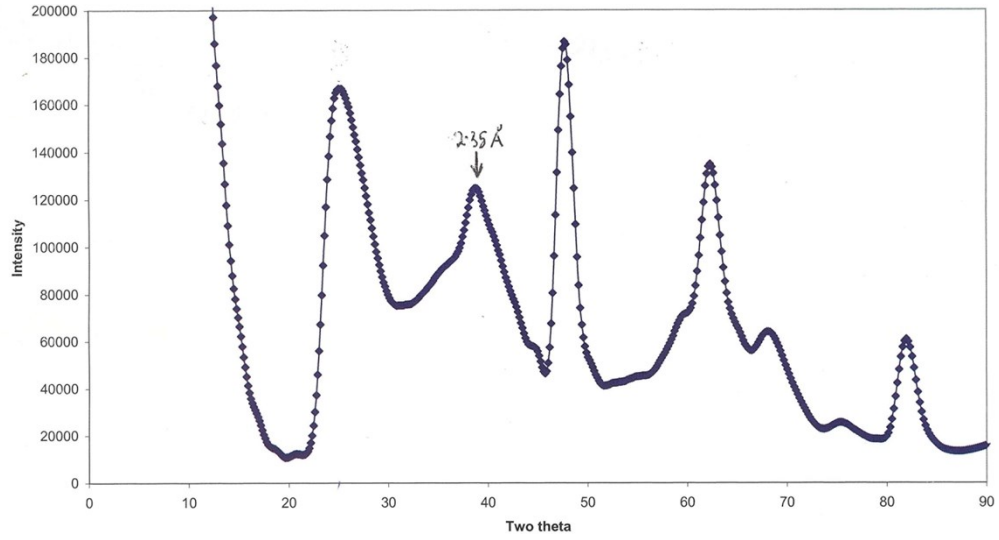

Figure 2(d). As for Figure 2(a), for a lepidocrocite segment based on 13 x 1 x 17 multiples of the unit cell.

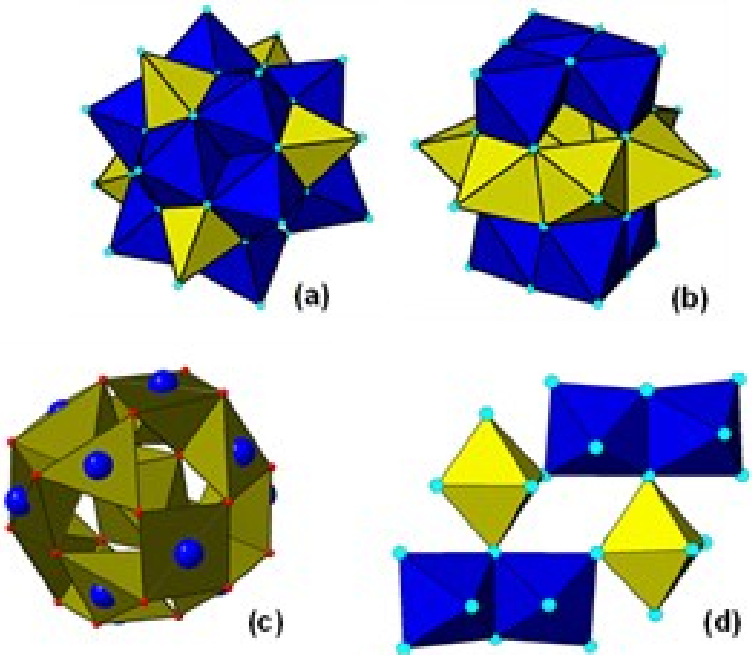

Figure S3. Titanium-oxo clusters that were used to generate PDFs. (a) $Ti_{18}O_{45}$, (b) $Ti_{12}O_{32}$, (c) $Ti_{15}O_{30}$, (d) Ti_6O_{28}.

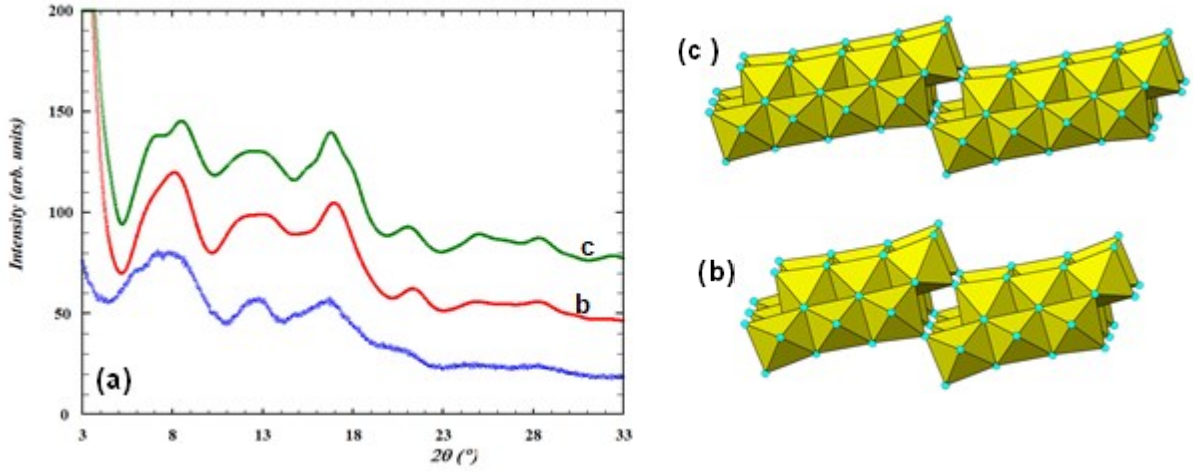

Figure S4 (a) Experimental PXRD (blue points) and Debye-calculated PXRD for (b) 30 Ti-centred octahedral cluster from $H_2Ti_3O_7$ and (c) 40 Ti-centred octahedral cluster from $H_2Ti_4O_9$.