Supporting Information for

**Stable barium isotope fractionation in pore waters of estuarine sediments**

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**1 Supplementary Tables**

**Table S1.** Salinity, dissolved barium (Ba) concentrations, and their stable Ba isotopic composition (137Ba and 138Ba) data for the bottom waters and pore waters of the Pearl River Estuary in January 2017.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Station | Deptha | Salinity | Ba | 137Ba±2SDb | 138Ba±2SDc | nd |
|  | (cm) |  | (nmol kg-1) | (‰) | (‰) |  |
| P03 | −0.5 | 0.7 | 141.6 | 0.24±0.04 | 0.32±0.05 | 3 |
| 23.1°N |  |  |  | 0.24±0.06 | 0.31±0.08 | 3 |
| 113.5°E | 1 | 0.4 | 231.1 | 0.35±0.04 | 0.47±0.06 | 3 |
| 5.8 me | 2 | 0.6 | 194.2 | 0.34±0.05 | 0.46±0.06 | 3 |
|  | 3 | 0.8 | 201.2 |  |  |  |
|  | 4 | 0.9 | 343.5 | 0.18±0.06 | 0.24±0.08 | 3 |
|  |  |  |  | 0.14±0.01 | 0.18±0.01 | 3 |
|  | 5 | 0.9 | 595.5 | 0.24±0.04 | 0.32±0.06 | 3 |
|  | 6 | 0.9 | 710.3 | 0.21±0.07 | 0.29±0.09 | 3 |
|  |  |  |  | 0.17±0.05 | 0.23±0.06 | 3 |
|  | 8 | 0.9 | 424.8 |  |  |  |
|  | 10 | 0.8 | 960.2 | 0.17±0.05 | 0.22±0.07 | 3 |
|  |  |  |  | 0.18±0.02 | 0.23±0.02 | 3 |
|  | 12 | 0.8 | 1567.2 | 0.10±0.01 | 0.13±0.01 | 3 |
|  |  |  |  | 0.12±0.07 | 0.16±0.10 | 3 |
|  | 15 | 0.7 | 1335.6 | 0.15±0.04 | 0.20±0.05 | 3 |
|  |  |  |  | 0.19±0.03 | 0.25±0.04 | 3 |
| P06 | −0.5 | 8.0 | 211.1 | 0.11±0.03 | 0.14±0.04 | 3 |
| 22.9°N |  |  |  | 0.11±0.07 | 0.15±0.09 | 6 |
| 113.6°E | 1 | 9.0 | 383.6 | 0.38±0.07 | 0.51±0.09 | 3 |
| 21.3 me |  |  |  | 0.42±0.05 | 0.56±0.06 | 3 |
|  | 2 | 9.0 | 865.8 | 0.17±0.01 | 0.22±0.02 | 3 |
|  | 3 | 8.8 | 2123.5 |  |  |  |
|  | 4 | 8.6 | 2723.6 | 0.12±0.01 | 0.15±0.02 | 3 |
|  |  |  |  | 0.13±0.11 | 0.18±0.14 | 3 |
|  | 5 | 8.2 | 3107.1 | 0.09±0.02 | 0.12±0.03 | 3 |
|  |  |  |  | 0.14±0.03 | 0.19±0.04 | 3 |
|  | 6 | 7.7 | 3410.9 | 0.12±0.07 | 0.16±0.10 | 3 |
|  |  |  |  | 0.17±0.04 | 0.23±0.05 | 3 |
|  | 8 | 7.1 | 3207.7 | 0.08±0.05 | 0.11±0.07 | 3 |
|  |  |  |  | 0.07±0.04 | 0.09±0.06 | 3 |
|  | 10 | 6.6 | 2523.3 | 0.12±0.03 | 0.16±0.03 | 3 |
|  |  |  |  | 0.15±0.04 | 0.21±0.05 | 3 |
|  | 12 | 6.2 | 1996.2 | 0.12±0.05 | 0.16±0.07 | 3 |
|  |  |  |  | 0.16±0.10 | 0.21±0.13 | 3 |
|  | 15 | 5.7 | 1717.3 | 0.16±0.06 | 0.22±0.07 | 3 |
|  |  |  |  | 0.13±0.09 | 0.18±0.12 | 3 |
| A03 | −0.5 | 21.2 | 149.8 | 0.15±0.07 | 0.19±0.10 | 6 |
| 22.6°N |  |  |  | 0.17±0.07 | 0.22±0.10 | 3 |
| 113.7°E | 1 | 22.0 | 208.1 |  |  |  |
| 10.5 me | 2 | 22.2 | 220.7 | 0.52±0.04 | 0.69±0.05 | 2 |
|  | 3 | 22.7 | 253.0 | 0.51±0.07 | 0.67±0.09 | 3 |
|  |  |  |  | 0.50±0.10 | 0.67±0.14 | 3 |
|  | 4 | 22.9 | 282.8 | 0.39±0.06 | 0.52±0.08 | 3 |
|  | 5 | 23.0 | 328.7 |  |  |  |
|  | 6 | 23.0 | 330.3 | 0.21±0.08 | 0.28±0.11 | 3 |
|  |  |  |  | 0.19±0.06 | 0.25±0.07 | 3 |
|  | 8 | 23.0 | 310.5 | 0.39±0.07 | 0.52±0.09 | 3 |
|  |  |  |  | 0.39±0.07 | 0.53±0.10 | 3 |
|  | 10 | 22.5 | 364.9 | 0.29±0.02 | 0.38±0.03 | 3 |
|  | 12 | 21.9 | 307.3 | 0.36±0.02 | 0.48±0.03 | 3 |
|  | 15 | 20.9 | 354.7 | 0.20±0.02 | 0.27±0.03 | 3 |
| A09 | −0.5 | 30.9 | 85.1 | 0.25±0.06 | 0.34±0.08 | 6 |
| 22.2°N |  |  |  | 0.29±0.07 | 0.39±0.09 | 3 |
| 113.8°E | 1 | 30.4 | 163.9 | 0.35±0.04 | 0.47±0.06 | 3 |
| 15.3 me | 2 | 30.9 | 178.9 | 0.37±0.07 | 0.49±0.09 | 3 |
|  |  |  |  | 0.35±0.09 | 0.47±0.12 | 3 |
|  | 3 | 31.0 | 167.2 | 0.33±0.02 | 0.44±0.03 | 3 |
|  | 4 | 31.0 | 157.5 | 0.28±0.02 | 0.37±0.03 | 3 |
|  |  |  |  | 0.28±0.08 | 0.38±0.11 | 3 |
|  | 5 | 31.0 | 155.9 |  |  |  |
|  | 6 | 31.0 | 156.6 | 0.24±0.10 | 0.32±0.13 | 3 |
|  |  |  |  | 0.22±0.02 | 0.29±0.03 | 3 |
|  | 8 | 31.0 | 157.2 | 0.27±0.04 | 0.35±0.05 | 3 |
|  | 10 | 31.0 | 166.8 | 0.21±0.09 | 0.28±0.12 | 3 |
|  | 12 | 31.0 | 173.4 | 0.18±0.02 | 0.24±0.02 | 3 |
|  | 15 | 31.0 | 180.6 | 0.18±0.01 | 0.24±0.02 | 3 |
|  |  |  |  | 0.18±0.07 | 0.24±0.09 | 3 |

aDepth of −0.5 cm indicates data of the bottom waters collected at 4.0, 19.0, 7.0, and 12.0 m water depth, respectively, at stations P03, P06, A03, and A09, which were previously published in Cao et al. (2021).

b SD is the standard deviation estimated from the double spike bracketing measurements of a single sample solution.

c 138Ba±2SD is converted from 137Ba±2SD by multiplying by 1.33 assuming mass-dependent fractionation.

d n is the number of double spike bracketing measurements of a single sample solution.

e Data in meter indicate the bottom depth of each sampling station.

**Table S2.** Stable barium isotopic composition (137Ba and 138Ba) data for various Ba carriers of selected sediment samples in the Pearl River Estuary in January 2017.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Station | Depth | Extractant | Ba carrier extracted | 137Ba±2SDa | 138Ba±2SDb | nc |
|  | (cm) |  |  | (‰) | (‰) |  |
| P03 | 12 | 25 mL 2 N NH4Cl | barite | 0.02±0.03 | 0.03±0.05 | 3 |
|  |  |  |  | 0.03±0.03 | 0.04±0.04 | 3 |
|  |  | 25 mL CDBd | Mn and Fe oxides | 0.08±0.00 | 0.11±0.01 | 3 |
| P06 | 6 | 25 mL 2 N NH4Cl | barite | 0.00±0.02 | 0.00±0.03 | 3 |
|  |  |  |  | 0.06±0.06 | 0.08±0.08 | 3 |
|  |  | 25 mL CDBd | Mn and Fe oxides | 0.05±0.06 | 0.07±0.08 | 3 |
| A03 | 1 | 25 mL 2 N NH4Cl | barite | 0.09±0.01 | 0.12±0.01 | 3 |
|  |  | 25 mL CDBd | Mn and Fe oxides | 0.07±0.01 | 0.09±0.01 | 3 |
| A09 | 2 | 25 mL 2 N NH4Cl | barite | 0.00±0.03 | 0.00±0.04 | 3 |
|  |  |  |  | 0.04±0.08 | 0.05±0.11 | 3 |
|  |  | 25 mL CDBd | Mn and Fe oxides | 0.08±0.05 | 0.11±0.06 | 3 |

a SD is the standard deviation estimated from the double spike bracketing measurements of a single sample solution.

b 138Ba±2SD is converted from 137Ba±2SD by multiplying by 1.33 assuming mass-dependent fractionation.

c n is the number of double spike bracketing measurements of a single sample solution.

d CDB is a mixed solution of 0.15 N Na-citrate, 0.5 N NaHCO3 (pH 7.6), and 1.125g Na-dithionite.

**Table S3.** Dissolvednitrate (NO3-), manganese (Mn), iron (Fe), and sulfate (SO42-) concentration and barite saturation state (BSS) data for the pore waters of the Pearl River Estuary in January 2017.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Station | Depth | NO3-a | Mn | Fe | SO42- | BSS |
|  | (cm) | (mol L-1) | (mol L-1) | (mol L-1) | (mmol kg-1) |  |
| P03 | 1 | 5.56 | 10.34 | 2.70 |  |  |
| 23.1°N | 2 | 1.09 | 16.89 | 22.40 | 0.67 | 0.31 |
| 113.5°E | 3 | 1.58 | 22.32 | 70.78 | 0.58 | 0.25 |
| 5.8 mb | 4 | 1.74 | 29.75 | 166.94 | 0.58 | 0.41 |
|  | 5 | 1.92 | 31.14 | 277.08 | 0.48 | 0.60 |
|  | 6 | 1.78 | 39.34 | 247.85 | 0.30 | 0.45 |
|  | 8 | 2.37 | 53.37 | 285.12 | 0.05 | 0.05 |
|  | 10 | 0.00 | 59.90 | 327.09 | 0.06 | 0.13 |
|  | 12 | 0.00 | 82.48 | 319.37 | 0.05 | 0.18 |
|  | 15 | 0.00 | 87.76 | 318.27 | 0.05 | 0.14 |
| P06 | 1 | 62.15 | 75.04 | 0.82 | 6.78 | 1.68 |
| 22.9°N | 2 | 33.87 | 131.70 | 64.95 |  |  |
| 113.6°E | 3 | 1.75 | 149.07 | 480.64 | 5.06 | 7.06 |
| 21.3 mb | 4 | 0.67 | 167.12 | 491.06 | 4.69 | 8.53 |
|  | 5 | 1.46 | 163.68 | 484.03 | 3.19 | 6.86 |
|  | 6 | 0.34 | 148.54 | 450.41 | 1.40 | 3.44 |
|  | 8 | 0.48 | 135.06 | 377.20 | 1.05 | 2.58 |
|  | 10 | 0.00 | 131.60 | 431.09 | 0.39 | 0.80 |
|  | 12 | 0.00 | 123.56 | 372.64 | 0.40 | 0.66 |
|  | 15 | 0.00 | 112.17 | 482.65 | 0.44 | 0.66 |
| A03 | 1 | 10.18 | 14.36 | 0.13 |  |  |
| 22.6°N | 2 | 5.95 | 55.88 | 0.14 | 22.66 | 1.55 |
| 113.7°E | 3 | 1.91 | 64.39 | 0.31 | 17.83 | 1.37 |
| 10.5 mb | 4 | 1.43 | 86.48 | 0.36 | 19.61 | 1.70 |
|  | 5 | 0.29 | 115.54 | 1.14 |  |  |
|  | 6 | 0.77 | 121.25 | 0.56 | 18.61 | 1.84 |
|  | 8 | 0.76 | 124.57 | 0.77 | 16.66 | 1.55 |
|  | 10 | 0.11 | 134.26 | 0.15 | 14.89 | 1.66 |
|  | 12 | 0.12 | 141.64 | 6.52 | 11.69 | 1.13 |
|  | 15 | 0.00 | 152.81 | 36.33 | 8.60 | 1.00 |
| A09 | 1 | 0.93 | 62.81 | 0.13 |  |  |
| 22.2°N | 2 | 0.14 | 89.54 | 0.18 | 25.47 | 1.00 |
| 113.8°E | 3 | 0.00 | 71.03 | 0.49 | 22.59 | 0.83 |
| 15.3 mb | 4 | 0.00 | 60.65 | 21.79 | 21.13 | 0.73 |
|  | 5 | 0.00 | 55.38 | 42.70 | 23.97 | 0.82 |
|  | 6 | 0.00 | 59.26 | 50.78 | 24.94 | 0.85 |
|  | 8 | 0.00 | 47.20 | 73.64 | 24.84 | 0.85 |
|  | 10 | 0.00 | 35.98 | 37.85 | 23.96 | 0.87 |
|  | 12 | 0.00 | 34.17 | 17.06 |  |  |
|  | 15 | 0.00 | 20.21 | 32.94 | 25.59 | 1.01 |

a NO3- values of 0.00 indicate sample concentrations lower than the detection limit of 0.1 mol L-1.

b Data in meter indicate the bottom depth of each sampling station.

**Table S4.** Bulk barium (Ba), manganese (Mn), iron (Fe), and aluminum (Al) concentration data, Ba/Al, Mn/Al, and Fe/Al ratio data, and bulk total organic carbon (TOC) concentration data for the sedimentary solid phase of the Pearl River Estuary in January 2017.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Station | Depth | Ba | Mn | Fe | Al | Ba/Al | Mn/Al | Fe/Al | TOC |
|  | (cm) | (mg g-1) | (mg g-1) | (mg g-1) | (mg g-1) |  |  |  | (wt%) |
| P03 | 1 | 0.38 | 0.59 | 47.22 | 104.01 | 0.0037 | 0.0057 | 0.45 | 1.36 |
| 23.1°N | 2 | 0.35 | 0.53 | 43.00 | 91.81 | 0.0038 | 0.0058 | 0.47 | 1.25 |
| 113.5°E | 3 | 0.34 | 0.57 | 39.49 | 85.41 | 0.0040 | 0.0066 | 0.46 | 1.29 |
| 5.8 ma | 4 | 0.35 | 0.60 | 37.75 | 81.69 | 0.0043 | 0.0073 | 0.46 | 1.15 |
|  | 5 | 0.39 | 0.67 | 42.03 | 91.60 | 0.0043 | 0.0073 | 0.46 | 1.40 |
|  | 6 | 0.38 | 0.66 | 42.82 | 93.39 | 0.0042 | 0.0071 | 0.46 | 1.09 |
|  | 8 | 0.36 | 0.63 | 58.84 | 97.60 | 0.0037 | 0.0064 | 0.60 | 1.21 |
|  | 10 | 0.37 | 0.66 | 38.20 | 82.08 | 0.0045 | 0.0080 | 0.47 | 0.96 |
|  | 12 | 0.40 | 0.73 | 37.06 | 79.85 | 0.0050 | 0.0091 | 0.46 | 0.96 |
|  | 15 | 0.41 | 0.84 | 42.75 | 94.64 | 0.0043 | 0.0089 | 0.45 | 1.14 |
| P06 | 1 | 0.26 | 0.42 | 28.59 | 55.44 | 0.0046 | 0.0076 | 0.52 | 0.65 |
| 22.9°N | 2 | 0.28 | 0.52 | 36.21 | 68.71 | 0.0040 | 0.0075 | 0.53 | 0.58 |
| 113.6°E | 3 | 0.34 | 0.69 | 43.68 | 96.55 | 0.0036 | 0.0071 | 0.45 | 0.87 |
| 21.3 ma | 4 | 0.35 | 0.71 | 45.43 | 102.13 | 0.0034 | 0.0069 | 0.44 | 0.97 |
|  | 5 | 0.28 | 0.59 | 39.43 | 73.23 | 0.0038 | 0.0080 | 0.54 | 0.46 |
|  | 6 | 0.28 | 0.44 | 26.35 | 45.11 | 0.0061 | 0.0098 | 0.58 | 0.36 |
|  | 8 | 0.28 | 0.62 | 35.60 | 57.33 | 0.0049 | 0.0109 | 0.62 | 0.29 |
|  | 10 | 0.34 | 0.59 | 31.99 | 62.51 | 0.0054 | 0.0094 | 0.51 | 0.60 |
|  | 12 | 0.29 | 0.53 | 27.53 | 56.28 | 0.0052 | 0.0093 | 0.49 | 0.99 |
|  | 15 | 0.33 | 0.75 | 40.96 | 82.10 | 0.0040 | 0.0092 | 0.50 | 0.98 |
| A03 | 1 | 0.32 | 0.52 | 40.78 | 94.61 | 0.0034 | 0.0055 | 0.43 | 0.68 |
| 22.6°N | 2 | 0.32 | 0.50 | 41.06 | 94.77 | 0.0034 | 0.0053 | 0.43 | 0.66 |
| 113.7°E | 3 | 0.27 | 0.44 | 32.49 | 74.59 | 0.0036 | 0.0059 | 0.44 |  |
| 10.5 ma | 4 | 0.26 | 0.40 | 31.55 | 72.63 | 0.0036 | 0.0055 | 0.43 | 0.66 |
|  | 5 | 0.34 | 0.54 | 45.47 | 101.47 | 0.0033 | 0.0053 | 0.45 | 0.66 |
|  | 6 | 0.34 | 0.55 | 43.35 | 102.17 | 0.0034 | 0.0054 | 0.42 | 0.64 |
|  | 8 | 0.25 | 0.44 | 30.85 | 71.47 | 0.0036 | 0.0061 | 0.43 |  |
|  | 10 | 0.30 | 0.48 | 37.23 | 87.99 | 0.0034 | 0.0054 | 0.42 | 0.73 |
|  | 12 | 0.35 | 0.56 | 45.55 | 105.61 | 0.0033 | 0.0053 | 0.43 | 0.72 |
|  | 15 | 0.35 | 0.68 | 46.51 | 103.52 | 0.0033 | 0.0066 | 0.45 | 0.94 |
| A09 | 1 | 0.26 | 0.53 | 39.19 | 62.69 | 0.0041 | 0.0084 | 0.63 | 0.73 |
| 22.2°N | 2 | 0.31 | 0.55 | 37.16 | 59.84 | 0.0052 | 0.0092 | 0.62 | 0.70 |
| 113.8°E | 3 | 0.28 | 0.50 | 35.44 | 58.89 | 0.0048 | 0.0086 | 0.60 | 0.56 |
| 15.3 ma | 4 | 0.31 | 0.62 | 41.15 | 73.93 | 0.0042 | 0.0083 | 0.56 | 0.63 |
|  | 5 | 0.28 | 0.55 | 37.05 | 63.19 | 0.0045 | 0.0087 | 0.59 | 0.64 |
|  | 6 | 0.27 | 0.52 | 36.12 | 63.67 | 0.0043 | 0.0082 | 0.57 | 0.69 |
|  | 8 | 0.28 | 0.56 | 38.99 | 65.14 | 0.0042 | 0.0086 | 0.60 | 0.69 |
|  | 10 | 0.28 | 0.51 | 37.68 | 63.46 | 0.0044 | 0.0080 | 0.59 | 0.71 |
|  | 12 | 0.29 | 0.55 | 38.16 | 67.88 | 0.0043 | 0.0082 | 0.56 | 0.76 |
|  | 15 | 0.29 | 0.50 | 37.73 | 66.76 | 0.0043 | 0.0075 | 0.57 | 0.73 |

a Data in meter indicate the bottom depth of each sampling station.