Supporting Information for:

Controls on the generation and geochemistry of neutral mine drainage: Evidence from Force Crag mine, Cumbria, UK

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Table S1. Total and filtered (0.45 μm) cation concentrations for FC29 (Level 1 discharge water at inlet to treatment system) and FC16 (Coledale Beck upstream of mine site), showing median (standard deviation), minimum and maximum (n) values. Shaded cells indicate significant differences (Mann-Whitney U test; $p < 0.001$) between total and filtered concentrations; no significant difference ($p > 0.1$) between total and filtered concentrations in all other cases.

	FC29		FC16	
	Total	**Filtered**	**Total**	**Filtered**
Ca (mg/L)	10.2 (2.51) 4.0 – 14.8 (*132*)	10.1 (2.51) 4.0 – 14.8 (*117*)	0.46 (0.08) 0.30 – 0.60 (*34*)	0.45 (0.08) 0.30 – 0.60 (*34*)
Mg (mg/L)	3.60 (0.78) 1.63 – 5.10 (*132*)	3.60 (0.77) 1.62 – 5.10 (*117*)	0.67 (0.13) 0.49 – 0.90 (*34*)	0.67 (0.13) 0.49 – 0.90 (*34*)
Na (mg/L)	2.9 (0.28) 2.2 – 4.2 (*132*)	2.9 (0.29) 2.2 – 4.2 (*117*)	3.0 (0.59) 1.9 – 4.5 (34)	3.0 (0.58) 1.9 – 4.5 (34)
Zn (μg/L)	3190 (724) 1253 – 4490 (*132*)	3030 (700) 1231 – 4400 (*117*)	20.0 (4.17) 13.0 – 30.0 (*34*)	20.0 (3.94) (10.0 – 30.0 (*34*)
Pb (μg/L)	34.0 (10.7) 8.0 – 83.4 (*97*)	1.3 (8.6) 0.1 – 38.3 (*83*)	0.86 (0.77) 0.45 – 3.27 (*16*)	0.64 (0.70) 0.36 – 3.18 (*16*)
Cd (μg/L)	14.8 (3.3) 6.3 – 21.5 (*100*)	14.1 (3.3) 4.8 – 20.9 (*85*)	0.05 (0.04) 0.05 – 0.16 (*16*)	0.05 (0.04) 0.05 – 0.20 (*16*)
Ni (μg/L)	16.1 (3.2) 8.5 – 24.7 (*100*)	16.0 (3.3) 8.0 – 24.3 (*85*)	1.61 (0.22) 1.39 – 2.08 (*16*)	1.59 (0.22) 1.39 – 2.07 (*16*)
Al (μg/L)	58.0 (55.3) 16.0 – 576.3 (*131*)	13.3 (13.4) 5.0 – 94.0 (*86*)	138.8 (46.5) 64.9 – 250.0 (*34*)	133.3 (45.7) 60.7 – 250.0 (*34*)
Fe (μg/L)	503 (127) 138 – 760 (*131*)	127 (25) 71 – 201 (*117*)	11.3 (7.2) 4.1 – 35.0 (*18*)	8.8 (6.7) 3.4 – 31.3 (*17*)
Mn (μg/L)	536 (131) 212 – 790 (*132*)	521 (131) 206 – 790 (*117*)	20.0 (4.6) 14.8 – 30.0 (*34*)	20.0 (4.6) 14.6 – 30.0 (*34*)
Cu (μg/L)	4.00 (1.83) 2.36 – 16.94 (*97*)	2.00 (1.21) 0.41 – 5.86 (*73*)	0.83 (0.19) 0.39 – 1.31 (*16*)	0.77 (0.19) 0.41 – 1.30 (*16*)
As (μg/L)	2.39 (0.49) 1.43 – 3.24 (*42*)	1.45 (0.30) 0.69 – 1.99 (*42*)	0.24 (0.05) 0.17 – 0.35 (*16*)	0.22 (0.05) 0.14 – 0.34 (*16*)
Si (mg/L)	3.0 (0.53) 1.5 – 3.9 (*132*)	2.9 (0.52) 1.5 – 3.9 (*117*)	0.8 (0.09) 0.6 – 1.0 (*34*)	0.8 (0.09) 0.6 – 1.0 (*34*)
Ba (μg/L)	84.8 (26.6) 54.0 – 215.5 (*72*)	85.3 (16.3) 52.0 – 133.5 (*59*)	13.1 (3.8) 10.7 – 24.3 (*12*)	n.d.
Sr (μg/L)	23.0 (3.2) 13.0 – 30.0 (*72*)	22.5 (3.2) 12.6 – 30.0 (*59*)	3.50 (0.34) 3.17 – 4.16 (*11*)	n.d.

Notes: (1) No data for K shown since all values, for both total and filtered, below detection limit of 1 mg/L. (2) Cd data for FC16 includes concentrations (11 for total and 9 for filtered) less than the detection limit of 0.1 µg/L, recorded as 0.05 µg/L for the purposes of calculation.

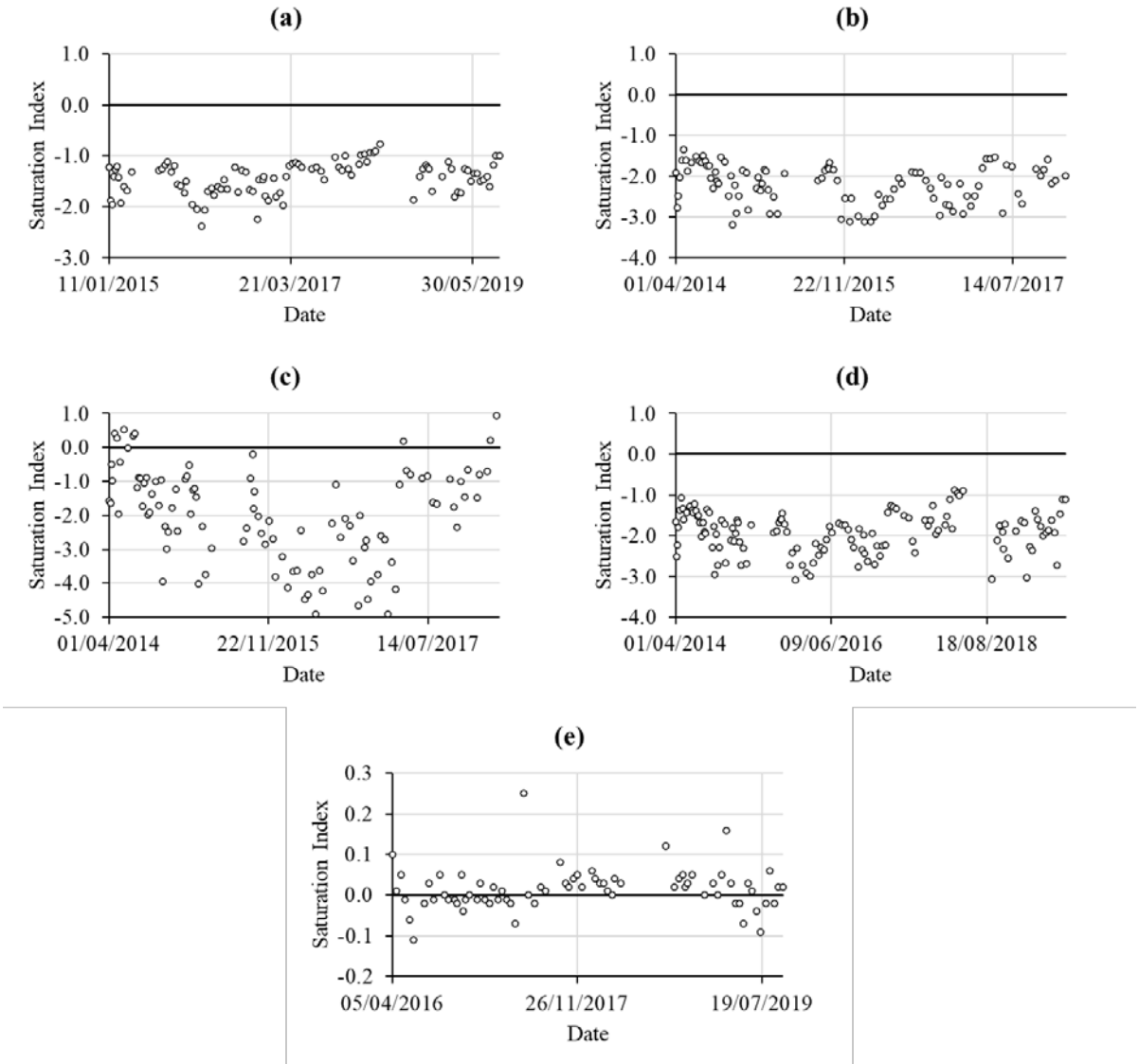

Figure S1. Saturation Indices (calculated in PhreeqC) for minerals in the Force Crag mine Level 1 discharge (at location FC29), showing (a) cerussite, (b) smithsonite, (c) ferrihydrite (amorphous), (d) siderite and (e) barite.

Table S2. Molar balance calculations for one litre of water, showing the molar proportions of the different mineral dissolution / precipitation reactions (in bold, relative to sphalerite) within the mine that explain the difference in composition between input water (FC16) and outlet water (FC29). For ferrihydrite, the general formula $Fe(OH)_3$ was used. Cd, Ni and Cu were not taken into consideration as the amounts are too small to make a difference. Mg was not included because the relative proportions contributed by dolomite and chlorite dissolution could not be constrained. Column J shows calculated composition of FC29 for each constituent according to the sequence of calculations shown below the molar balance table, and column K indicates there is no difference between calculated and actual FC29 composition.

	A	B	C	D	E	F	G	H	J	K
1		**FC16 actual composition**	**Sphalerite dissolution**	**galena dissolution**	**pyrite dissolution**	**calcite dissolution**	**ferrihydrite precipitation**	**FC29 actual composition**	**FC29 calculated composition**	**Difference between actual and calculated (%)**

2	Molar conc.		**4.87E-05**	**1.08E-04**	**4.97E-05**	**2.44E-04**	**-4.09E-05**			
3	Molar ratio		**1.00**	**2.22**	**1.02**	**5.00**	**0.84**			
4	SO_4	2.50E-05	4.87E-05	1.08E-04	9.94E-05			2.81E-04	2.81E-04	0.0
5	Ca	1.15E-05				2.44E-04		2.55E-04	2.55E-04	0.0
6	Fe	2.03E-07			4.97E-05		-4.09E-05	9.04E-06	9.04E-06	0.0
7	Zn	3.06E-07	4.87E-05					4.90E-05	4.90E-05	0.0
8	Pb	4.15E-09		1.08E-04			-1.08E-04	1.64E-07	1.64E-07	0.0
9	HCO_3^-	8.20E-06				4.87E-04		2.86E-04	2.86E-04	0.0
10	H^+	1.07E-05			1.99E-04			2.82E-07		

Table S2. Continued.

Cell Ref.	**Sequence of calculations**
C7	FC29 Zn concentration minus FC16 Zn concentration
C4	Equal to cell C7 value, since 1:1 molar ratio of Zn:S in sphalerite dissolution
D8	Zn concentration released by ZnS dissolution, multiplied by the PbS:ZnS ratio (cell D3). Initially, assumed ratio of sphalerite:galena dissolution (based on mined masses) used to calculate Pb release (i.e. double that of Zn release from ZnS); subsequently, PbS:ZnS ratio iteratively adjusted to resolve molar balance
D4	Equal to value in cell D8, since 1:1 molar ratio of Pb:S in galena dissolution
E4	Calculated as FC29 SO_4 concentration (H4) minus the sum of: FC16 SO_4 concentration (cell B4) + SO_4 released from sphalerite dissolution (cell C4) + SO_4 released from galena dissolution (cell D4)
E10	Calculated from SO_4 released from pyrite dissolution (cell E4): 4 moles H^+ for each mole of pyrite oxidised
E6	Calculated from SO_4 released from pyrite dissolution (cell E4): 2 moles of Fe for each mole of S in pyrite
F5	FC29 Ca concentration minus FC16 Ca concentration
F9	Cell F5 value multiplied by two, since 1:2 ratio of Ca:HCO_3^- in the reaction $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$, which is the main dissolution reaction at approximately pH ≥5 (Younger et al., 2002)
G6	Calculated as FC29 Fe concentration (cell H6) minus the sum of: FC16 Fe concentration (cell B6) + Fe released from pyrite dissolution (cell E6)
G8	Pb scavenged by ferrihydrite, calculated as FC29 Pb concentration (cell H8) minus sum of: FC16 Pb concentration (cell B8) + Pb released from galena dissolution (cell D8)
G10	Note that proton release from ferrihydrite precipitation not shown here as it is accounted for in pyrite dissolution reaction (cell E10)
J4	Sum of: FC16 SO_4 concentration (cell B4) + SO_4 concentrations from sphalerite, galena and pyrite dissolution (cells C4, D4, E4, respectively)
J5	Sum of: FC16 Ca concentration (cell B5) + Ca from calcite dissolution (cell F5)
J6	Sum of: FC16 Fe concentration (cell B6) + Fe from pyrite dissolution (cell E6) + Fe attenuated via ferrihydrite precipitation (cell G6). Note cell G6 has negative value to indicate attenuation

J7	Sum of: FC16 Zn concentration (cell B7) + Zn from sphalerite dissolution (cell C7)
J8	Sum of: FC16 Pb concentration (cell B8) + Pb from galena dissolution (cell D8) + Pb scavenged by ferrihydrite (cell G8). Note cell G8 has negative value to indicate attenuation
J9	Calculated as follows: firstly, the sum of FC16 HCO_3^- concentration (cell B9) + HCO_3^- concentration from $CaCO_3$ dissolution (cell F9) is calculated; subtracted from this are (1) the H^+ released by pyrite dissolution (cell E10) and (2) the H^+ released through pH increase from FC16 to FC29 (i.e. cell B10 minus cell H10), since protons released from pyrite dissolution and pH increase will consume HCO_3^-

	Additional notes
A2	Molar concentration refers to the molar concentration of the primary metal of interest released or attenuated in each of the mineral reactions (shown in cells C2 to G2)
A3	Molar ratio is the ratio of the molar concentration of each of Pb (cell D2), Fe (cell E2), Ca (cell F2) and Fe (cell G2) to the molar concentration of Zn (cell C2). For Fe precipitation this is shown as a positive value for convenience (cell G3)

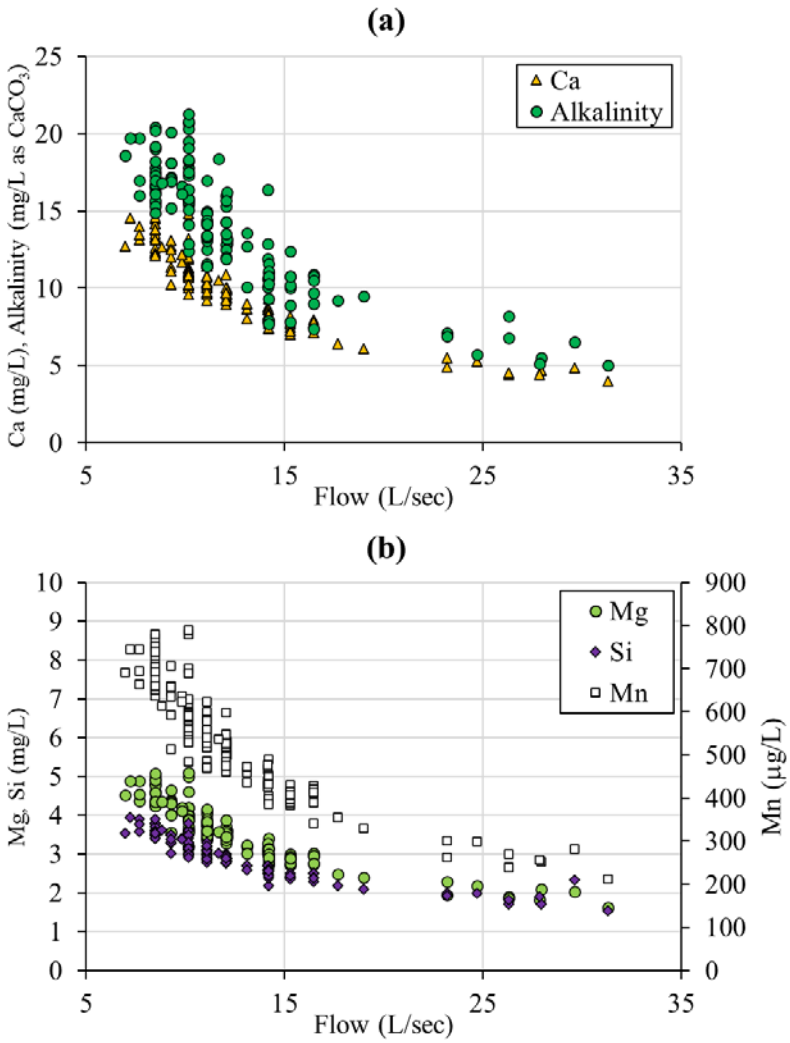

Figure S2. Relationship between flow of the Level 1 mine water discharge at Force Crag with (a) Ca and alkalinity concentration and (b) Mg, Si and Mn concentrations.

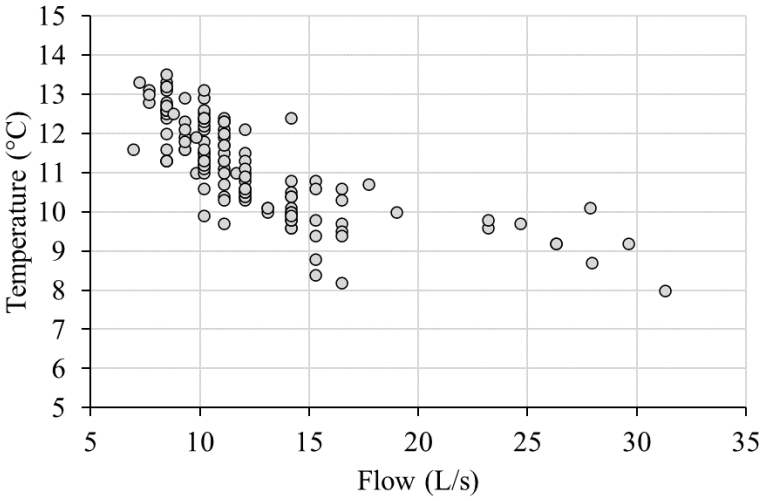

Figure S3. Relationship between temperature and flow of water leaving the Force Crag mine (FC28/29).

Table S3. Full and partial Spearman Rho correlation coefficients (r^2) and significance level (p) between mine water temperature and selected variables (see manuscript text for discussion; "Filt." = filtered concentration of metal).

Variable	Temp vs variable		Temp. vs variable (flow controlled)	
	r^2	p	r^2	p
Flow	-0.833	0.000	-	-
Pb	-0.485	0.000	0.015	0.884
Filt. Pb	-0.757	0.000	0.482	0.000
Zn	0.815	0.000	0.550	0.000
Cd	0.787	0.000	0.462	0.000
Ni	0.729	0.000	0.346	0.000
Al	-0.444	0.000	0.333	0.000
Filt. Al	-0.792	0.000	-0.243	0.026
Fe	0.732	0.000	0.458	0.000
Filt. Fe	-0.103	0.269	-0.099	0.296
Cu	-0.767	0.000	0.252	0.014
Filt. Cu	-0.681	0.000	-0.024	0.844
Ba	-0.800	0.000	0.321	0.007
SO_4^{2-}	0.834	0.000	0.606	0.000