

Supplementary Material

1 SUPPLEMENTARY DATA

Table S1. Si and trace metal	concentrations in high resolution	pore water samples.	No measurements were made	where data are not available.
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	Denth	Ge	Si	Ge/Si	Fe	Mn
Core	cm	pmol/L	µmol/L	umol/mol	µmol/L	nmol/L
MC-1D	1	380	249	1.53	63	57
MC-1D	3	696	324	2.15	106	90
MC-1D	3	707	308	2.30	128	100
MC-1D	5	471	352	1.34	118	124
MC-1D	7	356	367	0.97	40	161
MC-1D	9	379	391	0.97	87	183
MC-1D	13	203	390	0.52	55	202
MC-1D	13	249	422	0.59	60	228
MC-1D	16	262	452	0.58	59	265
MC-1D	24	199	462	0.43	53	375
MC-1D	29	180	492	0.37	39	321
MC-1D	33	181	517	0.35	39	398
MC-2A	0	531	297	1.78	88	36
MC-2A	1	730	340	2.15	156	54
MC-2A	2	1177	363	3.24	159	75
MC-2A	4	432	353	1.22	118	226
MC-2A	8	380	356	1.07	83	123
MC-2A	15	214	440	0.49	72	217
MC-2A	29	117	517	0.23	43	354
MC-2A	33	111	525	0.21		
	0	226	220	1 46	10	2
	0	614	200	1.40	10	70
	5	251	270	0.05	112	110
	5	206	370	0.95	01	113
	10	200	469	0.72	04	222
MC-2D	20	200	400	0.37	94 62	223
NIC-2D	20	171	457	0.37	03	200
MC-3D	1	859	273	3.15	128	66
MC-3D	2	695	320	2.17	117	83
MC-3D	2	556	282	1.97	97	102
MC-3D	15	540	451	1.20	77	259
MC-3D	22	196	447	0.44	38	250
MC-3D	30		464		46	619
MC-3D	35	139	508	0.27	29	374
MC-5C-1	1	518	309	1 67	1	0
MC-5C-1	2	531	514	1.07	261	175
MC-5C-1	4	522	546	0.96	201	352
MC-5C-1	8	446	463	0.96	306	321
MC-5C-1	13	315	426	0.30	79	218
MC-5C-1	10	252	420	0.74	67	258
MC-5C-1	23	177	460	0.38	51	200
MC-5C-1	23	120	400	0.38	30	230
MC-5C-2	21 15	120		0.27	50	210
MC-5C-2	6.5	-+ 13 525				
MC-5C-2	1/5	2/1				
MC-5C-2	25.5	130				
MC-5C-2	34.5	89				

Table S2.	Ammonia concentrations in high resolution pore water samples and overlying water. Cores MC-1B, MC-2B, and MC-4B are distinct from corr	es
analyzed f	or Ge and Si, but were collected alongside the cores discussed above.	

Core	Depth, cm	NH ₃ ,	Core	Depth, cm	NH ₃ ,
MC-1B	0.5	24	MC-1B		8
MC-1B	2.5	51	MC-2B	OL W	8
MC-1B	4.5	78	MC-4B	OLW	24
MC-1B	6.5	93	-		
MC-1B	8.5	120	MC-2A	0	44
MC-1B	12.5	158	MC-2A	1	37
MC-1B	16	187	MC-2A	2	33
MC-1B	20.5	217	MC-2A	3	59
MC-1B	27	276	MC-2A	4	62
			MC-2A	5	83
MC-2B	0.5	29	MC-2A	7	102
MC-2B	3.5	63	MC-2A	8	97
MC-2B	5.5	116	MC-2A	9	127
MC-2B	10.5	136	MC-2A	10	123
MC-2B	15.5	176	MC-2A	11	160
MC-2B	20.5	203	MC-2A	12	137
MC-2B	25.5	238	MC-2A	14	169
MC-2B	30.5	263	MC-2A	15	172
MC-2B	36	302	MC-2A	17	209
MC-2B	42.5	337	MC-2A	20	234
			MC-2A	24	261
MC-4B	0.5	17	MC-2A	27	264
MC-4B	3.5	57	MC-2A	29	274
MC-4B	6.5	86	MC-2A	30	294
MC-4B	9.5	139	MC-2A	33	297
MC-4B	15.5	201			
MC-4B	18.5	222	MC-4B	34	339
MC-4B	22.5	273	MC-4B	40	379
MC-4B	28.5	299	MC-4B	43	430

 Table S3.
 Sulfate concentrations in seawater, high resolution pore water samples, and overlying water. Measurement uncertainty is 4 %.

Sampla	Depth,	SO ₄ ,
Sample	m	mmol/L
SPOT SSW	0	27.4
SPOT 885m	885	27.2
MC-5B-1 (Core inc.)	885	26.4
5B-Final (Core inc.)	885	26.5
MC-2C OLW	885	29.6
MC-2D OLW	885	27.2
MC-5C OLW	885	27.8
MC-1D OLW	885	26.5
MC-2A OLW	885	26.1
Coro	Depth,	SO ₄ ,
COIE	cm	mmol/L
MC-1D	1	26.5
MC-1D	3	24.4
MC-1D	5	26.1
MC-1D	9	26.3
MC-1D	16	26.0
MC-1D	24	24.5
MC-1D	29	24.9
MC-1D	33	23.5
MC-2A	0	26.1
MC-2A	4	25.6
MC-2A	12	25.4
MC-2A	20	24.7
MC-2A	29	25.4

Table S4. Ge and Si concentrations during San Pedro Basin core incubations.

		Corr. time.	Ge.	Si.	Ge/Si.
Sample	Time, h	d/m *	pmol/L	µmol/L	µmol/mol
MC-3A				-	
1	0	0	73	103	0.71
2	8.0	2.8	83	112	0.74
3	17.5	6.2	86	125	0.69
4	40.3	14.5	104	130	0.80
5	64.3	23.5	116	145	0.81
Final	65.8	24.1	118	142	0.83
<u>MC-5D</u>					
1	0	0	83	105	0.79
2	6.0	1.8	86	108	0.79
3	23.4	7.2	88	115	0.76
4	45.4	14.2	87	120	0.73
5	68.4	21.7	94	127	0.74
Final	68.4	21.7	98	129	0.76
<u>MC-4C</u>					
1	0	0	83	106	0.78
2	3.3	1.0	83	110	0.75
3	3.5	1.1	85	109	0.77
4	23.0	7.3	88	120	0.74
5	46.0	14.9	87	122	0.71
6	69.8	22.9	92	130	0.71
7	92.8	30.8	101	136	0.74
8	118.5	39.8	102	143	0.72
9	140.5	47.6	109	147	0.74
<u>MC-5A</u>					
1	0	0	81	105	0.77
2	5.5	1.9	82	112	0.73
3	23.0	8.1	84	120	0.70
4	45.0	16.1	84	125	0.67
5	70.0	25.3	87	134	0.65
6	93.0	34.0	83	140	0.60
7	117.5	43.4	86	147	0.58
8	139.5	52.1	85	155	0.55
<u>MC-5B</u>					
1	0	0	74	104	0.71
2	5.5	1.5	74	108	0.69
3	23.0	6.4	69	114	0.61
4	45.0	12.6	78	120	0.66
5	70.0	19.9	78	126	0.62
6	93.0	26.8	86	131	0.65
7	117.5	34.2	84	139	0.61
8	139.0	40.8	87	142	0.61

* Calculated as sum of incubation time in days divided by height of the overlying incubated water column in m at a given time. The height of the water column decreases throughout the incubation due to water removal by sampling. This calculation corrects for the effect of decreasing water volume, and is used to calculate the Ge and Si fluxes reported in Table 3 of main text.

Table S5. Ge and Si concentrations during Santa Monica Basin core incubations. No measurements were made where data are not available.

Sample	Time, h	Corr. time, d/m *	Ge, pmol/L	Si, µmol/L	Ge/Si, µmol/mol
D3-S2			-	-	-
1	11.5	4.9	96	126	0.76
2	24.6	10.6	104	131	0.79
3	31.2	13.6	107	133	0.80
4	49.7	22.2	114	140	0.81
5	119.2	56.0	145	154	0.94
<u>D4-S1</u>					
1	9.8	3.5	95	129	0.74
2	22.7	8.3		134	
3	29.6	10.9	105	137	0.76
4	48.5	18.3		143	
5	118.4	46.4	147	165	0.89
<u>D4-S4</u>					
1	9.8	4.4	99	129	0.76
2	22.8	10.5		135	
3	29.6	13.9	102	138	0.74
4	48.5	23.4		146	
5	118.2	59.7	147	170	0.86
<u>D5-S1</u>					
1	8.5	2.9	91	131	0.70
2	21.6	7.4		136	
3	28.3	9.8	96	138	0.69
4	46.8	16.6		139	
5	116.9	42.9	151	189	0.80
<u>D5-S4</u>					
1	8.6	2.4	88	131	0.67
2	23.0	6.4		134	
3	28.3	8.0	90	136	0.66
4	46.9	13.5		145	
5	116.8	34.6	116	163	0.71

* Calculated as sum of incubation time in days divided by height of the overlying incubated water column in m at a given time. The height of the water column decreases throughout the incubation due to water removal by sampling. This calculation corrects for the effect of decreasing water volume, and is used to calculate the Ge and Si fluxes reported in Table 3 of main text.

SUPPLEMENTARY TABLES AND FIGURES 2

2.1 **Tables**

Table S6. Core incubation model input parameters.

Parameter	Range	PDF	Source
F _{lith} (nmol m ⁻² d ⁻¹)	0.70 ± 0.26	normal	1
Ge/Si _{bSi} (µmol/mol)	0.70 ± 0.10	normal	2
δ ⁷⁴ Ge _{initial} (‰)	3.06 ± 0.17	normal	3
δ ⁷⁴ Ge _{bSi} (‰)	3.28 ± 0.52	normal	4
δ ⁷⁴ Ge _{lith} (‰)	0.58 ± 0.21	normal	5
δ ⁷⁴ Ge _{pw} (‰)	2.13 ± 0.25	normal	6
$\Delta^{74}\text{Ge}_{\text{FeOx-diss}}$ (‰)	-4.61.6	uniform	7
$\Delta^{74}\text{Ge}_{\text{auth-diss}}$ (‰)	-0.3 - 0.3	uniform	8

(1) Calculated from FeOx flux reported by Leslie et al. (1990) and UCC Ge/Fe ratio (Rudnick & Gao, 2014) - see supp. text; (2) Baronas et al. (2016); (3) Mean of all measured pre-incubation overlying water values (Table 1); (4) Mean of meaured seawater values (Table 1); (5) Rouxel & Luais (2017); (6) Mean of all pore water values below 5 cm depth (incl. the single SMB measurement); (7) Pokrovsky et al. (2014); (8) Based on the negligible δ^{74} Ge_{pw} gradient in SPB sediments (Fig. 1)

Table S7. Core incubation model results for San Pedro and Santa Monica Basin cores. Values are reported as median with 25-75th percentiles in parentheses.

	San Pedro Basin						Santa Monica Basin	
Core	MC-3A	MC-5D	MC-4C	MC-5A	MC-5B	D3S2	D4S4	D5S1
n _{initial} (nmol)	62 (59 - 66)	81 (77 - 85)	82 (78 - 86)	69 (65 - 73)	80 (77 - 84)	67 (63 - 72)	60 (55 - 65)	73 (69 - 78)
n _{inc} (nmol)	34 (32 - 36)	8.1 (7.5 - 8.6)	20 (19 - 22)	1.01 (0.94 - 1.07)	17 (16 - 18)	18 (17 - 19)	17 (16 - 18)	30 (28 - 32)
f _{lith}	0.39 (0.35 - 0.42)	0.49 (0.45 - 0.53)	0.56 (0.52 - 0.6)	0.57 (0.53 - 0.6)	0.55 (0.51 - 0.59)	0.65 (0.62 - 0.69)	0.57 (0.53 - 0.61)	0.4 (0.37 - 0.44)
f _{bSi}	0.61 (0.58 - 0.65)	0.51 (0.47 - 0.55)	0.44 (0.4 - 0.48)	0.43 (0.4 - 0.47)	0.45 (0.41 - 0.49)	0.35 (0.31 - 0.38)	0.43 (0.39 - 0.47)	0.6 (0.56 - 0.63)
f _{auth}	-0.81 (-1.320.43)	-0.22 (-0.440.09)	-0.2 (-0.370.08)	-0.23 (-0.430.1)	-0.16 (-0.310.07)	-0.11 (-0.220.05)	-0.1 (-0.20.04)	-0.19 (-0.360.08)
f _{FeOx}	0.8 (0.41 - 1.32)	-0.48 (-0.610.26)	-0.38 (-0.50.2)	-0.75 (-0.880.55)	-0.48 (-0.580.33)	0 (-0.12 - 0.16)	-0.17 (-0.270.04)	0.07 (-0.07 - 0.25)
f _{released}	0.98 (0.89 - 1.08)	0.29 (0.26 - 0.32)	0.41 (0.37 - 0.46)	0.02 (0.02 - 0.02)	0.34 (0.31 - 0.38)	0.86 (0.77 - 0.97)	0.71 (0.63 - 0.79)	0.85 (0.77 - 0.93)
F _{bSi} (nmol m ^{−2} d ^{−1})	1.11 (1.02 – 1.21)	0.71 (0.65 - 0.76)	0.53 (0.49 - 0.57)	0.52 (0.48 - 0.57)	0.55 (0.51 - 0.6)	0.35 (0.33 - 0.38)	0.51 (0.47 - 0.55)	1.02 (0.94 - 1.1)
F _{supply} (nmol m ⁻² d ⁻¹)	1.81 (1.69 - 1.94)	1.39 (1.29 - 1.5)	1.21 (1.11 - 1.31)	1.2 (1.11 – 1.3)	1.23 (1.13 - 1.33)	1.03 (0.94 - 1.12)	1.19 (1.09 - 1.29)	1.71 (1.6 – 1.84)
F _{auth} (nmol m ⁻² d ⁻¹)	-1.46 (-2.380.78)	-0.31 (-0.610.13)	-0.24 (-0.450.1)	-0.28 (-0.520.12)	-0.2 (-0.390.09)	-0.12 (-0.230.05)	-0.12 (-0.240.05)	-0.33 (-0.620.14)
F _{FeOx} (nmol m ⁻² d ⁻¹)	1.43 (0.74 - 2.35)	-0.65 (-0.850.35)	-0.45 (-0.620.24)	-0.88 (-1.060.64)	-0.58 (-0.730.39)	0 (-0.13 - 0.15)	-0.2 (-0.330.04)	0.11 (-0.12 - 0.41)
F _{inc} (nmol m ⁻² d ⁻¹)	1.77 (1.65 - 1.89)	0.41 (0.38 - 0.43)	0.5 (0.46 - 0.53)	0.02 (0.02 - 0.03)	0.42 (0.4 - 0.45)	0.89 (0.83 - 0.95)	0.84 (0.78 - 0.9)	1.45 (1.36 - 1.55)
δ ⁷⁴ Ge _{supply} (‰)	2.24 (2.09 - 2.39)	1.98 (1.85 – 2.13)	1.79 (1.66 - 1.92)	1.78 (1.65 - 1.92)	1.83 (1.7 - 1.97)	1.54 (1.42 - 1.66)	1.79 (1.66 - 1.92)	2.21 (2.07 - 2.36)
δ ⁷⁴ Ge _{FeOx} (‰)	-0.85 (-1.60.11)	-0.42 (-1.02 - 0.01)	-0.73 (-1.350.26)	-0.47 (-0.860.15)	-0.47 (-0.920.12)	-1.29 (-2.080.64)	-0.69 (-1.390.2)	-0.72 (-1.490.03)
∆ ⁷⁴ Ge _{FeOx-diss} (‰)	-3.1 (-3.852.35)	-2.39 (-3.011.95)	-2.51 (-3.152.02)	-2.23 (-2.651.9)	-2.27 (-2.761.91)	-2.83 (-3.642.17)	-2.46 (-3.21.97)	-2.94 (-3.722.24)
δ ⁷⁴ Ge _{inc} (‰)	-0.16 (-1.41 - 0.92)	3.08 (1.37 - 4.67)	1.54 (0.66 - 2.38)	27.2 (13 - 41.46) *	2.76 (1.98 - 3.52)	1.09 (0.67 - 1.4)	1.7 (1.27 – 2.09)	1.78 (1.33 - 2.16)

ue highly uncertain and likely inacurrate due to the extremely low Ge incubation flux (Finc) for this core. This value is therefore excluded from the summary table and figures in the main text

Table S8. Input parameters used to calculate $\delta^{74}Ge_{shelf-PW}$, the average global isotope composition of dissolved Ge in continental margin pore waters.

Parameter	Symbol	Value	Units	Source
Ge concentration in riverine sediments	[Ge] _{UCC}	1.4 ± 0.2	ppm	Rudnick & Gao (2014)
Dissolved riverine Ge flux	FGe^{riv}_{diss}	3.2 ± 1.2	Mmol/y	Baronas et al. (2017)
Fraction Ge released during continental weathering taken up into secondary phases	1- f _{diss} Ge	90-99%		Baronas et al. (2018)
Ge isotope composition of riverine sediments	$\delta^{74}Ge_{\text{lith}}$	0.58 ± 0.21‰		Rouxel & Luais (2017)
bSi dissolving in global continental margin sediments	FSi ^{bSi} shelf	12.7-83.7	Tmol/y	Treguer & De La Rocha (2013)
Detrital rain to the seafloor (San Pedro Basin)	F ^{detrital} SPB	350 ± 30	mg/(m ² d)	Collins et al. (2011)
Reducible Fe(OH) ₃ flux (San Pedro Basin)	F ^{FeOx} SPB	26	µmol/(m ² d)	Leslie et al. (1990)
Ge/Si ratio of biogenic silica	Ge/Si _{bSi}	0.5-0.7	µmol/mol	Rouxel & Luais (2017)
Ge isotope composition of biogenic silica	$\delta^{74}Ge_{bSi}$	2.5 - 3.5‰		Guillermic et al. (2017)

2.2 Figures



Figure S1. Summary of core incubation model results, showing the probability distributions of calculated values for each core.