Supplementary Information

A multi-technique investigation of the pH dependence of phosphate induced transformations of ZnO nanoparticles

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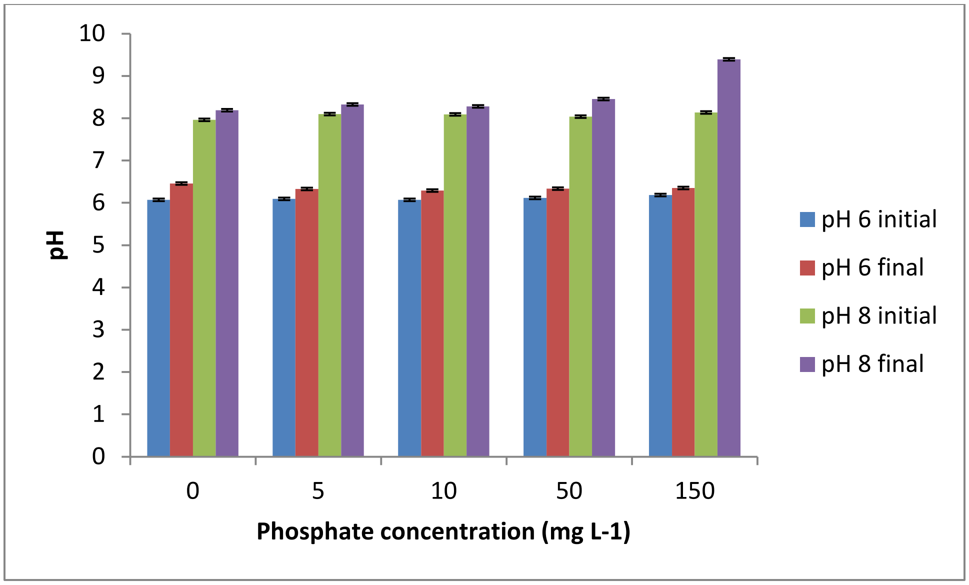
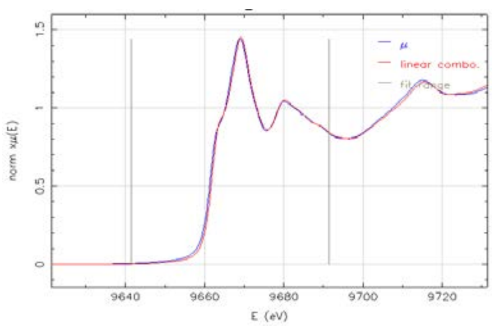
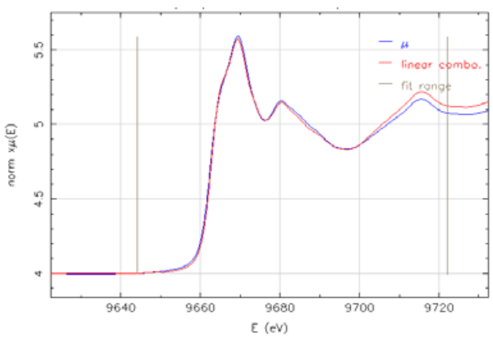


Figure S1. pH values at the beginning and end of aging as a function of initial pH and phosphate concentration. Results were similar regardless of aging duration so the different time points and replicates were averaged for each pH value and phosphate concentration.



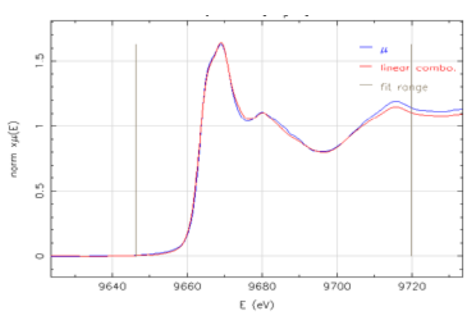
A – 90% ZnO, 10% Zn-phosphate

R	0.000304
Chi square	0.05186
Reduced chi square	0.0002284
ZnO	91.2
Zn-phosphate	8.8



B – 75% ZnO, 25% Zn-phosphate

R	0.000473
Chi square	0.09710
Reduced chi square	0.0004296
ZnO	73.9
Zn-phosphate	26.1



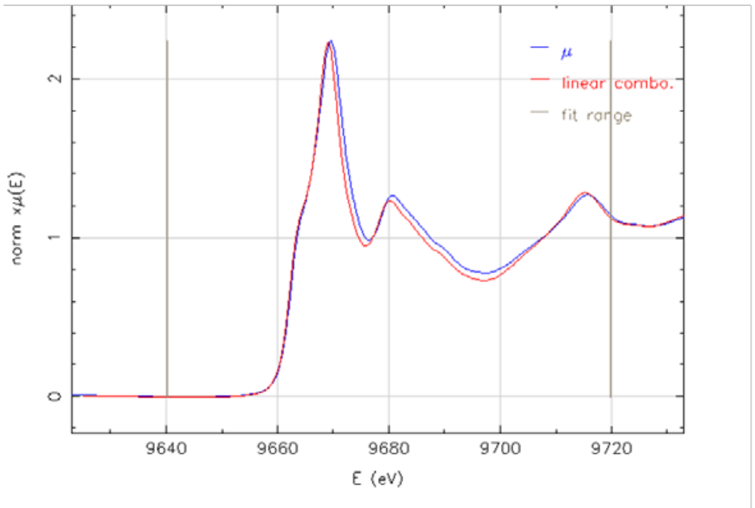
C – 50% ZnO, 50% Zn-phosphate

R	0.000320
Chi square	0.06283
Reduced chi square	0.0002869
ZnO	50.8
Zn-phosphate	49.2

Figure S2. Linear combination fits for X-ray absorption near edge spectra (XANES) of standards containing known proportions of ZnO and $Zn_3(PO_4)_2$.

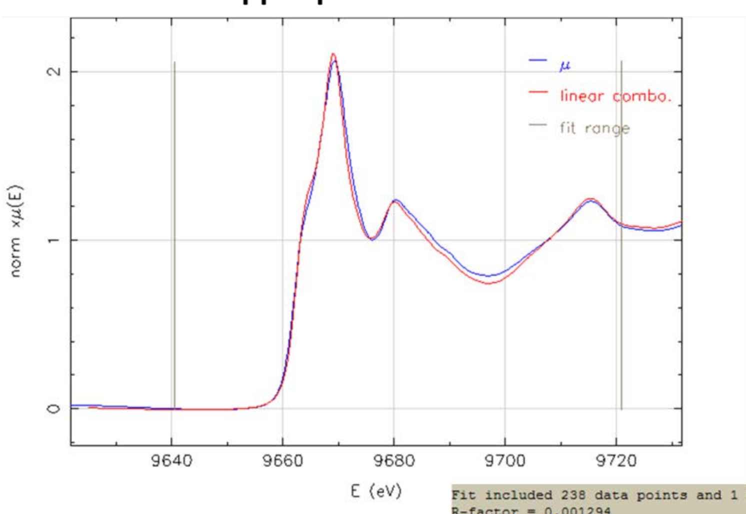
Figure S3. Example linear combination fits for X-ray absorption near edge spectra (XANES) aged ZnO manufactured nanomaterials. The treatment conditions are given above each panel (ppm = mg/L of phosphate).

5ppm-pH6-1d



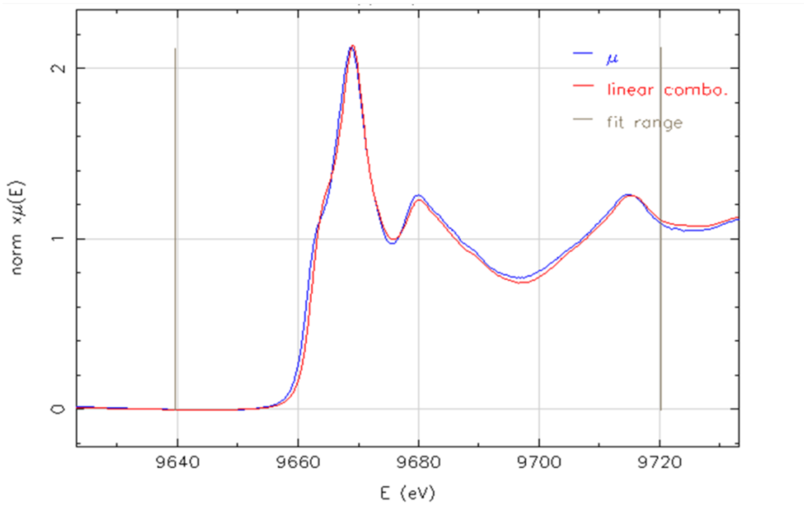

```
Fit included 236 data points and 1 variable
R-factor = 0.003623
chi-square = 0.88933
reduced chi-square = 0.0037524

   group                     weight
=======================================
  1: ZnO 1                   0.790(0.015)
  2: zinc phosphate 1        0.210(0.015)
```

5ppm-pH6-3d



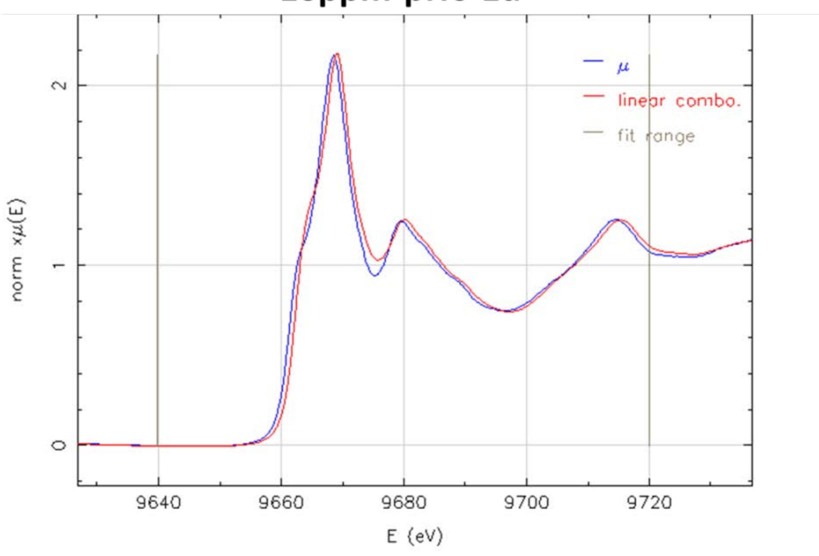

```
Fit included 238 data points and 1 variable
R-factor = 0.001294
chi-square = 0.31001
reduced chi-square = 0.0012971

   group                     weight
=======================================
  1: ZnO 1                   0.673(0.009)
  2: zinc phosphate 1        0.327(0.009)
```

5ppm-pH6-7d



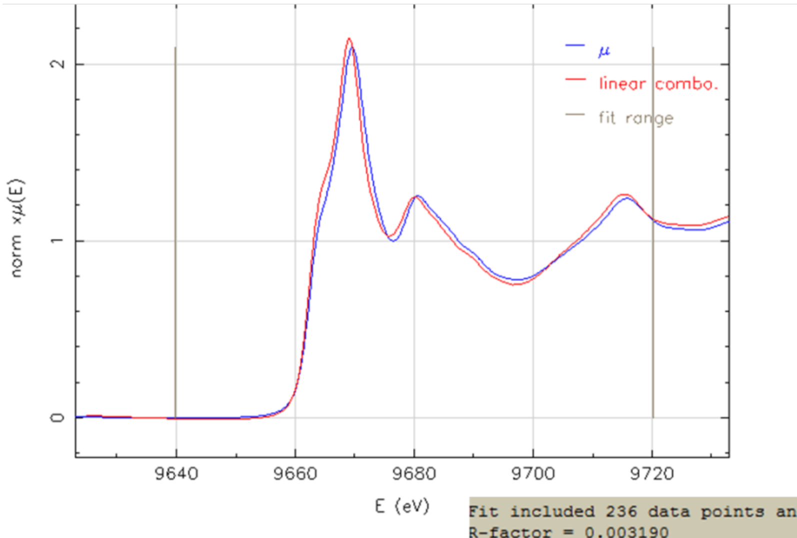

```
Fit included 222 data points and 1 variable
R-factor = 0.002121
chi-square = 0.50752
reduced chi-square = 0.0022965

   group                 weight
=======================================
  2: zinc phosphate 1    0.300(0.012)
  1: ZnO 1               0.700(0.012)
```

10ppm-pH6-1d



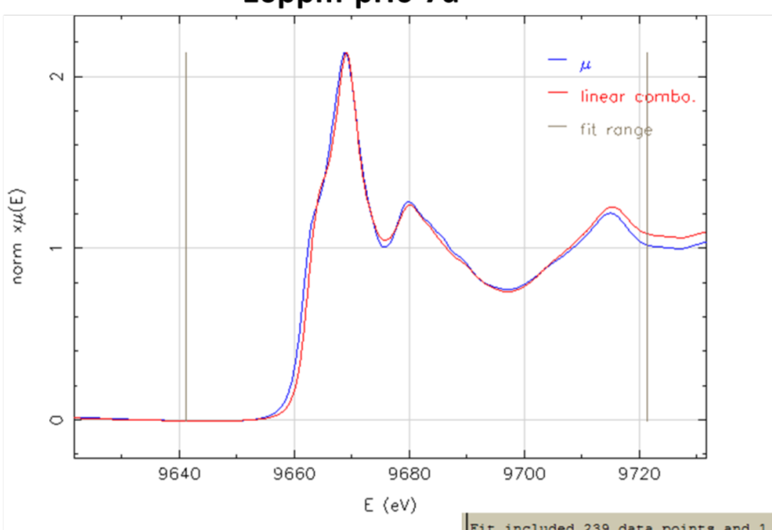

```
Fit included 221 data points and 1 variable
R-factor = 0.004497
chi-square = 1.05227
reduced chi-square = 0.0047614

   group                 weight
=======================================
  1: ZnO 1               0.672(0.016)
  2: zinc phosphate 1    0.328(0.016)
```

10ppm-pH6-3d



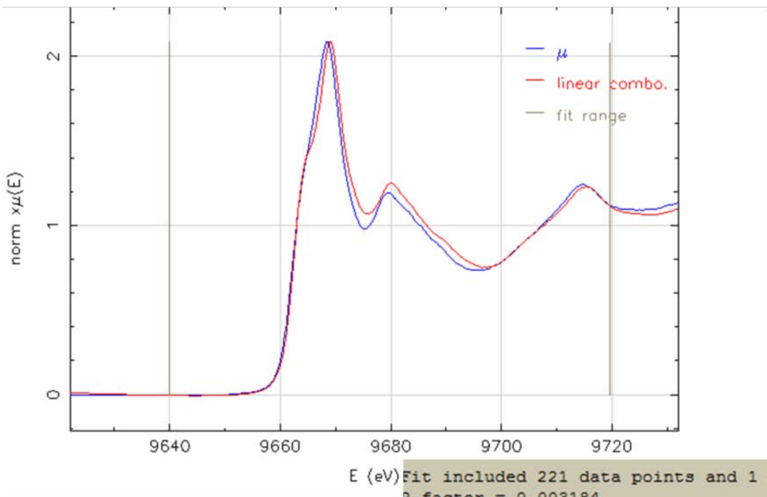

```
Fit included 236 data points and 1 variable
R-factor = 0.003190
chi-square = 0.77290
reduced chi-square = 0.0032612

  group                   weight
=======================================
  1: zinc phosphate 1    0.362(0.010)
  4: ZnO 1               0.638(0.010)
```

10ppm-pH6-7d



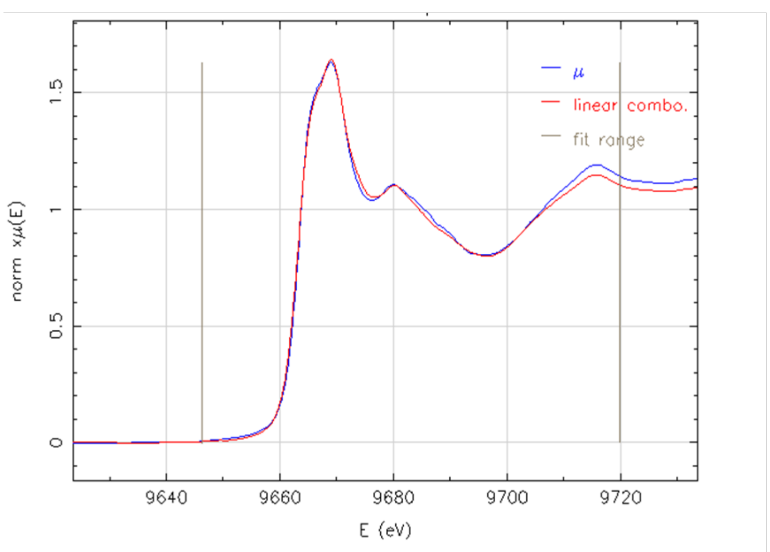

```
Fit included 239 data points and 1 variable
R-factor = 0.002691
chi-square = 0.72048
reduced chi-square = 0.0030020

  group                   weight
=======================================
  1: zinc phosphate 1    0.367(0.013)
  4: ZnO 1               0.633(0.013)
```

50ppm-pH6-1d



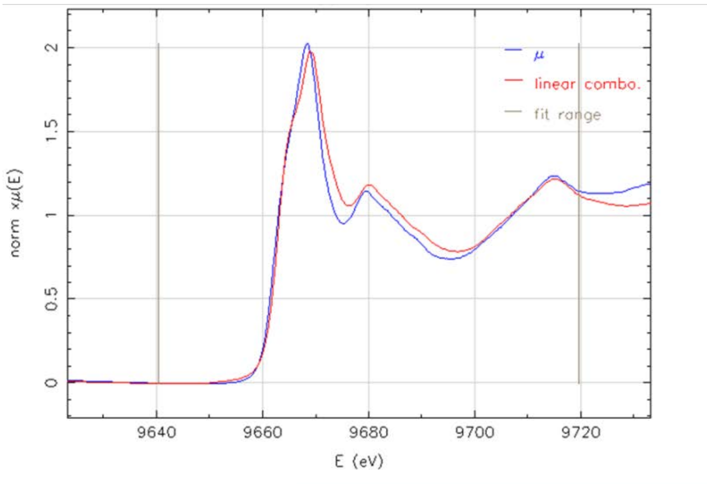

```
Fit included 221 data points and 1 variable
R-factor = 0.003184
chi-square = 0.72830
reduced chi-square = 0.0033105

  group                    weight
=======================================
 1: zinc phosphate 1     0.410(0.014)
 4: ZnO 1                0.590(0.014)
```

50ppm-pH6-7d



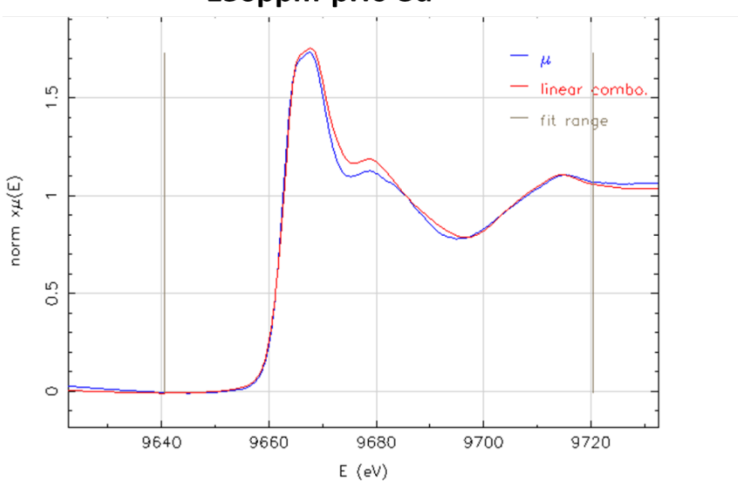
R	0.000320
Chi square	0.06283
Reduced chi square	0.0002869
ZnO	50.8
Zn-phosphate	49.2

150ppm-pH6-1d



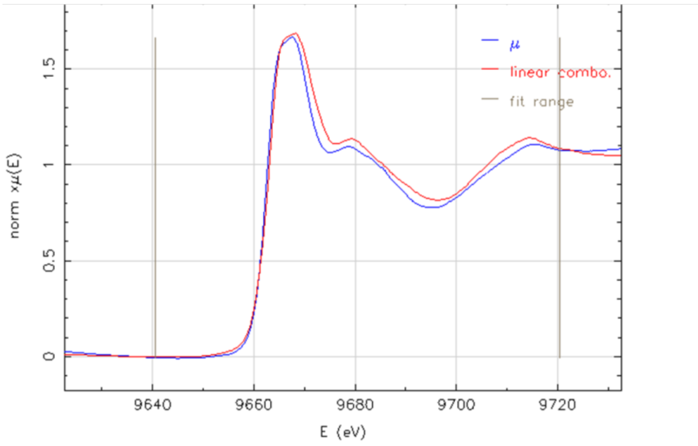

```
Fit included 220 data points and 1 variable
R-factor = 0.005601
chi-square = 1.23505
reduced chi-square = 0.0056138

   group                    weight
========================================
  2: ZnPO4 std.024.xns     0.600(0.019)
  4: ZnO 1                 0.400(0.019)
```

150ppm-pH6-3d



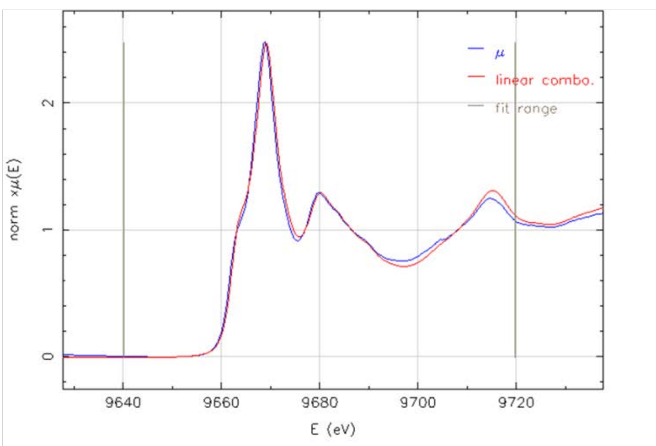

```
Fit included 236 data points and 1 variable
R-factor = 0.001284
chi-square = 0.30498
reduced chi-square = 0.0012868

   group                    weight
========================================
  33: Zn3PO4_4Layers.001.xns  0.610(0.015)
  31: Zno-1                   0.390(0.015)
```

150ppm-pH6-7d



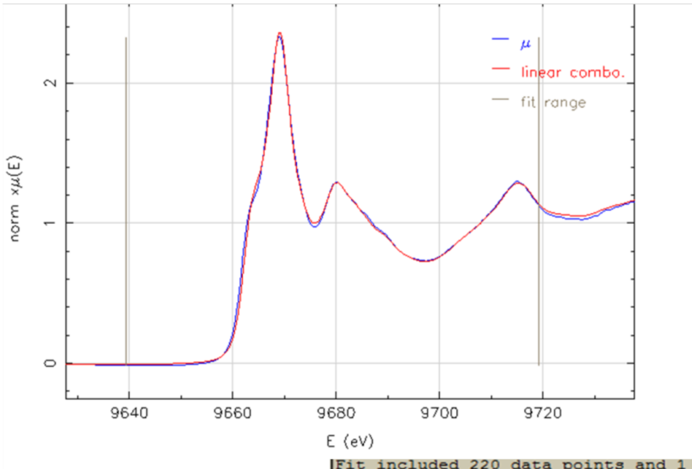

```
Fit included 236 data points and 1 variable
R-factor = 0.002926
chi-square = 0.66734
reduced chi-square = 0.0028158

   group                  weight
========================================
  2: ZnPO4 std.024.xns   0.673(0.024)
  31: Zno-1              0.327(0.024)
```

5ppm-pH8-1d



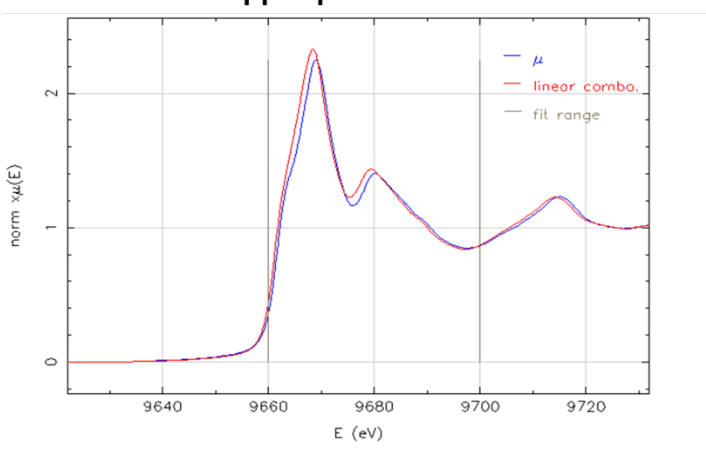

```
Fit included 220 data points and 1 variable
R-factor = 0.001816
chi-square = 0.44799
reduced chi-square = 0.0020363

   group                    weight
========================================
  1: Zn phosphate std.001.xns  0.095(0.008)
  3: ZnO std.023.xns     0.905(0.008)
```

5ppm-pH8-3d



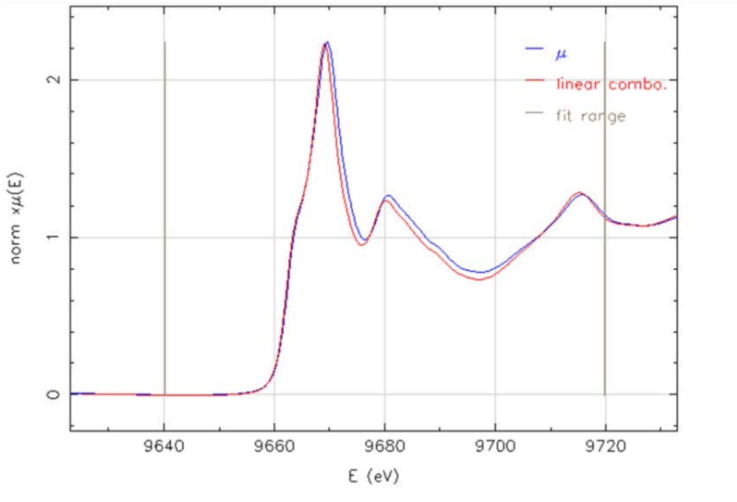

```
Fit included 220 data points and 1 variable
R-factor = 0.000596
chi-square = 0.14821
reduced chi-square = 0.0006768

   group                weight
=======================================
  1: Zn phosphate std.001.xns  0.176(0.004)
  4: ZnO std.023.xns    0.824(0.004)
```

5ppm-pH8-7d



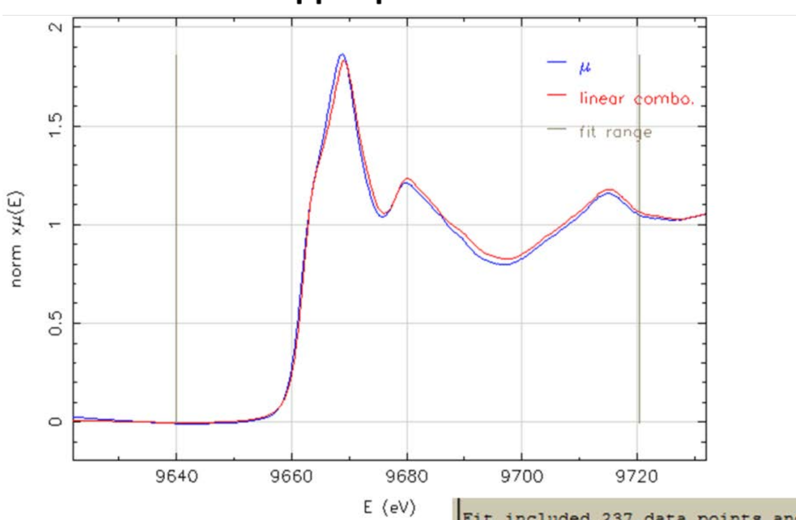
Chi square	1.0414
Reduced schi square	0.0078301
ZnO	82.5
Zn3(PO4)2	17.5

10ppm-pH8-1d



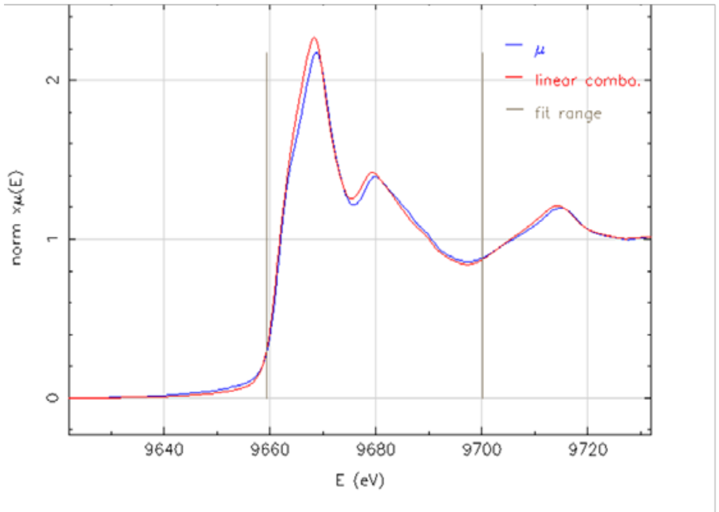

```
Fit included 236 data points and 1 variable
R-factor = 0.003623
chi-square = 0.88933
reduced chi-square = 0.0037524

  group                    weight
========================================
 1: ZnO 1                  0.790(0.015)
 2: zinc phosphate 1       0.210(0.015)
```

10ppm-pH8-3d



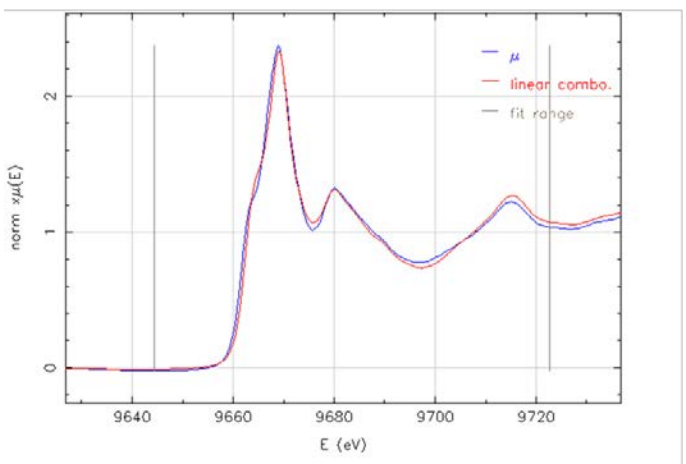

```
Fit included 237 data points and 1 variable
R-factor = 0.000993
chi-square = 0.24543
reduced chi-square = 0.0010356

  group                    weight
========================================
 2: ZnPO4 std.024.xns      0.221(0.016)
 3: ZnO std.002.xns        0.779(0.016)
```

50ppm-pH8-1d



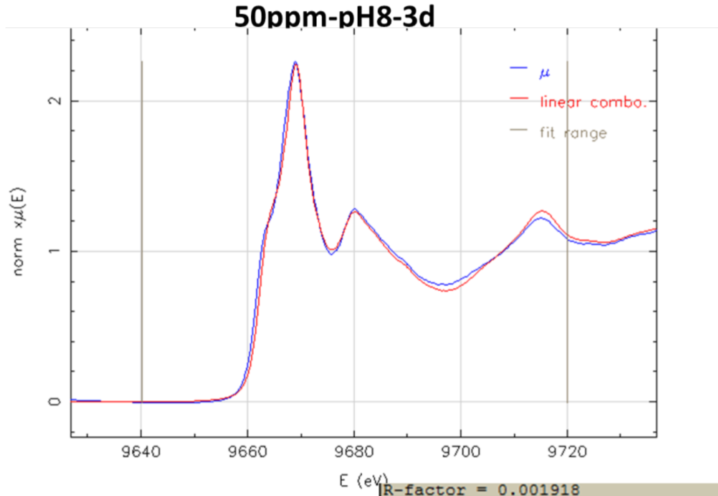
Chi square	0.46576
Reduced schi square	0.0034246
ZnO	73.1
Zn3(PO4)2	26.9

10ppm-pH8-7d



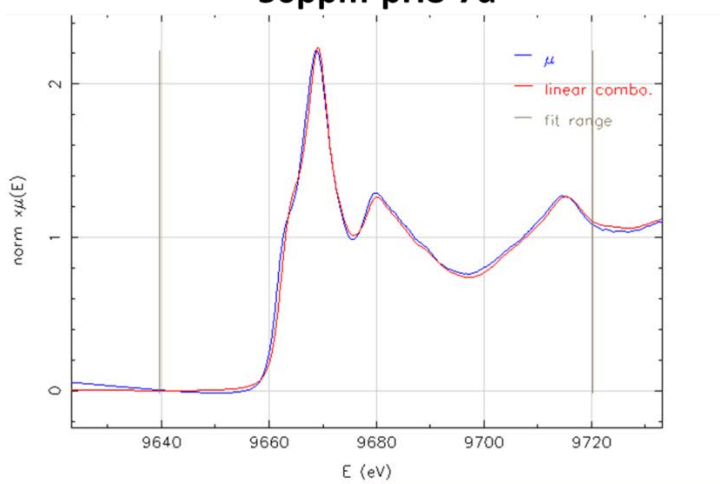

```
Fit included 226 data points and 1 variable
R-factor = 0.001964
chi-square = 0.52810
reduced chi-square = 0.0023471

   group                   weight
=======================================
  1: Zn phosphate std.001.xns   0.249(0.008)
  4: ZnO std.023.xns     0.751(0.008)
```

50ppm-pH8-3d



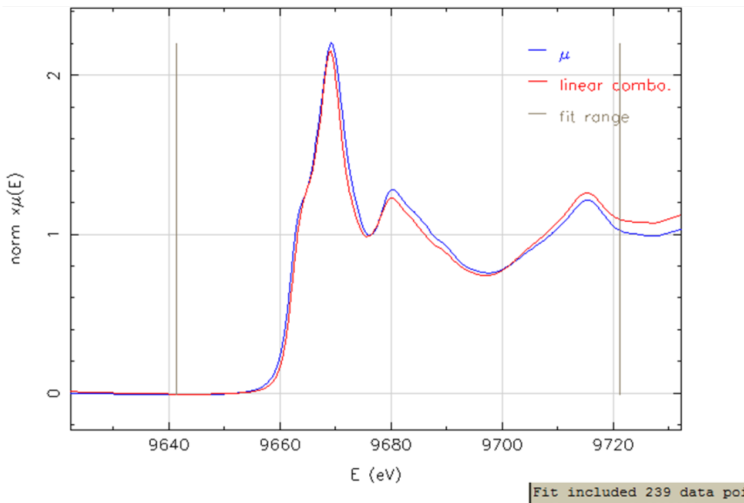

```
R-factor = 0.001918
chi-square = 0.47724
reduced chi-square = 0.0021595

  group                    weight
=======================================
  1: Zn phosphate std.001.xns  0.279(0.011)
  3: ZnO 1                   0.721(0.011)
```

50ppm-pH8-7d



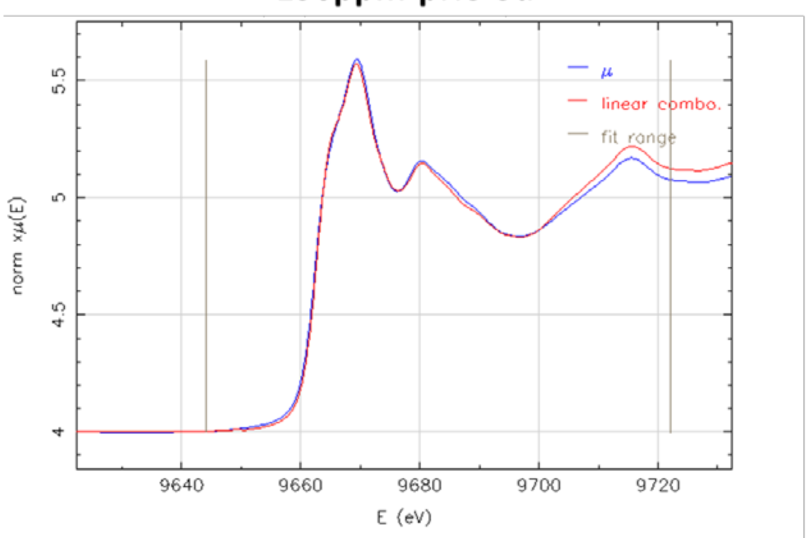

```
Fit included 222 data points and 1 variable
R-factor = 0.001798
chi-square = 0.44738
reduced chi-square = 0.0020243

  group                    weight
=======================================
  1: Zn phosphate std.001.xns  0.286(0.011)
  3: ZnO 1                   0.714(0.011)
```

150ppm-pH8-1d



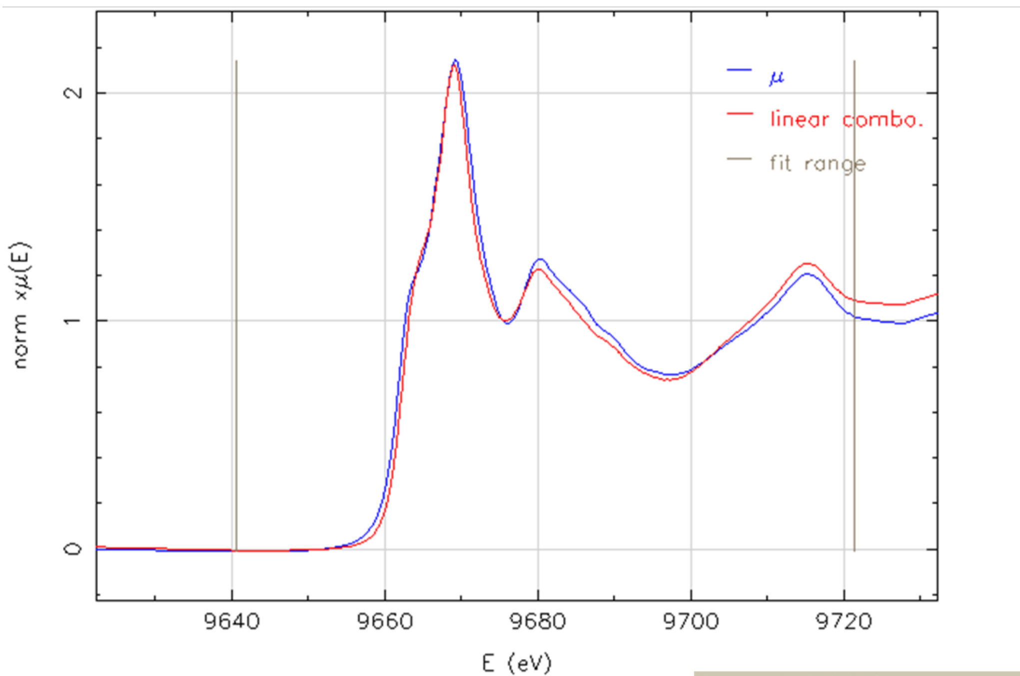

```
Fit included 239 data points and 1 variable
R-factor = 0.002852
chi-square = 0.76160
reduced chi-square = 0.0031866

   group                   weight
========================================
  1: ZnO 1                 0.718(0.014)
  2: zinc phosphate 1      0.282(0.014)
```

150ppm-pH8-3d



R	0.000473
Chi square	0.09710
Reduced chi square	0.0004296
ZnO	73.9
Zn-phosphate	26.1

150ppm-pH8-7d




```
Fit included 240 data points and 1 variable
R-factor = 0.002644
chi-square = 0.69882
reduced chi-square = 0.0029117

   group                    weight
=======================================
  1: ZnO 1                  0.691(0.013)
  2: zinc phosphate 1       0.309(0.013)
```

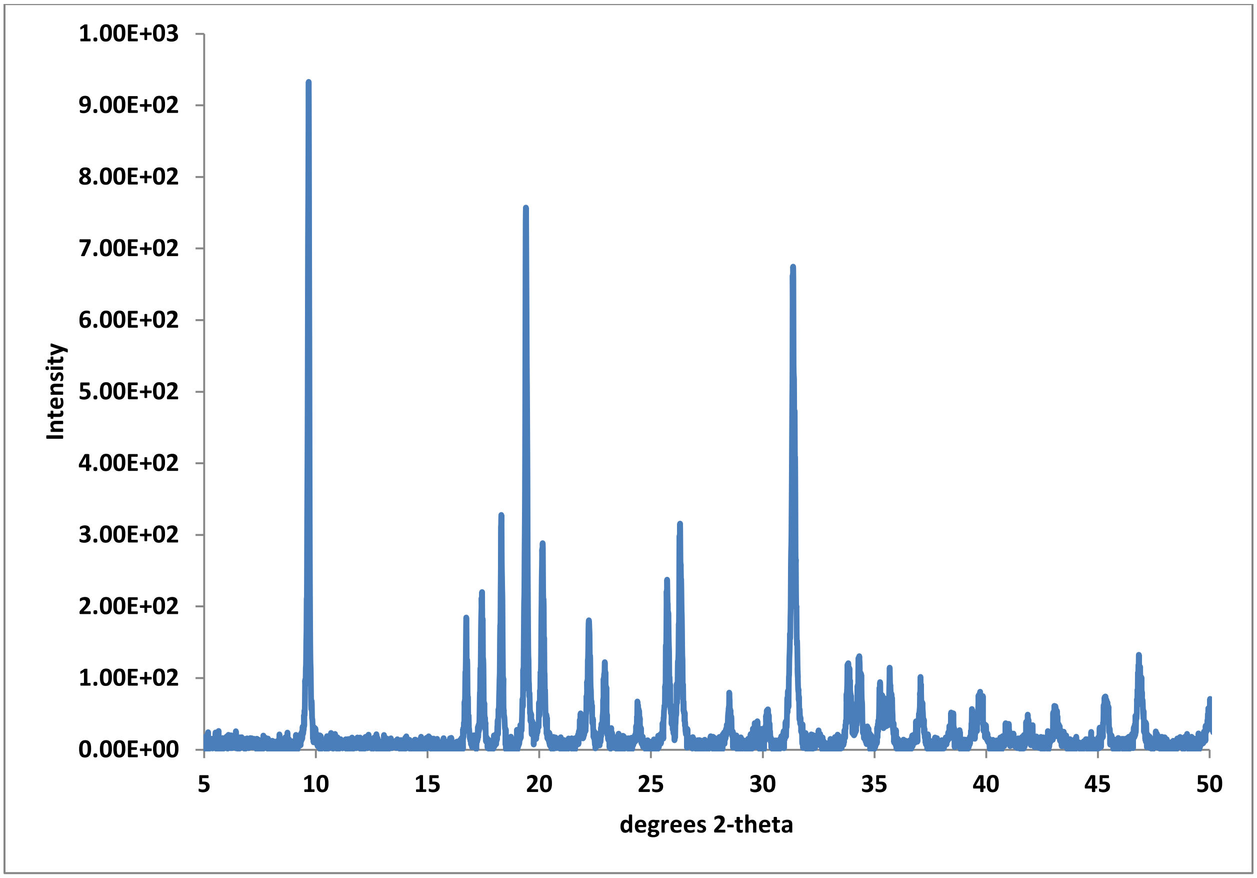


Figure S4. X-ray diffraction pattern for hopeite reported on the RUFF database (http://rruff.info/, RUFF ID R050254).

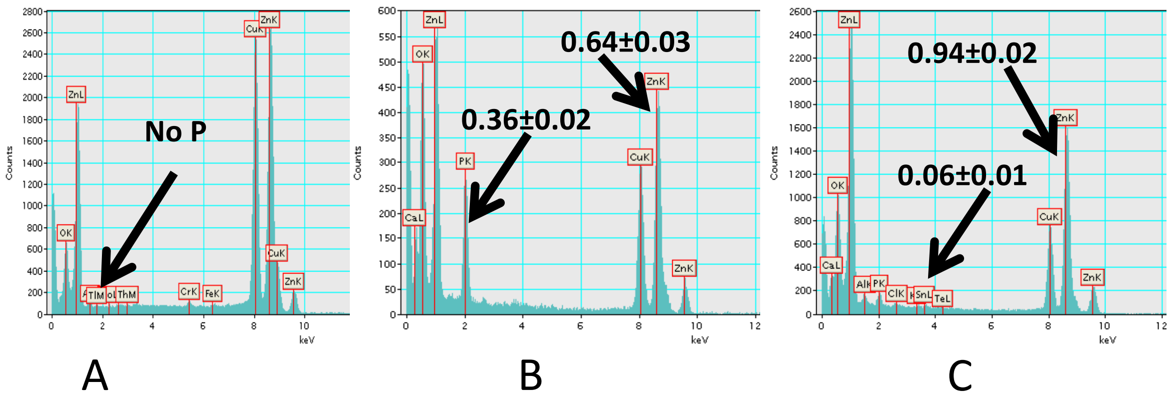


Figure S5 X-ray energy dispersive spectra for pristine material (A) micron sized fraction of aged material (B) and nano sized fraction of aged material (C). The ratios of P and Zn are indicated on the figure.

Additional interpretation of NMR spectra.

The NMR spectra provide additional detail regarding particles aged at pH 8, showing that one reason for the low hopeite formation is that a greater number of other species were formed in competition. Whereas the species with the chemical shift of 8.0 ppm (**Fig 6**) was the only by-product at pH 6, only 47% of the pH 8 material being accounted for by the analogous species (7.8 ppm) with 27% of the pH 8 aged material was accounted for by a third component (5.3 ppm) not evident in particles aged at pH 6. The signals we observe near 4.2 ppm bear qualitative similarlities with that of α-$Zn_3(PO_4)_2$ with respect to both isotropic chemical shift (3.9 ppm) and individual principal values (See **Table S1**). Our T_1s were all considerably shorter than those reported by Roming et al. [36] for α-$Zn_3(PO_4)_2$, likely because our materials include water molecules which place ^{1}H near the phosphate ^{31}P. Indeed Roming et al. [36] report a T_1 of 48 s for 'as-prepared' zinc phosphate, in the range of our values ranging from 33 to 67 s for the signal near 4.2 ppm we assign to hopeite.

Table S1: Isotropic chemical shifts (δ_{iso}) and tensors ($\delta_{11,}$ $\delta_{22,}$ and δ_{33}) , T_1 relaxation times, cross-polarization buildup times (τ_{cp}) and $T_{1H,\rho}$ relaxation times for ZnO MNMs aged at pH 6 and pH 8 and standards.

Species	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	span (ppm)	T_1 (s)	τ_{cp} (ms)	$T_{1H,\rho}$ (ms)
pH 6 B	8.0	46.0 ±.5	-7 ± 4	-15 ± 4	61 ±4	102	1.2	26
pH 6 A	4.3	38.6 ±.3	1.2 ±.4	-27.0 ± .1	66 ± .3	67	.65	5.7
hopeite	4.2	38.8 ± .4	2.5 ± .3	-28.6 ± .1	67.4 ± .6	33	.67	24
pH 8 A	4.5	37.65±.07	1.3 ± .3	-25.5 ± .4	63.2 ± .4	67		
pH 8 B	5.3	33 ± 2	-9 ± 1	-9 ± 2	42 ± 3			
pH 8 D[b]	7.8	39 ± 2	6 ± 2	-21.6 ± .6	60.1 ± .9	71		
$Zn_3(PO_4)_2$	3.9	39.8 ±.2	6.7 ± .7	-34.9 ± .5	74.7 ± .3			
α-$Zn_3(PO_4)_2$ [c]	3.9	37.0	6.4	-31.7	68.7	1948		
β-$Zn_3(PO_4)_2$ [c]	7.6	27.7	3.8	-8.8	36.5	946		

The T_1s of each of the ^{31}P signals were evaluated by varying the delay between scans from 900 s to 4 s in 9 steps and fitting the resulting signal amplitudes to the function $A=M_o(1-e^{-t/T1})$ where 'A' is the signal amplitude obtained using an interscan delay of 't', M_o is the maximum amplitude expected after infinite delay and T_1 is the longitudinal relaxation time.

[a] Data for the particles aged at pH 6 and hopeite were obtained using 100 s delays between direct polarization ^{31}P scans or 20 s between cross-polarized scans and acquisition times of 80 ms. Data for particles aged at pH 8 were obtained similarly except that they employed 200 s delays between direct polarization scans.

[b] pH 8 C: a fourth component is needed to describe the spectrum of material aged at pH 8 in 150 mg L^{-1} phosphate. However due to extensive overlap we do not have a unique description for it at present. A shoulder is seen at 7.1 ppm (**Figure 6**) but simulation of the pH 8 150 mg L^{-1} spectrum with four components yields best agreement when the fourth component included is broad and centered at 10.6 ppm (data not shown).

[c] Our isotropic chemical shifts ranging from 4 - ≈10 ppm and spans smaller than 70 ppm demonstrate that the phosphate is orthophosphate not a polyphosphate, as Roming et al. [30] report isotropic shifts of 3.9 ppm and 7.6 ppm associated with spans of 68.7 ppm and 36.4 ppm for α- and β- $Zn_3(PO_4)_2$, respectively but spans greater than 80 ppm for most of the components of their $Zn_2P_2O_7$ samples 80.7, 84.4, 84.6, 81.2, 99.1 and 69.3 ppm. Similarly, our relatively modest signal spans are most consistent with un-protonated PO_4^{3-} groups, as Rothwell et al. [31] found that for Ca^{2+} salts, HPO_4^{2-} and $H_2PO_4^{-1}$ have broader spans of 123 ppm and 127 ppm for HPO_4^{2-} species and 97 ppm, 125 ppm for $H_2PO_4^-$ species vs. 34 ppm and 33 ppm for PO_4^{3-} species.