1 **Supporting Information for:**

2 **Mechanisms of inorganic carbon-14 attenuation in contaminated**

3 **groundwater: Effect of solution pH on isotopic exchange and carbonate**

4 **precipitation reactions.**

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13 **This consists of four sections.**

14   **Section 1.0 Figures and tables**

15   **Table S1** Input solution compositions for PHREEQC precipitation modelling

| Predicted Saturation Index	PHREEQC input
+2.92	Temp 20; pH 9; 0.03 M Na_2CO_3 equilibrated with atmospheric $CO_2(g)$, 0.02 M $CaCl_2$
+2.51	Temp 20; pH 9; 0.015 M Na_2CO_3 equilibrated with atmospheric $CO_2(g)$, 0.015 M $CaCl_2$
+2.12	Temp 20; pH 9; 0.0075 M Na_2CO_3, 0.005 M NaOH equilibrated with atmospheric $CO_2(g)$, 0.006 M $CaCl_2$
+1.58	Temp 20; pH 9; 0.005 M Na_2CO_3, 0.005 M NaOH equilibrated with atmospheric $CO_2(g)$, 0.0015 M $CaCl_2$
+0.96	Temp 20; pH 9; 0.0025 M Na_2CO_3, 0.005 M NaOH equilibrated with atmospheric $CO_2(g)$, 0.0005 M $CaCl_2$
+0.48	Temp 20; pH 9; 0.0025 M Na_2CO_3, 0.005 M NaOH equilibrated with atmospheric $CO_2(g)$, 0.00015 M $CaCl_2$
+0.01	Temp 20; pH 9; 0.0025 M Na_2CO_3, 0.005 M NaOH equilibrated with atmospheric $CO_2(g)$, 0.00005 M $CaCl_2$
-0.98	Temp 20; pH 9; 0.0025 M Na_2CO_3, 0.005 M NaOH equilibrated with atmospheric $CO_2(g)$, 0.000005 M $CaCl_2$

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18   **1.2 X-ray diffraction results**

19   Figure 1 shows the x-ray diffraction pattern for the calcium carbonate used in isotopic exchange

20   experiments (see main text, section 2.2).

16/64 1 kaolinite
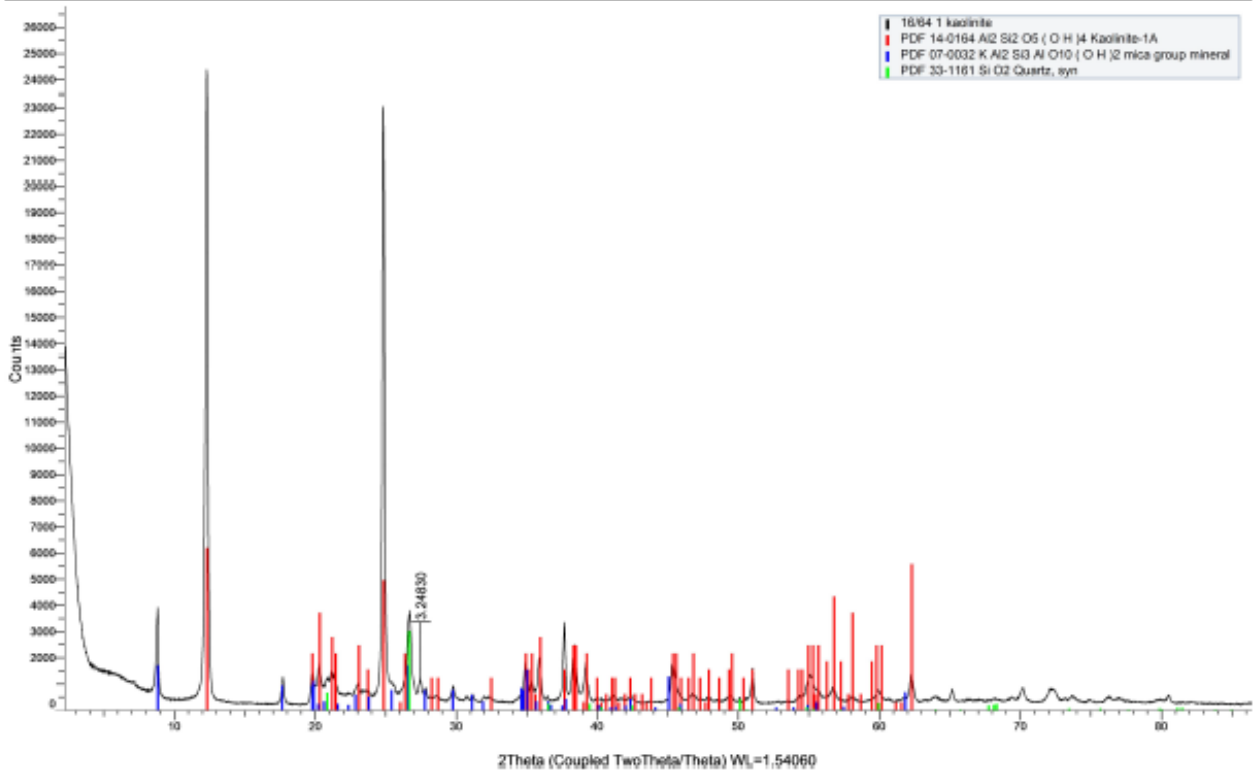
Figure S1 X-ray diffraction pattern showing the sample data (black line) and standard fit for kaolinite (red), mica (blue) and quartz (green)

16/64 1 calcite
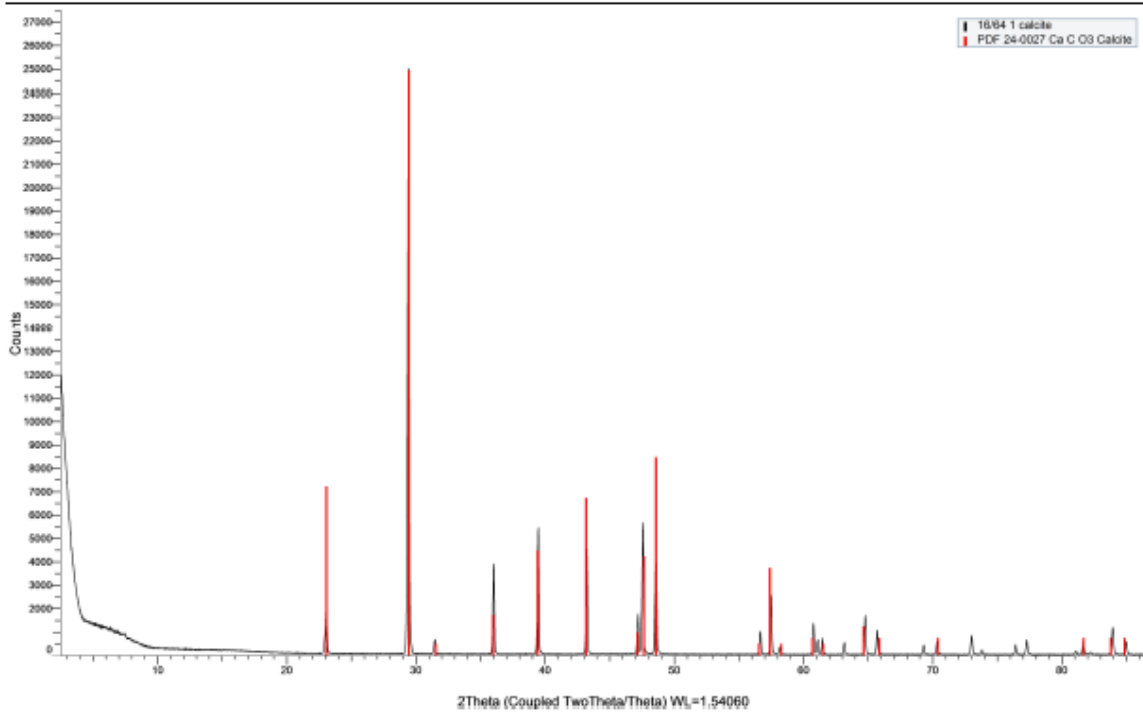
23   **Figure S2** X-ray diffraction pattern showing the sample data (black line) and calcite standard (red
24   line)

25   **Section 2.0 Determining the value of the rate constant (k_{r2})**

26   The key equation, Equation S1 below, allows a k_{obs} value to be calculated for different pH

27   using the rate constant which is then substituted into the first order rate equation to find values for

28    $[^{14}C]$ at defined time points. The experimental data are plotted with the modelled loss curves (main

29   text, Section 4.2, Figure 5) using this technique.

$$k_{obs}=\frac{k_{r2}}{\left(1+\frac{K_{a1}}{[H^+]}+\frac{K_{a1}K_{a2}}{[H^+]^2}\right)}$$ *Equation S1*

30   K_{obs} is a function of the outgassing rate and pH dependent partitioning of ^{14}C between the

31   aqueous carbonate phases

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$$k_{r2}=k_{obs}\cdot\left(1+\frac{K_{a1}}{[H^+]}+\frac{K_{a1}K_{a2}}{[H^+]^2}\right)$$ *Equation S2*

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35 **Table 2** Calculated values of k_{r2} using Equation S2 and k_{obs} values

pH	K_{obs}	Calculated k_{r2} values
7.2	0.254	1000
7.8	0.060	1000
8.8	0.028	5000
9.3	0.008	5000
10.5	0.004	10,000
12.6	0.002	2×10^8

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37   By inputting the k_{obs} values from the experimental data into Equation S2 a series of possible

38 k_{r2} values were obtained, for the purpose of this study $k_{r2} = 4500$ hr^{-1} has been applied to model the

39 experimental data (see main text, Section 4.2).

40 **Section 3.0 Solution compositions for input files for PHREEQC modelling**

41 SOLUTION 1 SWALLACE et al (2012) – site data

42 pH 9 charge;units g/L; Na 0.31;N 0.57;C 0.12 CO2(g) -3.5;S 0.02;end

43 SOLUTION 2 Theoretical composition when groundwater equilibrated with MgCO3

44 pH 9 charge;units g/L; Na 0.31;N 0.57;C 0.18 CO2(g) -3.5;S 0.02; Mg 0.03; end

45 SOLUTION 3 Groundwater composition of well near to leak source – site data

46 Ph 6.5 ;UNITS mg/L; K 4.3; Na 25;Ca 38; Mg 5; Cl 57 charge ; S 20; N 20; C 75 CO2(g) -3.5;end

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48 **Section 4.0 Calculating the thickness of the calcite surface layer**

49   Isotopic exchange between a solution and a solid phase is likely to be surface, or near

50   surface phenomena. The nominal thickness of the surface layer of calcite involved in isotope

51   exchange with DIC has been estimated by assuming that, at equilibrium, the isotope ratio in the

52   active layer is equal to the isotope ratio in the solution. Further it is assumed that net exchange of a

53   proportion, X, of the ^{14}C initially in solution corresponds to net exchange of same proportion of the

54   carbonate species initially in solution (i.e. isotope exchange across the solid solution boundary

55   occurs as a result of dynamic equilibrium between dissolution and precipitation reactions).

56   If the concentration of aqueous carbonate species in isotope exchange experiments is

57    $[C_{(aq.carb)}]$, then net exchange of the proportion, X, of the ^{14}C initially in solution corresponds to net

58   exchange of X.$[C_{(aq.carb)}]$ mM of carbonate. This corresponds to X.$[C_{(aq.carb)}]$.m_w g/L of calcium

59   carbonate (where m_w is the molar mass of calcium carbonate in g/mol). If that calcium carbonate

60   precipitates as calcite it will have a volume of X.$[C_{(aq.carb)}]$.$m_w/\rho_{calcite}$ cm^3/L (where $\rho_{calcite}$ is the density

61   of calcite in g/cm^3). If the mass of calcite per unit volume of solution is $m_{calcite}$ (g/L), and this has a

62   specific surface area of $A_{calcite}$ (cm^2/g), then the calcite surface area per unit volume is $m_{calcite}.A_{calcite}$

63   (cm^2/L). Thus, the thickness, δ (cm), of the active layer involved in solid phase isotope exchange is:

64        $$\delta = (X.[C_{(aq.carb)}].m_w)/(\rho_{calcite}.m_{calcite}.A_{calcite})$$

65   The isotope exchange experiments were equilibrated with a solution containing 1.25 mM

66   HCO_3^-/CO_3^{2-}. This concentration was substantially unchanged by addition of the ^{14}C spike. Calcite

67   has a density of 2.711 g/cm^3 and molecular weight of 100.09 g/mol. The measure SSA of the calcite,

68    $A_{calcite}$, used in the solid phase isotopic exchange experiments is 2900 cm^2/g. Thus, in the systems

69   containing 20 and 50 g/L of calcite, where 10% and 30% of the ^{14}C DIC was exchanged onto the solid,

70   the nominal thickness of the surface layer of calcite involved in isotope exchange is 0.80x10^{-7} cm =

71   8.0 Å and 0.95x10^{-7} cm = 9.5 Å.