

1 *Supporting information*

2 Coprecipitation of  $^{14}\text{C}$  and Sr with carbonate  
3 precipitates: The importance of  
4 recrystallization pathways

5  
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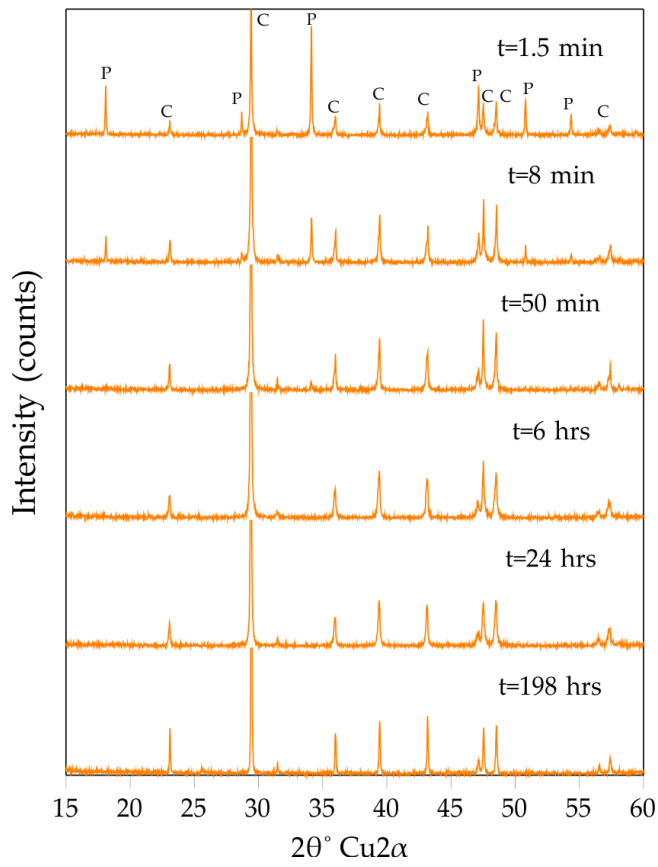
11 \*National Nuclear Laboratory, Sellafield, Cumbria

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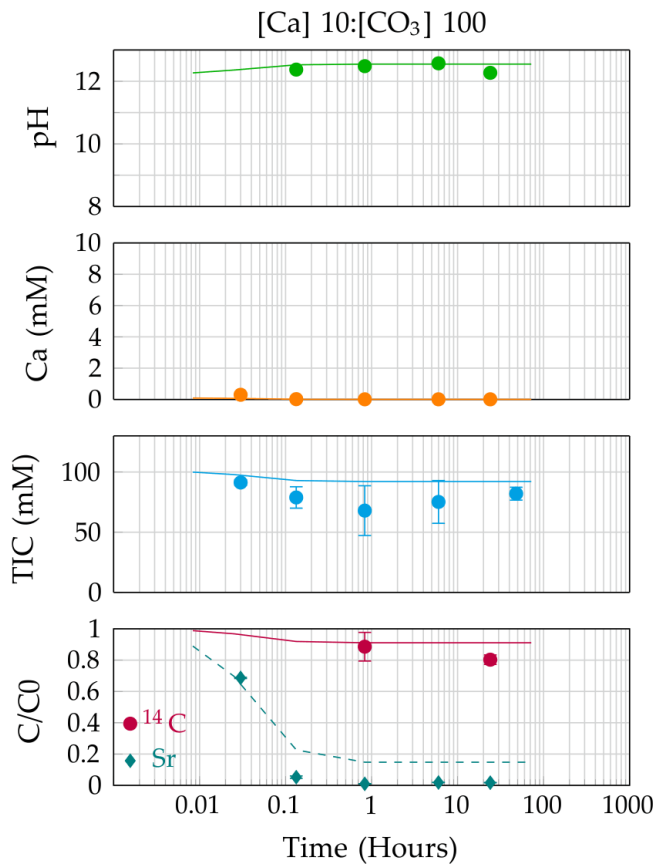
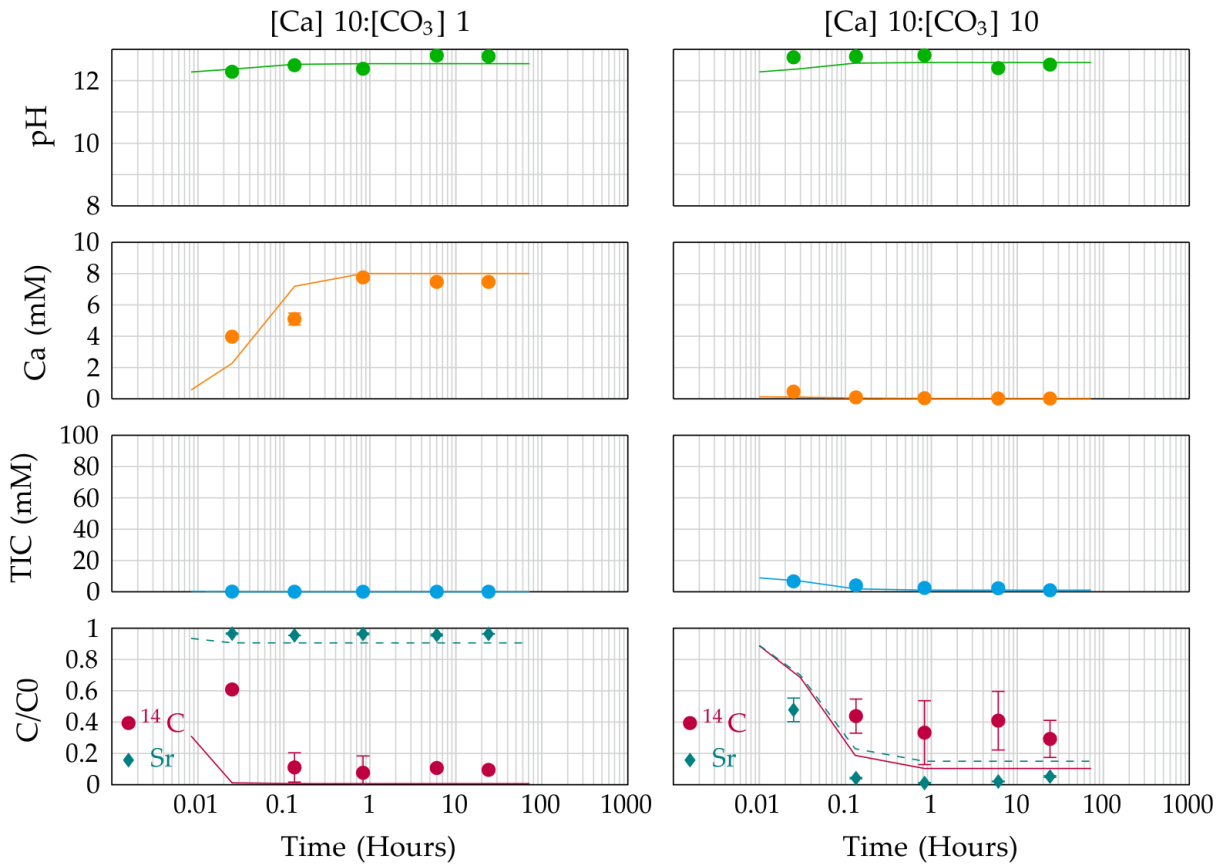
15 **S.I. Section 1: XRD data traces**



16

17 *Figure S1 Stacked XRD traces displaying key mineral phases throughout the [Ca]10:[CO3]1 experiment (C=Calcite,*  
18 *P=Portlandite)*

19 **S.I. Section 2: Complete closed system data**



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21 *Figure S2 Data from the closed system experiment series potted alongside model data computed in PHREEQC*

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24 **S.I. Section 3: Data tables**

25 *Table S1 Combined data from the [Ca]10:[CO3]1 experiment*

t (Hrs)	pH	Ca (mM)	Na (mM)	Sr (ppm)	Sr (mM)	Activity (Bq)	14C C/C0	Sr C/C0	TIC (mM)
0.0083		4.14	10.82	9.64	0.01	78.33	0.78	0.96	0.41
0.025	12.21	4.79	10.87	9.47	0.01	39.43	0.39	0.95	0.24
0.13	12.22	5.86	10.91	9.40	0.01	12.04	0.12	0.94	0.28
0.83	12.25	6.87	10.97	9.37	0.01	0.27	0.00	0.94	0.20
6	12.21	5.57	11.05	9.33	0.01	8.13	0.08	0.93	0.28
24	11.98	1.17	10.98	8.55	0.01	8.69	0.09	0.85	0.39
48	11.52	0.01	11.09	0.14	0.00	41.63	0.42	0.01	4.48
72	9.71	0.01	11.13	0.15	0.00	46.00	0.46	0.01	9.19
198	8.99	0.02	11.72	0.36	0.00	18.00	0.18	0.04	11.78

26

27

28 *Table S2 Combined data from the [Ca]10:[CO3]5 experiment*

t (Hrs)	pH	Ca (mM)	Na (mM)	Sr (ppm)	Sr (mM)	Activity (Bq)	14C C/C0	Sr C/C0	TIC (mM)
0.0083		1.41	19.82	9.58	0.01	88.15	0.88	0.96	3.84
0.025	12.09	1.09	19.62	4.47	0.01	41.69	0.42	0.45	1.25
0.13	12.19	1.72	19.92	2.81	0.00	9.70	0.10	0.28	0.31
0.83	12.27	3.14	19.58	2.78	0.00	10.48	0.79	0.28	0.20
6	12.20	1.74	19.60	2.73	0.00	10.20	0.41	0.27	0.23
24	11.93	0.02	19.88	0.62	0.00	14.39	0.14	0.06	2.97
48	11.40	0.01	20.25	0.26	0.00	34.71	0.35	0.03	8.41
72	10.07	0.01	20.13	0.27	0.00	43.13	1.39	0.03	14.18
198	9.24	0.02	21.61	0.52	0.00	29.10	0.29	0.05	19.99

29

30 *Table S3 Combined data from the [Ca]10:[CO3]10 experiment*

t (Hrs)	pH	2σ	Ca (mM)	2σ	Na (mM)	2σ	Sr (ppm)	2σ	Sr (mM)	Activity (Bq)	2σ	<sup>14</sup> C C/C0	2σ	Sr C/C0	2σ	TIC (mM)	2σ
0.0083			1.15	0.24	36.21	11.90	7.99	2.18	0.01	87.07	11.40	0.87	0.09	0.80	0.20	7.89	2.64
0.025	12.20	0.14	0.44	0.45	35.96	11.90	2.35	2.53	0.00	63.53	10.72	0.64	0.09	0.24	0.25	6.99	4.21
0.13	12.20	0.06	0.08	0.02	33.31	9.50	0.35	0.38	0.00	38.45	13.15	0.38	0.11	0.03	0.04	4.78	0.46
0.83	12.21	0.07	0.03	0.01	33.24	9.24	0.17	0.16	0.00	32.94	6.11	0.33	0.05	0.02	0.02	3.88	0.72
6	12.16	0.07	0.02	0.01	33.34	9.49	0.26	0.02	0.00	33.62	4.96	0.34	0.04	0.03	0.00	4.98	0.33
24	12.04	0.17	0.01	0.00	33.95	9.88	0.28	0.08	0.00	35.41	15.71	0.35	0.13	0.03	0.01	9.29	1.04
48	11.73	0.16	0.01	0.02	32.83	52.96	0.26	0.40	0.00	46.34	14.19	0.46	0.12	0.03	0.04	13.83	4.57
72	10.91	0.33	0.01	0.00	35.05	10.89	0.22	0.05	0.00	45.16	16.18	0.45	0.13	0.02	0.00	19.81	1.79
198	9.37	0.09	0.03	0.03	35.71	10.06	0.29	0.06	0.00	45.83	13.89	0.46	0.12	0.03	0.01	24.39	9.05

31

32

33 *Table S4 Combined data from the [Ca]10:[CO3]100 experiment*

t (Hrs)	pH	2σ	Ca (mM)	2σ	Na (mM)	2σ	Sr (ppm)	2σ	Sr (mM)	Activity (Bq)	2σ	<sup>14</sup> C C/C0	2σ	Sr C/C0	2σ	TIC (mM)	2σ
0.0083			1.06	0.21	182.88	22.23	9.09	1.11	0.01	98.76	8.34	0.99	0.07	0.91	0.09	87.04	3.79
0.025	12.07	0.07	0.79	0.04	184.05	14.86	3.56	0.30	0.00	90.49	2.90	0.90	0.02	0.36	0.02	88.17	0.26
0.13	12.12	0.03	0.04	0.01	184.52	18.05	0.45	0.06	0.00	84.13	3.56	0.84	0.03	0.04	0.01	85.41	1.85
0.83	12.12	0.04	0.02	0.00	185.77	8.25	0.23	0.01	0.00	86.92	11.91	0.87	0.10	0.02	0.00	83.11	3.12
6	12.03	0.08	0.02	0.00	183.93	14.00	0.24	0.01	0.00	91.73	6.38	0.92	0.05	0.02	0.00	81.83	6.38
24	11.92	0.06	0.01	0.00	181.42	12.31	0.19	0.01	0.00	90.14	5.56	0.90	0.05	0.02	0.00	89.25	3.71
48	11.50	0.03	0.01	0.00	186.11	12.71	0.19	0.01	0.00	87.93	7.44	0.88	0.06	0.02	0.00	96.53	6.48
72	10.85	0.03	0.01	0.00	185.80	12.62	0.18	0.01	0.00	85.16	1.93	0.85	0.02	0.02	0.00	102.30	4.57
198	10.08	0.12	0.01	0.00	193.12	14.29	0.20	0.02	0.00	94.92	0.77	0.95	0.01	0.02	0.00	120.03	2.44

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38 **S.I. Section 4: Full text PHREEQC input script**

```
39 # -----Nancollas and Reddy Calcite rate block-----
40 RATES
41 Calcite
42 -start
43   10 si_cc = si("Calcite")
44   20 if (m <= 0 and si_cc < 0) then goto 200
45   30 rate = 0.576 * 118.2 * 5.4 * (3.6e-9 - act("Ca+2") * act("CO3-2"))
46   80 moles = rate * time
47   140 if (moles > m) then moles = m
48   150 if (moles >= 0) then goto 200
49   160 temp = tot("Ca")
50   170 mc = tot("C(4)")
51   180 if mc < temp then temp = mc
52   190 if -moles > temp then moles = -temp
53   200 save moles
54 -end
55 # -----Johannsen 1999 Ca(OH)2 rate block-----
56 Ca(OH)2
57 -start
58   1 si_caoh = si("Ca(OH)2")
59   20 if (m <= 0 and si_caoh < 0) then goto 200
60   30 SA = 4.5 * m/m0
61   100 rate = 2.1 * SA * (4.76e-6 - act("Ca+2") * act("OH-")^2)
62   110 moles = rate * time
63   200 SAVE moles
64 -end
65 # -----Empirical Linear CO2 in-gassing-----
66 CO2(g)
67 -start
68   1 si_co2 = si("CO2(g)")
69   2 PCO2 = 7.2e-5 #1/6 atm
70   3 CO2eq = PCO2 * 0.032
71   4 SA = 56 #cm2
72   20 if (m <= 0 and si_co2 < -3.4) then goto 200
73   25 rate = 5.4e-4 * CO2eq - 5.4e-4 * (MOL("H2CO3")/10)
74   26 rate = rate * SA
75   30 moles = rate * TIME
76   200 SAVE moles
77 -end
78 INCREMENTAL_REACTIONS TRUE
79 #SOLID_SOLUTIONS 1
80 #CaSrCO3
81 # -comp Calcite 0 #1
82 # -comp strontianite 0 #0.00107
83 # -distribution_coefficients 0.057 0.057 0.015 0.0
84 #-----Starting solution 100ml 0.01M NaOH, 1ppm SrCl2 & 1mmol
85 Na2CO3 -----
86 solution 1 # pure water
87 temp 20.0
88 pH 12.2
89 water 1 kg
90 units mmol/L
91 Na 3 charge
92 C(4) 1
93 Sr 0.114
94 Cl 0.228
95
96 KINETICS
97 CO2(g)
```

```

98          -m0 1
99 Ca(OH)2
100          -m0 0.00918
101 Calcite
102          -m0 0
103          -parms 50 0.6
104 -cvode TRUE
105 #-steps 259200 in 432 steps
106 #-steps 3000 in 100 steps
107 #-steps 0.5 1.5 8 50 360 1440 2880 4320 minutes
108 -steps 0.5 1 6.5 42 310 1080 1440 1440 7680 minutes
109 SELECTED_OUTPUT
110 -file Complete Solution.xls
111 -reset false
112 USER_PUNCH
113     -headings t pH Ca(mmol) Na(mmol) TIC SrC/C0 nCalcite 14C/C0
114     -start
115 10 PUNCH total_time/60/60
116 20 PUNCH -LA("H+")
117 30 PUNCH TOT("Ca")*1000
118 40 PUNCH TOT("Na")*1000
119 50 PUNCH TOT("C(4)")*1000
120 60 PUNCH 1-((KIN("Calcite")*1000)*0.00108/0.0114)
121 70 PUNCH KIN("Calcite")
122 80 PUNCH act("CO2")*1000
123 -end
124 USER_GRAPH 1
125 -axis_scale x_axis 0.001 auto auto auto logscale
126 -axis_scale y_axis auto
127 -axis_titles "time (h)" "[Ca] (mmol)"
128 -initial_solutions false
129 -connect_simulations true
130 -start
131 10 GRAPH_X total_time/3600
132 20 GRAPH_Y TOT("Ca")*1000
133 USER_GRAPH 2
134 -axis_scale x_axis 0.001 auto auto auto logscale
135 -axis_scale y_axis auto
136 -axis_titles "time (h)" "pH"
137 -initial_solutions false
138 -connect_simulations true
139 -start
140 10 GRAPH_X total_time/3600
141 20 GRAPH_Y -LA("H+")
142 END
143

```



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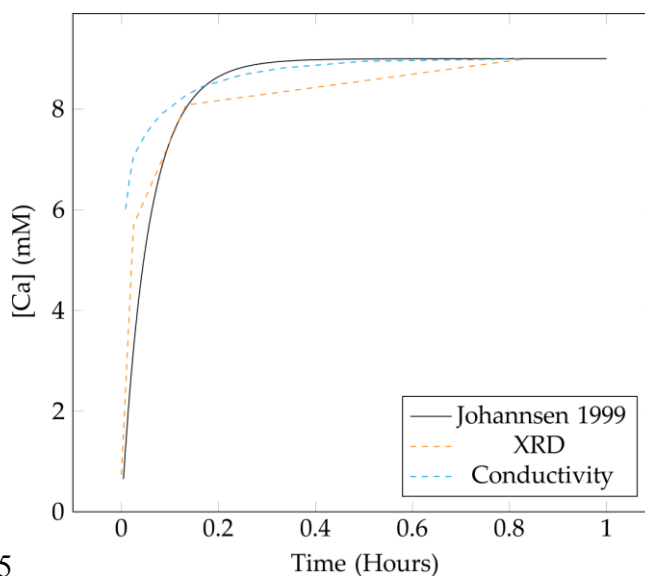
145 ***S.I. Section 5: Ca(OH)<sub>2</sub> dissolution rate***

146 Surface area of the Ca(OH)<sub>2</sub> starting material was calculated from triplicate BET analyses using a  
147 Micromeritics Gemini VII 2390a instrument. A sample size of 0.479 g was used and dried  
148 overnight at a temperature of 105°C while being flushed with nitrogen gas. The sample was then  
149 re-weighed to account for any moisture loss. A dead-space volume measurement was taken using  
150 helium which was then removed via vacuum and triplicate measurements were taken, using  
151 nitrogen as an absorbent at -196 °C. Results are presented in Table S1.

152 *Table S5 BET analysis of the Ca(OH)<sub>2</sub> starting material*

	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	BET Constant (C)	r <sup>2</sup>
a	4.2236 ± 0.043	274.1	0.9996
b	4.1449 ± 0.041	211.9	0.9996
c	4.1594 ± 0.043	254.2	0.9996
Average	4.176 ± 0.068	246.73	0.9996

153 In the paper the dissolution rate of calcium hydroxide was modelled using a formula from  
154 Johannsen and Rademacher<sup>1</sup>. The output from this model was compared to XRD data obtained  
155 for the % calcite in the solid phase, converted to [Ca] by multiplying the % by the expected final  
156 concentration/100. As well as conductivity data obtained from dissolving 10 mmol of Ca(OH)<sub>2</sub> in  
157 100ml of 0.01M NaOH. The conductivity data was converted to % dissolved by dividing by the  
158 stable conductivity achieved after 30 minutes and multiplying by 100. This was then converted  
159 to [Ca] by multiplying by the expected final concentration/100.



160

5

161 *Figure S3 Comparison of published  $\text{Ca}(\text{OH})_2$  dissolution rate to experimental data. XRD data obtained through Rietveld*  
 162 *refinement on powders generated during the experimental series, and conductivity data obtained during separate*  
 163 *triplicate experiments.*

164 **S.I. Section 6: Calcite Surface area**

165 The surface area of neo-formed calcite could not be derived from BET analysis due to low  
 166 precipitate yields as well as the presence of  $\text{Ca}(\text{OH})_2$  alongside the early formed precipitate.

167 Surface areas were instead calculated from the average crystal dimensions from SEM images  
 168 using an assumed calcite density of  $2.7 \text{ g cm}^{-3}$  and assuming a cubic shape for rhombic crystals  
 169 and a cylindrical shape for prismatic crystals. The rhombic crystals yielded a surface area of  $5.37$   
 170  $\text{m}^2 \text{ g}^{-1}$  while the prismatic crystals displayed a significantly larger surface area of  $76.19 \text{ m}^2 \text{ g}^{-1}$ . If  
 171 it assumed that by the end of testing  $10 \text{ mmol}$  of  $\text{Ca}$  forms  $\text{CaCO}_3$  (formula weight  $100 \text{ g mol}^{-1}$ )  
 172 then the rhombic end-point population would have an expected surface area of:

173 
$$SA = 5.37 \cdot (0.01 \cdot 100) = 5.37 \text{ m}^2 \text{ L}^{-1} \quad (\text{S } 1)$$

174 The initial rhombic calcite has a larger specific surface area but smaller mass so the overall  
 175 surface area is minimal (the initial concentration of seed crystals in the  $\text{Ca}(\text{OH})_2$  was calculated  
 176 at  $8.16\%$  of the  $1 \text{ mmol Ca}(\text{OH})_2$ ):

177 
$$SA = 76.19 \cdot (0.01 \cdot 100) \cdot 0.0816 = 6.2 \text{ m}^2 \text{ L}^{-1} \quad (\text{S } 3)$$

178 *Table S6 Surface area and crystal sizes taken from literature values and SEM images*

Source	Crystal Length ( $\mu\text{m}$ )	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Morphology
2	4-20	0.7	Rhombic
3	<0.5	14-17	Nano-Rhombic
4	10	0.3	Prismatic
5	0.7	8.63	Prismatic
This study	0.41	5.2	Rhombic
This study	0.5	76	Prismatic

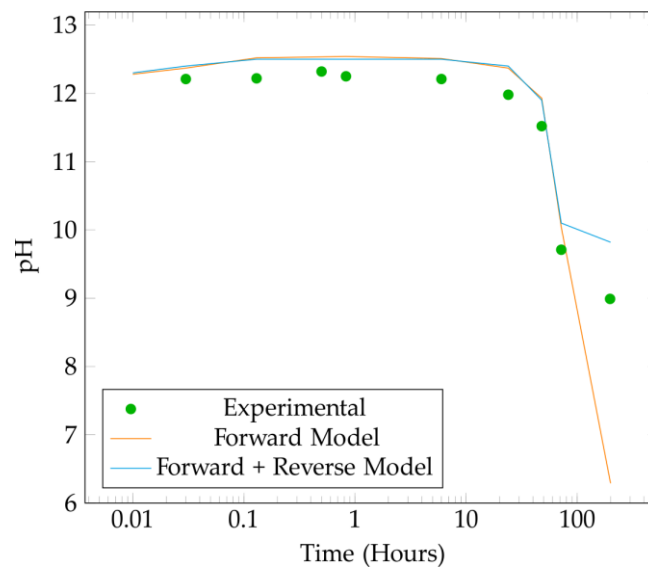
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180 ***S.I. Section 7: CO<sub>2</sub> dissolution***

181 CO<sub>2</sub> dissolution was determined to be the rate limiting step on the availability of TIC in solution  
 182 (Modelling Section). This process was modelled using a modified version of equation (S. 5) from  
 183 Noyes et al<sup>6</sup>. The forward component of this rate was adjusted to account for depletion of CO<sub>2</sub> in  
 184 the headspace of the reaction vessel. A P<sub>CO<sub>2</sub></sub> of 1/6 atm ( $7.2 \times 10^{-6}$ ) was used which agrees with  
 185 empirical observations of the in-gassing rate. The reverse component of (S. 5) only becomes  
 186 significant when appreciable CO<sub>2(aq)</sub> has accumulated in solution. Due to limitations in modelling  
 187 this component in PHREEQC this has been omitted from the model and the model was terminated  
 188 prior the accumulation of CO<sub>2(aq)</sub>. Thus (S. 5) can be rearranged to (S. 6) where [CO<sub>2(aq)</sub>]<sup>equilibrium</sup> is  
 189 adjusted to that expected to be in equilibrium with 1/6 atmospheric CO<sub>2(g)</sub>.

190  $J_{\text{CO}_2} = k_{\text{tr}} \cdot ([\text{CO}_{2(\text{aq})}]^{\text{equilibrium}} - [\text{CO}_{2(\text{aq})}])$  (S. 5)

191  $J_{\text{CO}_2} = k_{\text{tr}} \cdot [\text{CO}_{2(\text{aq})}]^{\text{equilibrium}} = 1.24 \times 10^{-9}$  (S. 6)



192

193 *Figure S4 Experimental CO<sub>2</sub> data from the [Ca]10:[CO<sub>3</sub>]1 experiment plotted against 3 model curves*

194 Figure 4 displays the effect of changing the reverse component on the final pH. The “Forward  
 195 Model” (run without a reverse component) over predicts the drop in pH caused by CO<sub>2</sub> in-gassing.  
 196 When the reverse component was included (“Forward + Reverse Model”) the predicted pH drop  
 197 was reduced and close to the experimental data. This was a slight overestimation however due to  
 198 the use of [H<sub>2</sub>CO<sub>3</sub>] in the model rather than [CO<sub>2</sub>(aq)] (PHREEQC does not contain a term for  
 199 [CO<sub>2</sub>(aq)]). The “Adjusted model” was run with 0.1x[H<sub>2</sub>CO<sub>3</sub>], this accounted for the under  
 200 prediction in the Model.

201 ***S.I. Section 8: Sr distribution coefficients***

$$D_{sr} = \frac{[Sr]/[Ca]_{ppt}}{[Sr]/[Ca]_{sol}}$$

204 *Table S7 Average strontium distribution coefficients for each triplicate series*

Experiment	Ca <sub>ppt</sub>	Ca <sub>sol</sub>	Sr <sub>ppt</sub>	Sr <sub>sol</sub>	D <sub>sr</sub>
10_1	9.980	0.020	0.011	4.15×10 <sup>-4</sup>	0.0508
10_5	9.984	0.016	0.011	5.93×10 <sup>-4</sup>	0.0287
10_10	9.912	0.034	0.011	3.28×10 <sup>-4</sup>	0.1120
10_100	9.988	0.012	0.011	2.25×10 <sup>-4</sup>	0.0606
Average	9.966	0.020	0.011	3.90×10 <sup>-4</sup>	0.0566

205  
 206

207 **S.I. Section 9: Sellafield groundwater composition**

208 *Table S8 Concentration of selected Sellafield groundwater ions and the range of reported <sup>14</sup>C and <sup>90</sup>Sr*  
 209 *activities.<sup>7</sup>*

GW species	Concentration
pH	7
Ca	0.96 mM
HCO <sub>3</sub>	1.23 mM
Mg	0.19 mM
K	0.18 mM
Na	1.12 mM
Cl	1.40 mM
SO <sub>4</sub>	0.21 mM
Sr	1.40 μM
<sup>14</sup> C	1-50 KBq L <sup>-1</sup>
<sup>90</sup> Sr	0.1-44 KBq L <sup>-1</sup>

210 **S.I. Section 10: Costing information for reagents**

211 Only Ca(OH)<sub>2</sub> will be required to run the proposed treatment scheme. TIC content in the  
 212 groundwater is sufficient and the addition of 840.3 g of Ca(OH)<sub>2</sub> per m<sup>3</sup> to achieve a 10:1 Ca:CO<sub>3</sub>  
 213 molar ratio would yield an approximate pH of 11.6 which would be sufficient to minimize de-  
 214 gassing of <sup>14</sup>C. The amount of Ca(OH)<sub>2</sub> costed would be sufficient to produce a Ca:CO<sub>3</sub> molar ratio  
 215 of 10:1

216 *Table S9 Costing information for the proposed treatment scheme. Prices quoted from Singleton Birch 01652*  
 217 *686000 (19/11/2015)*

Reagent	Amount require per m <sup>3</sup>	Cost per ton of reagent	Cost per m <sup>3</sup> of groundwater
Ca(OH) <sub>2</sub>	840.3 g	\$260	\$0.22

218

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221

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