minerals

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Article

Evolution of the Reaction and Alteration of Mudstone with Ordinary Portland Cement Leachates: Sequential Flow Experiments and Reactive-Transport Modelling

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Supplementary Materials

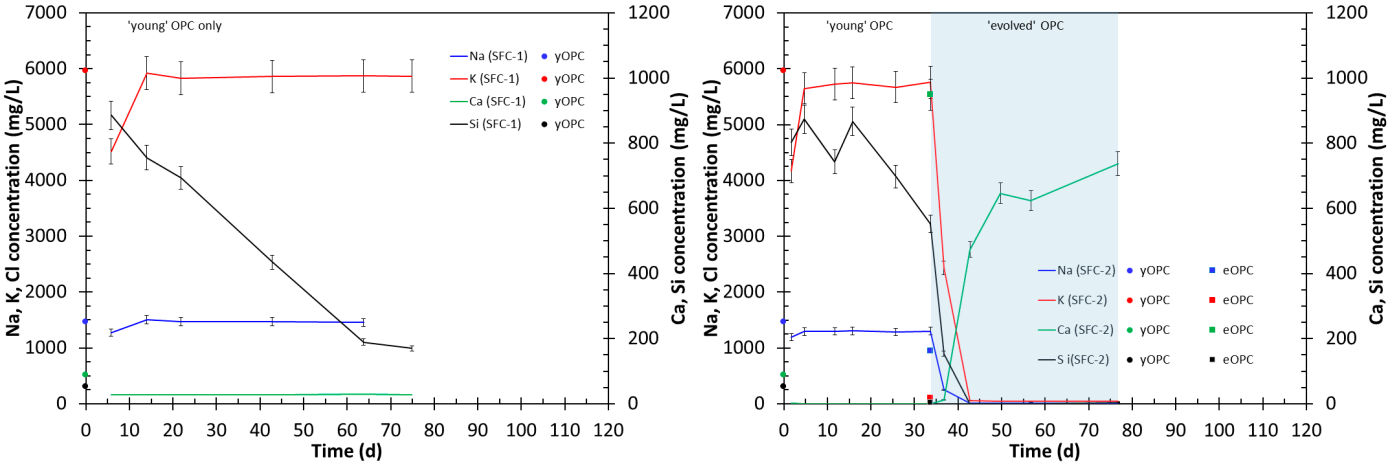

Figure S1. Major changes in fluid chemistry with time. (**a**) Horonobe mudstone with 'young' OPC leachate (SFC-1); (**b**) Horonobe mudstone with 'young' OPC, then 'evolved OPC leachate (SFC-2). Legend text: yOPC – 'young' OPC leachate; eOPC–'evolved' OPC leachate; HGW – Horonobe Groundwater. Lines indicate concentrations in reacted samples; Single points the original concentration in the reacting fluids. X-axis at same scale as Figure 4 for direct comparison of data.

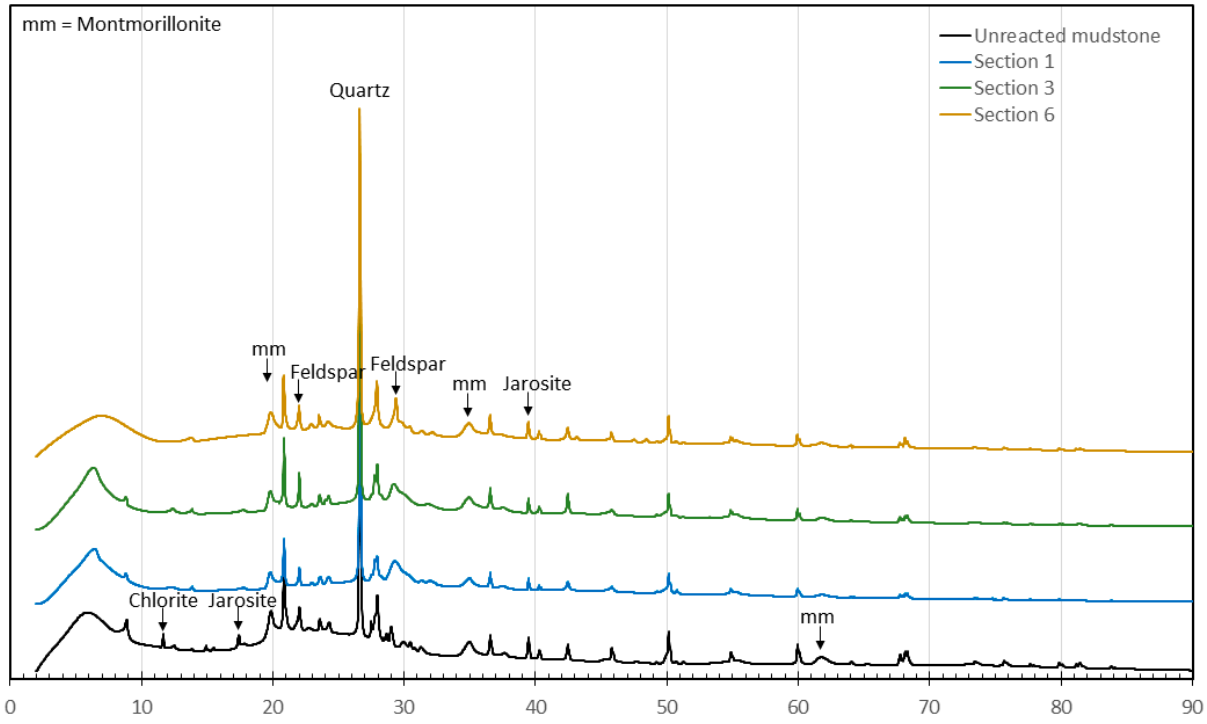

Figure S2. XRD analysis of unreacted and reacted mudstone samples experiment with 'young' OPC, then the 'evolved OPC leachate (SFC-2), Sections 1,2 and 6. Showing little difference between unreacted and reacted solids.

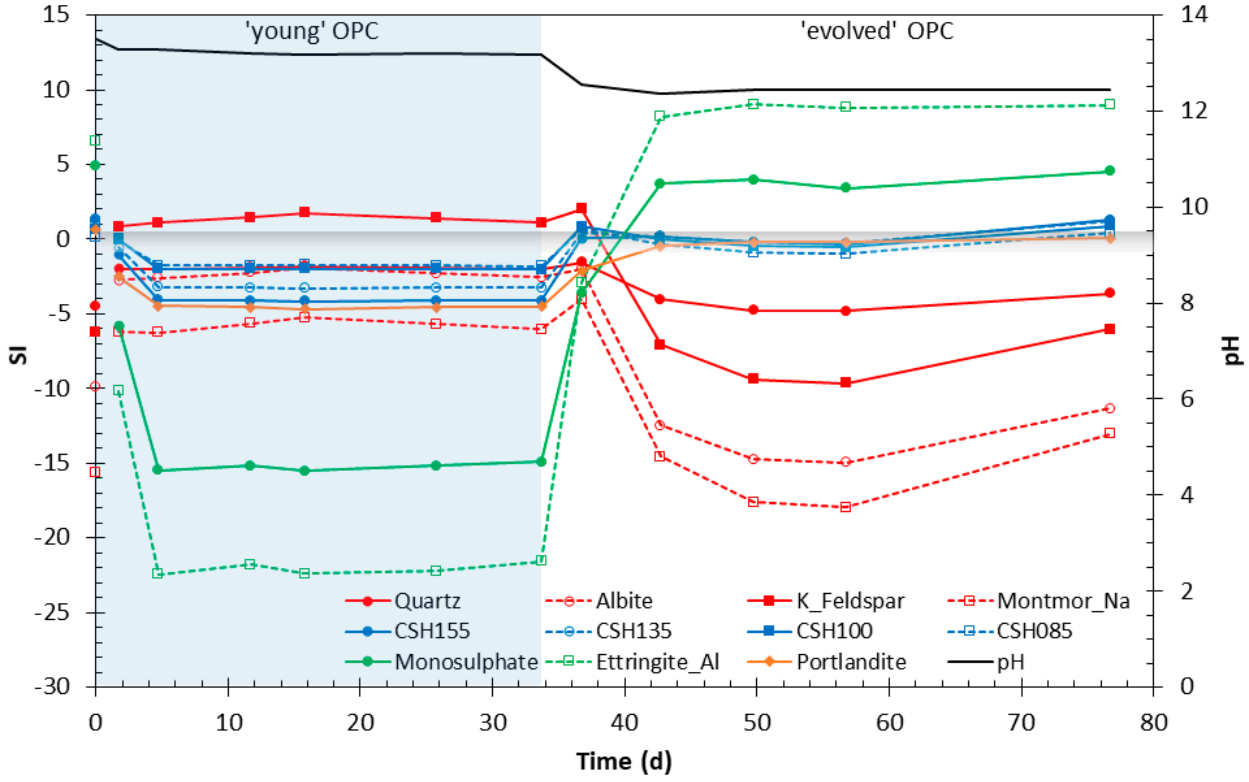

Figure S3. Selected primary mineral and C-S-H phase saturation states in reacted fluids, experiment with 'young' OPC, then the 'evolved OPC leachate (SFC-2).

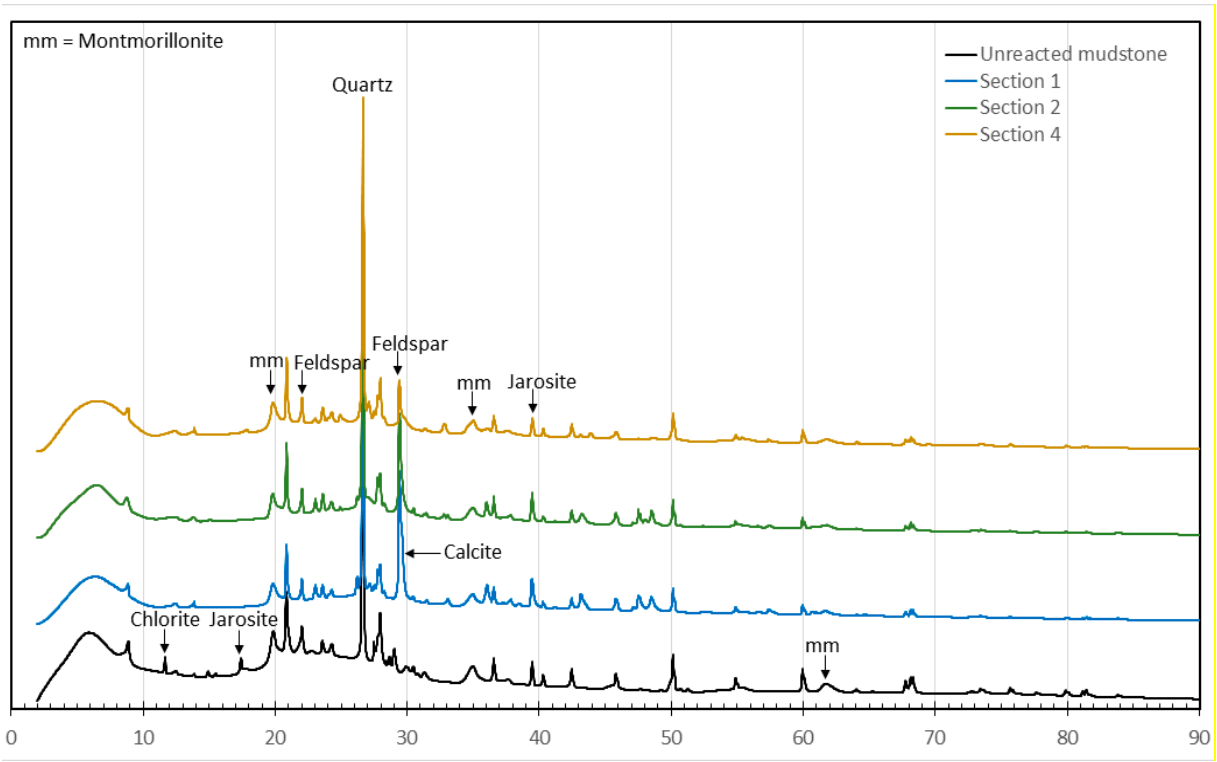

Figure S4. XRD analysis of unreacted and reacted mudstone samples experiment with 'young' OPC, then the 'evolved OPC leachate followed by HGW (SFC-3), Sections 1,2 and 6. Showing little difference between unreacted and reacted solids apart from presence of calcite (Sections 1,2).

CABARET model parameters.

In order to create the reacting fluids in situ within the CABARET model three hypothetical mineral assemblages were defined. These were then reacted at appropriate timesteps (0, ~40, and ~80 days) with 'pure' water to produce fluids with aqueous chemistry matching that of the OPC leachates and the Horonobe Groundwater.

Table S1. Calculated Log $K_{(297.15K)}$ for the hypothetical minerals; 'young' OPC leachate.

Mineral name	Formula	Dissolution reaction	Calculated Log K
A_YoungOPC_calcium	$Ca(OH)_2$	$[Ca(OH)_2] + 2[H^+] \Leftrightarrow [Ca^{++}] + 2[H_2O]$	22.8
A_YoungOPC_chlorine	HCl	$[HCl] \Leftrightarrow [H^+] + [Cl^-]$	−33.4
A_YoungOPC_alminium	$Al(OH)_3$	$[Al(OH)_3] + [H_2O] \Leftrightarrow [Al(OH)_4^-] + [H^+]$	−10.4
A_YoungOPC_carbon	H_2CO_3	$[H_2CO_3] \Leftrightarrow 2[H^+] + [CO_3^{--}]$	−36.9
A_YoungOPC_potassium	KOH	$[KOH] + [H^+] \Leftrightarrow [K^+] + [H_2O]$	12.4
A_YoungOPC_magnesium	$Mg(OH)_2$	$[Mg(OH)_2] + 2[H^+] \Leftrightarrow [Mg^{++}] + 2[H_2O]$	4.86
A_YoungOPC_sodium	NaOH	$[NaOH] + [H^+] \Leftrightarrow [Na^+] + [H_2O]$	11.9
A_YoungOPC_silicon	$Si(OH)_4$	$[Si(OH)_4] \Leftrightarrow [Si(OH)_{4(aq)}]$	−24.3
A_YoungOPC_water	H_2O	$[H_2O] \Leftrightarrow [H_2O]$	−0.002
A_YoungOPC_sulfuer	H_2SO_4	$[H_2SO_4] \Leftrightarrow 2[H^+] + [HSO_4^{--}]$	−47.3

Table 2. Calculated Log $K_{(297.15K)}$ for the hypothetical minerals; 'evolved' OPC leachate.

Mineral name	Formula	Dissolution reaction	Calculated Log K
A_OldOPC_calcium	$Ca(OH)_2$	$[Ca(OH)_2] + 2[H^+] \Leftrightarrow [Ca^{++}] + 2[H_2O]$	22.93
A_OldOPC_chlorine	HCl	$[HCl] \Leftrightarrow [H^+] + [Cl^-]$	−32.69
A_OldOPC_alminium	$Al(OH)_3$	$[Al(OH)_3] + [H_2O] \Leftrightarrow [Al(OH)_4^-] + [H^+]$	−9.735
A_OldOPC_carbon	H_2CO_3	$[H_2CO_3] \Leftrightarrow 2[H^+] + [CO_3^{--}]$	−35.90

A_OldOPC_potassium	KOH	$[KOH] + [H^+] \Leftrightarrow [K^+] + [H_2O]$	−7.604
A_OldOPC_magnesium	$Mg(OH)_2$	$[Mg(OH)_2] + 2[H^+] \Leftrightarrow [Mg^{++}] + 2[H_2O]$	4.054
A_OldOPC_sodium	NaOH	$[NaOH] + [H^+] \Leftrightarrow [Na^+] + [H_2O]$	−7.596
A_OldOPC_silicon	$Si(OH)_4$	$[Si(OH)_4] \Leftrightarrow [Si(OH)_{4(aq)}]$	−23.65
A_OldOPC_water	H_2O	$[H_2O] \Leftrightarrow [H_2O]$	−0.00068
A_OldOPC_sulfuer	H_2SO_4	$[H_2SO_4] \Leftrightarrow 2[H^+] + [HSO_4^{--}]$	−45.58

Table S3. Calculated Log $K_{(297.15K)}$ for the hypothetical minerals; Horonobe groundwater.

Mineral name	Formula	Dissolution reaction	Calculated Log K
A_HoroOPC_calcium	$Ca(OH)_2$	$[Ca(OH)_2] + 2[H^+] \Leftrightarrow [Ca^{++}] + 2[H_2O]$	13.7
A_HoroOPC_chlorine	HCl	$[HCl] \Leftrightarrow [H^+] + [Cl^-]$	−9.69
A_HoroOPC_alminium	$Al(OH)_3$	$[Al(OH)_3] + [H_2O] \Leftrightarrow [Al(OH)_4^-] + [H^+]$	9.52
A_HoroOPC_carbon	H_2CO_3	$[H_2CO_3] \Leftrightarrow 2[H^+] + [CO_3^{--}]$	−10.2
A_HoroOPC_potassium	KOH	$[KOH] + [H^+] \Leftrightarrow [K^+] + [H_2O]$	5.67
A_HoroOPC_magnesium	$Mg(OH)_2$	$[Mg(OH)_2] + 2[H^+] \Leftrightarrow [Mg^{++}] + 2[H_2O]$	14.1
A_HoroOPC_sodium	NaOH	$[NaOH] + [H^+] \Leftrightarrow [Na^+] + [H_2O]$	7.44
A_HoroOPC_silicon	$Si(OH)_4$	$[Si(OH)_4] \Leftrightarrow [Si(OH)_{4(aq)}]$	−3.04
A_HoroOPC_water	H_2O	$[H_2O] \Leftrightarrow [H_2O]$	−0.003
A_HoroOPC_sulfuer	H_2SO_4	$[H_2SO_4] \Leftrightarrow 2[H^+] + [HSO_4^{--}]$	−37.7

Table S4. Details of the dissolved chemical species included in the CABARET reactive transport model.

Aqueous Basis species	Aqueous Complex species		
H_2O	$Al(OH)_2^+$	CO_3^{--}	$MgSiO(OH)_3^+$
	$Al(OH)_{3(aq)}$	KCl(aq)	$NaAl(OH)_{4(aq)}$
Al^{+++}	$Al(OH)_4^-$	KCO_3^-	$NaCl_{(aq)}$
Ca^{++}	$CaAl(OH)_4^+$	$KHCO_3(aq)$	$NaCO_3^-$
Cl^-	$CaCl^+$	KOH(aq)	$NaHCO_{3(aq)}$
H^+	$CaCl_{2(aq)}$	$KSiO_2(OH)_2$-	$NaOH_{(aq)}$
HCO_3^-	$CaCO_{3(aq)}$	$KSiO(OH)_{3(aq)}$	$NaSiO_2(OH)_2^-$
K^+	$CaHCO_3^+$	$MgAl(OH)_4^-$	$NaSiO(OH)_{3(aq)}$
Mg^{++}	$CaOH^+$	$MgCO_{3(aq)}$	OH^-
Na^+	$CaSiO_2(OH)_{2(aq)}$	$MgHCO_3^+$	$SiO(OH)_3^-$
$Si(OH)_{4(aq)}$	$CaSiO(OH)_3^+$	$MgOH^+$	$SiO_2(OH)_2^{--}$
SO_4^{--}	$CO_{2(aq)}$	$MgSiO_2(OH)_{2(aq)}$	