The growth of $CaCO_3$ polymorphs in the presence of As(V): The stabilization of vaterite phase. Supplementary Information.

Morales Sánchez-Migallón J.,*[a] Gerding J.,[b] Gómez Barreiro J.,[a] Compaña J.M.,[a] Astilleros J. M.,[c-d] and Fernández-Díaz L. [c-d]

[a.] *Geology Department. Universidad de Salamanca, Salamanca, Spain..*
[b.] *Institute of Applied Economic Geology, Universidad de Concepción, Concepción, Chile.*
[c.] *Mineralogy and Petrology Department, Universidad Complutense, Madrid, Spain.*
[d.] *Instituto de Geociencias (CSIC-UCM), Madrid, Spain*

LOG INPUT USED IN PHREEQC:

SOLUTION 1

```
  temp      25
  pH        10.59
  pe        4
  redox     pe
  units     mol/l
  density   1
  -water    1 # kg
  Ca    0.1
  Cl    0.2
  C(4)  0.1
  Na    0.2
  As(5) 0.0

save solution 1
end
```

SOLUTION 2

```
  temp      25
  pH        9.44
  pe        4
  redox     pe
  units     mol/l
  density   1
  -water    1 # kg
  Ca    0.1
  Cl    0.2
  C(4)  0.1
  Na    0.2
  As(5) 0.000135

save solution 2
end
```

SOLUTION 3

```
  temp      25
  pH        8.91
  pe        4
  redox     pe
  units     mol/l
  density   1
  -water    1 # kg
  Ca    0.1
  Cl    0.2
  C(4)  0.1
  Na    0.2
  As(5) 0.000674

save solution 3
end
```

SOLUTION 4

```
  temp      25
  pH        8.03
  pe        4
  redox     pe
  units     mol/l
  density   1
  -water    1 # kg
  Ca    0.1
  Cl    0.2
  C(4)  0.1
  Na    0.2
  As(5) 0.001348

save solution 4
end
```

Vaterite	**CIF reference**	**CAL-0_4min**	**CAL-0_60min**	**CAL-10_60min**	**CAL-50_60min**	**CAL-100_60min**	**CAL-0_96h**	**CAL-10_96h**	**CAL-50_96h**	**CAL-100_96h**
a (Å)	12.358	12.412(2)	·	·	12.394(4)	12.404(3)	·	12.36(1)	12.384(2)	12.397(2)
b (Å)	7.106	7.134(1)	·	·	7.150(2)	7.153(1)	·	7.170(6)	7.1470(9)	7.1508(10)
c (Å)	25.741	25.759(3)	·	·	25.780(6)	25.804(4)	·	25.74(1)	25.759(3)	25.791(3)
alpha (˚)	90.43	90.31(2)	·	·	90.04(2)	89.92(1)	·	90.28(8)	90.119(9)	89.952(8)
beta (˚)	99.88	99.47(2)	·	·	99.56(1)	99.547(8)	·	99.3(1)	99.34(2)	99.576(4)
gamma (˚)	90.29	89.79(2)	·	·	90.12(3)	90.28(1)	·	90.2(1)	89.96(1)	90.282(5)
Volume ($Å^3$)	2226.84	2249.7(7)	·	·	2253.(1)	2257.7(8)	·	2251.(3)	2249.6(5)	2254.5(5)
D (Å)	·	700.(1)	·	·	338.(3)	321.(2)	·	1000.(2)	650.(1)	472.(3)
$\boldsymbol{\varepsilon}_{rms}$	·	0.00239(8)	·	·	0.0025(2)	0.0009(4)	·	0.0014(6)	0.0070(1)	0.00001(9)
Calcite	**CIF reference**	**CAL-0_4min**	**CAL-0_60min**	**CAL-10_60min**	**CAL-50_60min**	**CAL-100_60min**	**CAL-0_96h**	**CAL-10_96h**	**CAL-50_96h**	**CAL-100_96h**
a (Å)	4.987429	4.9902(4)	4.99078(9)	4.9899(1)	4.997(2)	4.994(3)	4.99128(2)	4.99180(2)	4.9911(4)	4.9977(7)
b (Å)	4.987429	4.9902(4)	4.99078(9)	4.9899(1)	4.997(2)	4.994(3)	4.99128(2)	4.99180(2)	4.9911(4)	4.9977(7)
c (Å)	17.05058	17.066(1)	17.0623(3)	17.0611(3)	17.076(7)	17.05(1)	17.0670(1)	17.0674(1)	17.066(1)	17.085(2)
alpha (˚)	90	90	90	90	90	90	90	90	90	90
beta (˚)	90	90	90	90	90	90	90	90	90	90
gamma (˚)	120	120	120	120	120	120	120	120	120	120
Volume ($Å^3$)	367.3	368.04(5)	368.05(1)	367.90(1)	369.3(3)	368.4(4)	368.225(3)	368.309(4)	368.17(5)	369.56(9)
D (Å)	·	3500.(1)	3690.(3)	4720.(7)	1100.(2)	1000.(4)	7600.(3)	16100.(4)	4400.(3)	11000.(3)
$\boldsymbol{\varepsilon}_{rms}$	·	0.00036(2)	0.000491(5)	0.000480(9)	0.0009(8)	0.0033(6)	0.00041(1)	0.00026(1)	0.00029(5)	0.00048(7)
Rietveld Indices		**CAL-0_4min**	**CAL-0_60min**	**CAL-10_60min**	**CAL-50_60min**	**CAL-100_60min**	**CAL-0_96h**	**CAL-10_96h**	**CAL-50_96h**	**CAL-100_96h**
GoF	·	1.1240494	1.9665729	2.2889085	2.421333	2.0498736	4.3208013	4.9308133	2.5961816	2.5339851
Rwp(%)	·	13.319871	7.8208976	9.197079	9.496611	7.625557	16.037338	17.74928	9.111792	8.895791
Rexp (%)	·	11.849897	3.9769173	4.0181065	3.922059	3.7200131	3.7116585	3.599666	3.5096896	3.5105932
Rietveld Weight Fraction (%)										
Vaterite	·	69.7(2)	·	·	98.1(3)	99.3(2)	·	8.6(2)	88.4(1)	97.4(2)
Calcite	·	30.3(7)	100	100	1.9(1)	0.68(9)	99.1(6)	91.3(6)	11.4(2)	2.6(5)
Halite	·	·	·	·	·	·	0.9(2)	0.1(7)	0.2(3)	0

Table S1. Rietveld refinement data from vaterite and calcite phases. CIF Reference selected for vaterite was 9017413 (Demichelis et al., 2013), for calcite was 4502441 (Zolotoyabko et al., 2010), and for halite was 9003308 (Walker et al., 2004). D (Å): Crystallite size; rms : root mean square microstrain; GoF: goodness of fit; Rwp: weighted profile residual; Rexp: expected R-factor. For crystallite size calculations, the Popa model was used with Isotropic parameters.

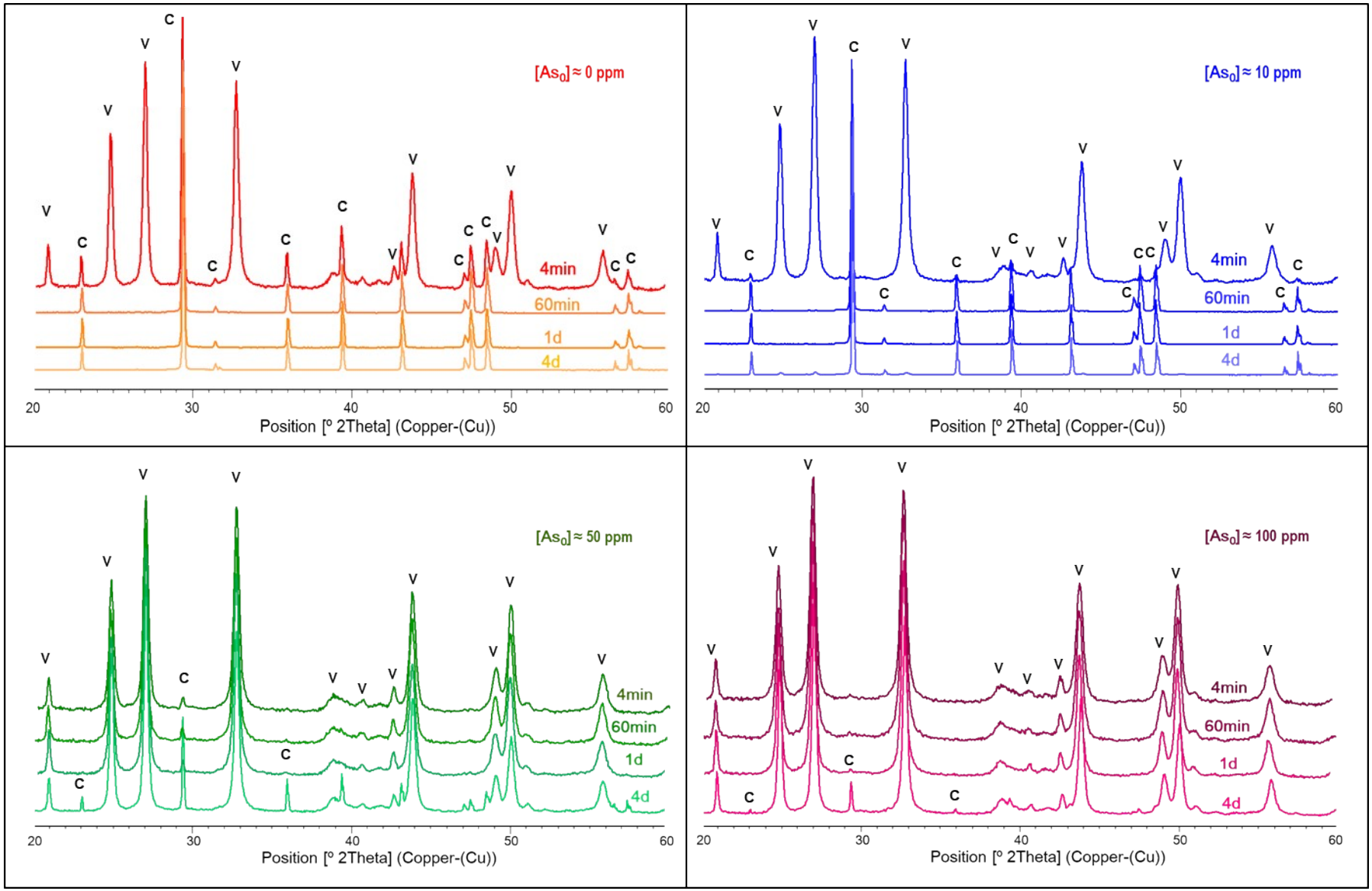

Figure S1. XRD patterns showing the evolution of each experiment

t (min)	As 0	Std.dev	As 10	Std.dev	As 50	Std.dev	As 100	Std.dev
0	10.6	0.8	9.4	1.0	9.0	1.0	8.0	0.7
4	10.0	0.8	8.9	1.0	7.6	0.8	7.3	0.6
60	9.6	0.6	8.2	0.7	7.1	0.9	6.9	0.4
1440	9.3	1.1	9.1	1.3	8.5	0.8	8.3	1.0
5760	9.2	1.3	9.2	1.2	8.6	0.5	8.5	0.9

Table S2. Mean values of pH measured for each experimental time.

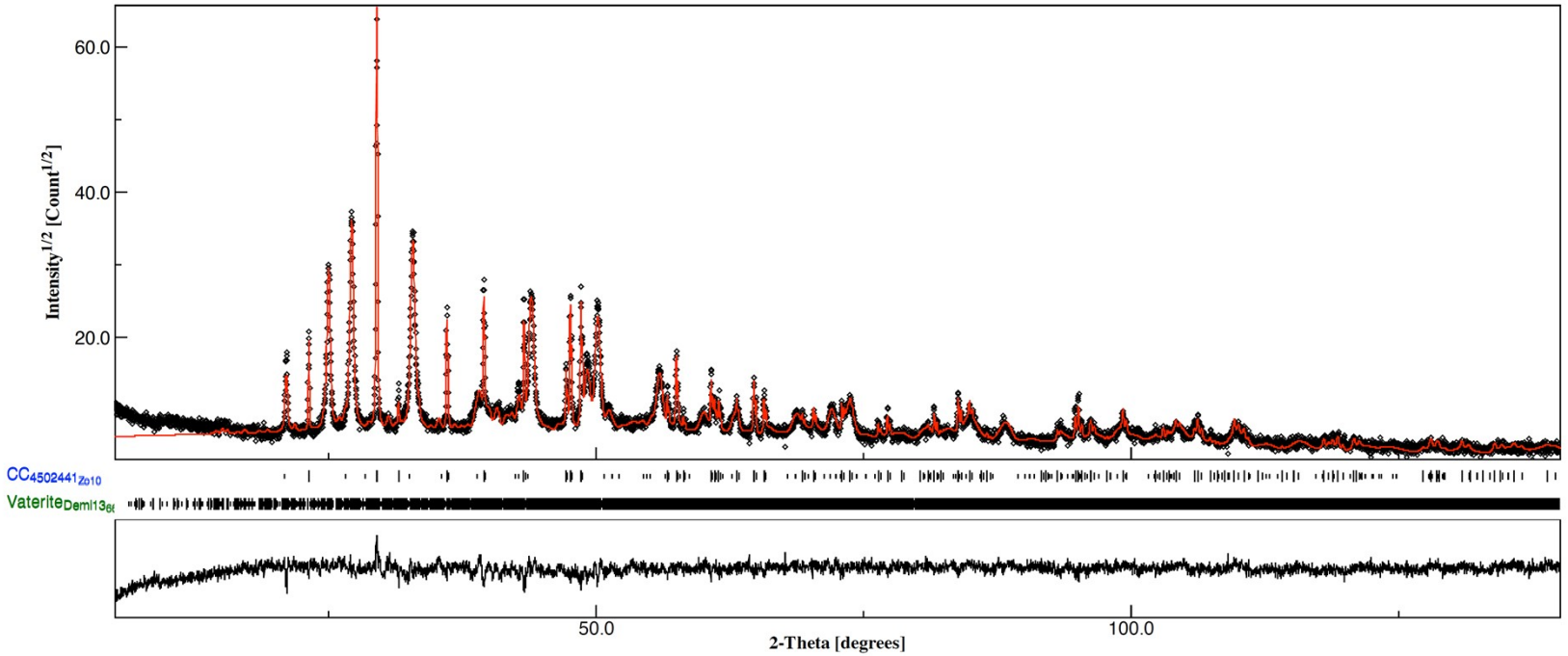

Figure S2. Rietveld refinement of sample Cal-0 (in absence of arsenic) after 4 minutes ageing.

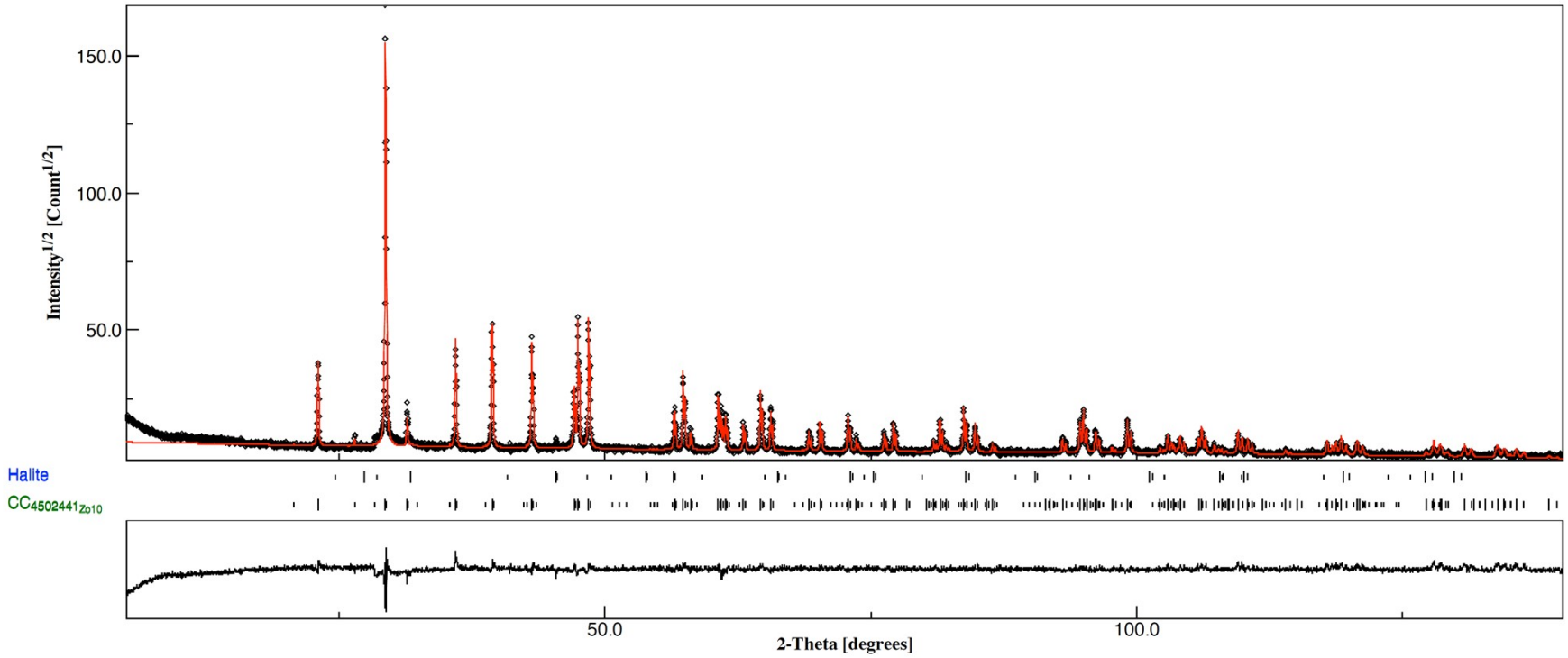

Figure S3. Rietveld refinement of sample Cal-0 (in absence of arsenic) after 24 hours ageing.

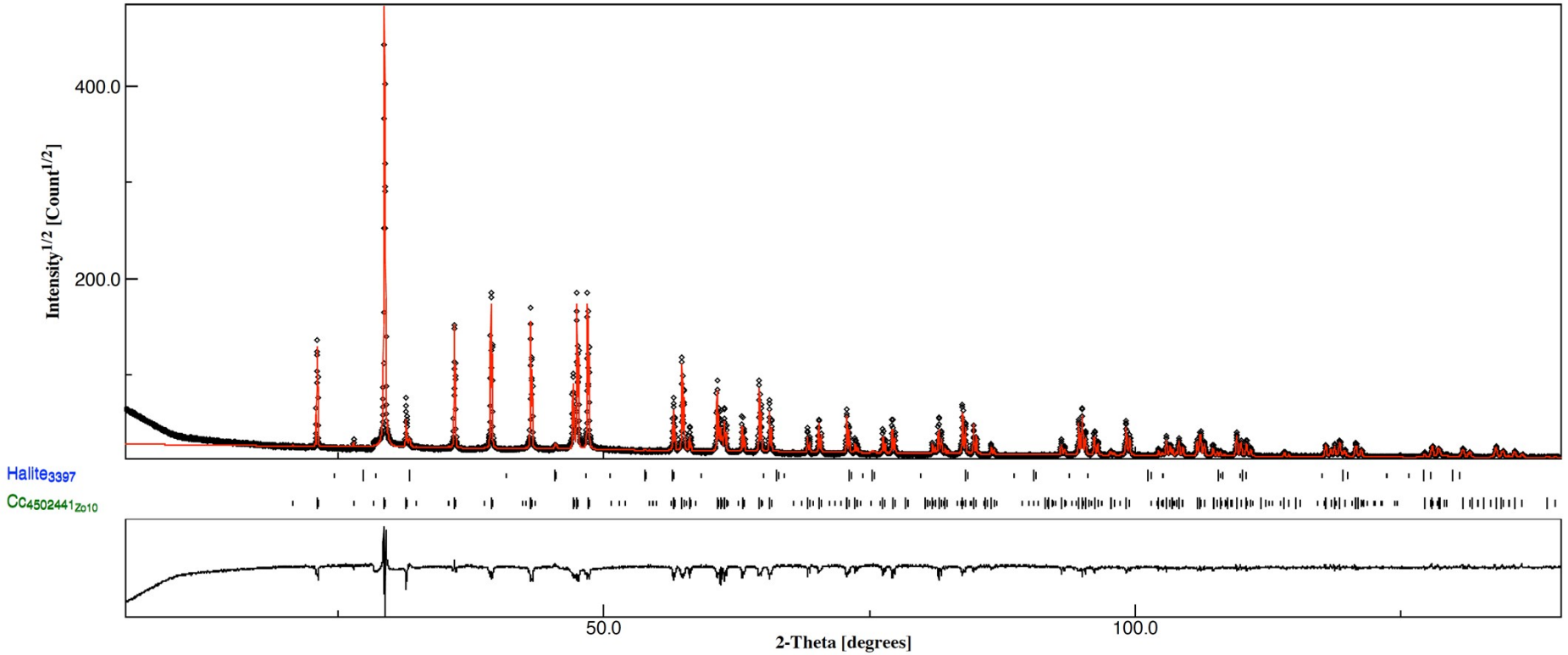

Figure S4. Rietveld refinement of sample Cal-0 (in absence of arsenic) after 96 hours ageing.

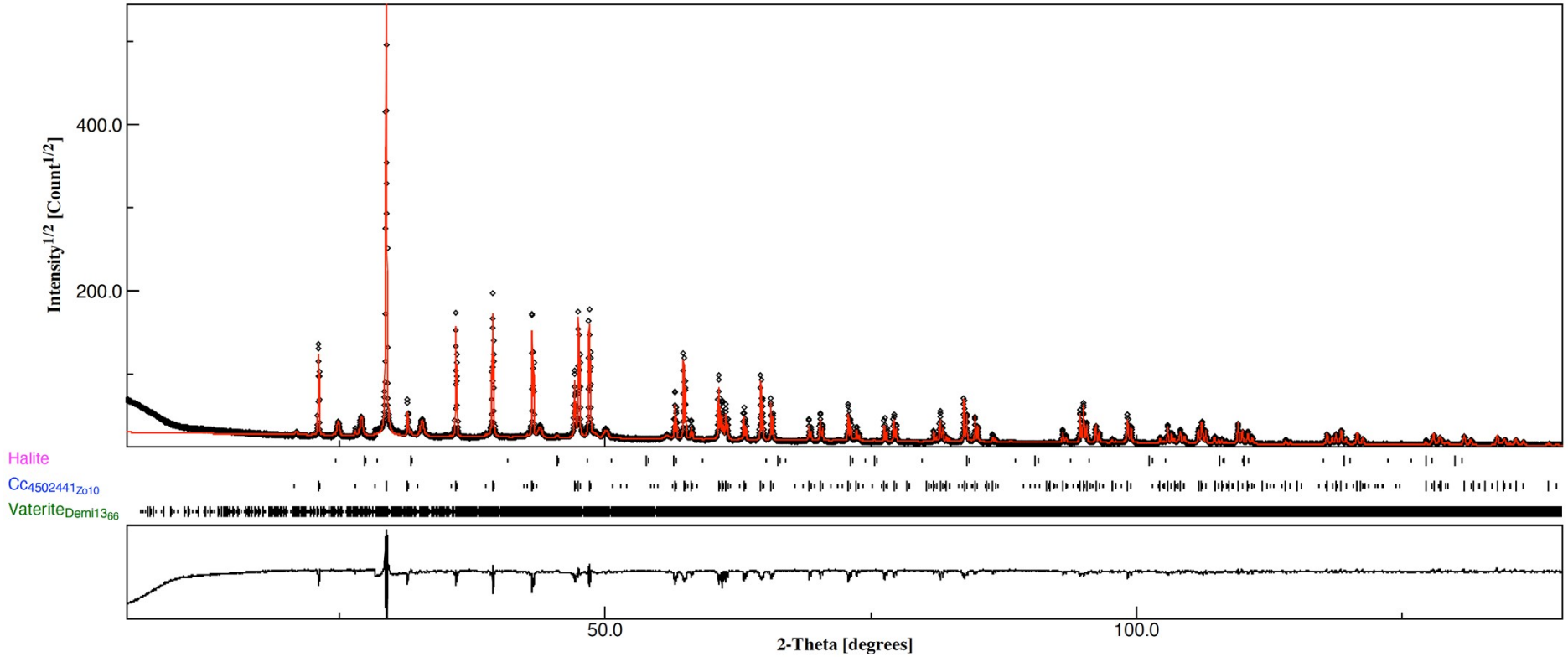

Figure S5. Rietveld refinement of sample Cal-10 (10 ppm of aqueous arsenic as initial concentration) after 96 hours ageing.

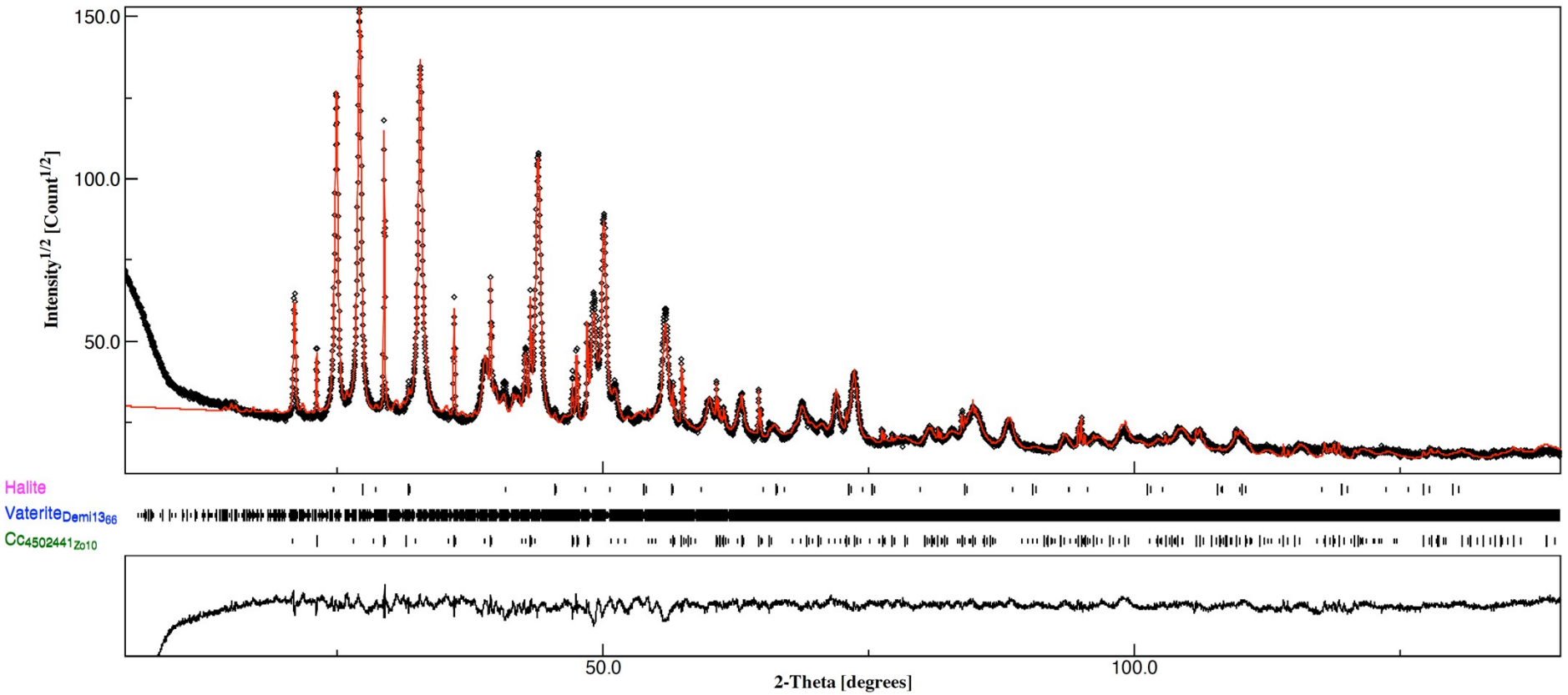

Figure S6. Rietveld refinement of sample Cal-50 (50 ppm of aqueous arsenic as initial concentration) after 96 hours ageing.

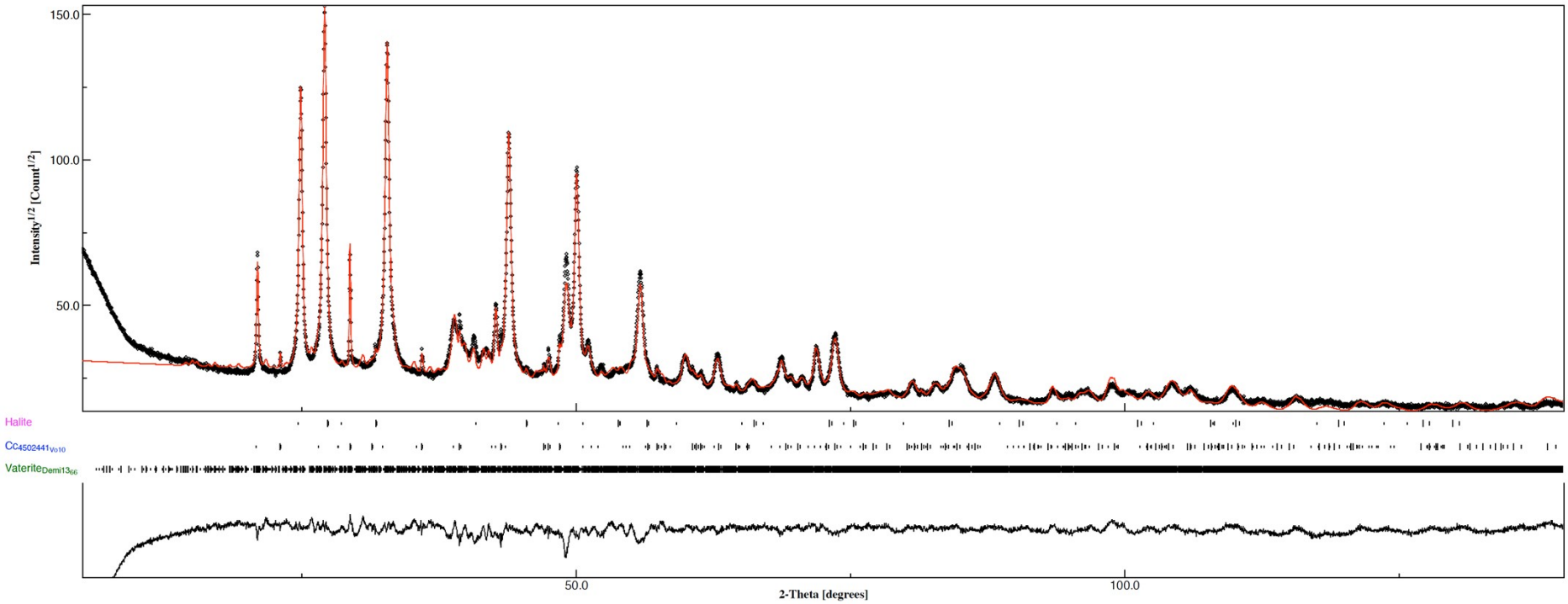

Figure S7. Rietveld refinement of sample Cal-100 (100 ppm of aqueous arsenic as initial concentration) after 96 hours ageing.

References:

1. R. Demichelis, P. Raiteri, J D. Gale & R. Dovesi, *Crystal Growth & Design*, 2013, **13(6)**, 2247-2251. https://doi.org/10.1021/cg4002972
2. E. Zolotoyabko, E.N. Caspi, J.S. Fieramosca, R.B. Von Dreele, F. Marin, G. Mor, L. Addadi, S. Weiner, Y. Politi, *Crystal Growth & Design*, 2010, **10,** 1207. https://doi.org/10.1021/cg901195t
3. D. Walker, P. K. Verma, L. M. Cranswick, R.L. Jones, S.M. Clark & S. Buhre *American Mineralogist*, 2004, **89(1)**, 204-210. https://doi.org/10.2138/am-2004-0124