

Barium Concentration and Stable Isotope Ratio Measurements of the Dissolved and Adsorbed Phases from Laboratory Batch Experiments and Himalayan River Samples from 2015-2016: Supporting Documentation

Knight, A. C. G.*¹, Bridgestock, L.^{1,2}, and Tipper, E. T.¹

¹Department of Earth Sciences, University of Cambridge, Cambridge, UK

²School of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK

Contents

1	Introduction	1
2	Laboratory Experiments	2
2.1	Riverine Series	2
2.1.1	Partitioning Subseries	2
2.1.2	Kinetic Subseries	2
2.2	Estuarine Series	2
2.3	Post-Reaction Processes	2
3	Himalayan River Sediment and Water Samples	3
4	Analytical Methods	3
4.1	Displacement of Pre-Existing Adsorbed Barium from Minerals	3
4.2	Mineral-Water Reactions	3
4.3	Extraction of the Adsorbed Phase	4
4.4	Determination of Element Concentrations	4
4.5	Barium Isotope Measurements	4
5	Details of Data Structure	4
5.1	Laboratory Data	5
5.2	Field Data	5

1 Introduction

This dataset contains barium concentration and stable isotope ratio measurements from laboratory batch experiments and Himalayan river samples. Controlled laboratory batch experiments were performed to understand the fractionation of stable barium isotopes during adsorption-desorption reactions between common environmental mineral adsorbents (clay minerals: kaolinite, montmorillonite; iron-oxyhydroxides: goethite, ferrihydrite) and surface waters (river water, groundwater and seawater). Field samples were used to validate the results of the experiments. The riverine suspended sediment and water samples were collected as part of the [PRESSurE project](#). Samples were collected from the surface of the water column at stationary sampling locations along the Saptakoshi and Sunkoshi rivers in Nepal. Further information on collection and processing of field samples is provided with a complimentary dataset [Knight et al., 2024].

*Corresponding author: acgk2@cam.ac.uk

Barium concentration measurements were performed via inductively coupled optical emission spectroscopy (ICP–OES) on an Agilent 5100 and isotope dilution via thermal ionisation mass spectrometry (TIMS) on a Thermo Fischer Scientific Triton Plus. Stable barium isotope ratios were determined via TIMS on a Thermo Fischer Scientific Triton Plus. A double–spike procedure was employed to correct for mass-dependent isotope fractionation. Barium isotope ratios ($\delta^{138/134}\text{Ba}$) are provided relative to the NIST 3104a standard. All analyses and experiments were conducted in the Department of Earth Sciences at the University of Cambridge.

2 Laboratory Experiments

Experiment Series	Experiment Subseries	Primary Variable
Riverine	Partitioning Kinetic	Adsorbent Concentration Reaction Duration
Estuarine	—	Salinity

Table 1: An overview of the laboratory batch experiment series.

2.1 Riverine Series

The riverine series was performed to understand the fractionation of stable barium isotopes in freshwater environments. Batch experiments were performed using terrestrial waters (a river water and groundwater) and common environmental mineral adsorbents (clay minerals: kaolinite, montmorillonite; iron-oxyhydroxides: goethite, ferrihydrite). These experiments were divided into two subseries.

2.1.1 Partitioning Subseries

The partitioning subseries was performed with the aim of understanding how the adsorbent concentration impacts the partitioning of barium between the adsorbed and dissolved phases. Variable mineral concentrations were used whilst maintaining a constant reaction duration (2000 min). The partitioning subseries was a prerequisite for further experiments to ensure a sufficient mass of barium (ca. 200 ng) was present in the adsorbed and dissolved phases for an isotope ratio measurement.

2.1.2 Kinetic Subseries

The kinetic subseries was performed to understand the impact of the reaction duration on the fractionation of barium isotopes. Experiment waters were added at the fixed adsorbent concentrations. The duration of the batch experiments ranges from 10 minutes to just over a month.

2.2 Estuarine Series

The estuarine series was performed to quantify the proportion of barium desorbed from river-derived suspended sediment in estuaries, and the associated fractionation of barium stable isotopes. Clay minerals (kaolinite, montmorillonite) were first equilibrated with a river water analogue (HS50), before being added to seawater. A constant reaction duration of 10 000 min was used with a constant clay concentration. Following the removal of seawater, half the experiments were re-equilibrated in river water (using the same volume as the initial equilibration stage and the same reaction duration).

2.3 Post–Reaction Processes

After each batch experiment, the reacted water and adsorbent were separated via centrifugation. The adsorbed elements were then displaced from the surface of the adsorbent (section 4.3). Adsorbed and dissolved phases were measured for barium concentrations (section 4.4) and isotope ratios (section 4.5).

3 Himalayan River Sediment and Water Samples

A total of 12 river water samples were selected from a more extensive time series of samples from the Sunkoshi and Saptakoshi rivers in Nepal as part of the [PRESSurE project](#). The river catchments are significant source areas of sediment and water for the Ganges-Brahmaputra system. Hydrological stations were installed on the rivers draining the epicentral area following the April 2015 Gorkha earthquake. The stations were operated for four consecutive monsoon seasons. All stations were equipped with a river stage height monitoring system and manned daily for sampling. Samples were taken at each location by a trained station manager using a USGS DH-48 depth-integrating fish sampler deployed with a rope from a bridge. Samples were collected during the pre-monsoon and monsoon (May–Sep) on a daily basis. During the post-monsoon and dry-season (Oct–Apr) samples were collected twice a week. The collected samples only integrate the first meter of the water column, as the fast velocity of the river ($>2\text{ ms}^{-1}$) prevented the sampler from being descended to the full depth. Each sample is composed of 6 sequential 500 mL water samples that were combined before filtering. Separation of the sediment and water was achieved via in-situ filtering through $0.22\text{ }\mu\text{m}$ polyethersulfone (PES) membrane filters.

Samples were manually scraped from the filter papers and oven-dried at $40\text{ }^\circ\text{C}$, before being weighed. Filtered water samples were acidified using 17M single-distilled HNO_3 to a pH of less than 2. Adsorbed cations were displaced from the sediment using two separate procedures: 1.0 M NH_4Cl or calcite-saturated 0.0167 M hexaamminecobalt (III) chloride (CoHex). A volume of 12.0 mL of NH_4Cl or CoHex was added to 0.200 g of suspended sediment in an acid-cleaned polypropylene centrifuge tube. The tube was then manually shaken, before being placed in an ultra-sonic bath for 20 min to ensure the sediment and reagent were well-mixed. The centrifuge tube was then placed on a shaker table for a period of 2 hr. The samples were centrifuged at 3100 g for 30 min to separate the sediment and supernatant. The supernatant was subsequently transferred via pipette into a separate acid-cleaned centrifuge tube. Another 12.0 mL of reagent was then added to the same sediment sample, and the whole process was repeated to maximise the desorption of adsorbed cations. Throughout the procedure, all supernatants were immediately filtered through $0.22\text{ }\mu\text{m}$ PES membrane filters, to ensure the effective separation of the sediment and supernatant. Barium concentrations and isotope ratios were determined via the same methods as the laboratory samples (section 4.4, section 4.5).

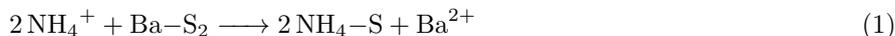
Further information on the collected field samples can be in the complimentary data set [Knight et al., 2024].

4 Analytical Methods

All analytical procedures were performed in clean laboratories designed for trace metal isotope analyses at the Department of Earth Sciences (University of Cambridge) under controlled conditions ($20\text{ }^\circ\text{C}$, 1 atm.). All reagents used were at room temperature unless specified.

4.1 Displacement of Pre-Existing Adsorbed Barium from Minerals

Kaolinite (KGa-2) and montmorillonite (SWy-2) used for the experiments were sourced from natural clay deposits and therefore adsorbed barium was already present. Repeated additions of 1.0 M NH_4Cl (Puratronic™, 99.999% trace metal basis) were performed to desorb the Ba^{2+} into solution:



Where S denotes a negatively charged surface site. The adsorbents were first weighed into polypropylene centrifuge tubes, followed by the addition of 1.0 M NH_4Cl . The centrifuge tubes were shaken to mix the adsorbent and NH_4Cl , before being placed in an ultrasonic bath for 30 min. The centrifuge tubes were then placed on a shaker table for 2 hr to allow the ion exchange reactions to proceed. Separation of the adsorbent from the supernatant was achieved by centrifuging the tubes at 3100 g for 30 min. The supernatants were transferred into separate polypropylene centrifuge tubes by pipette and immediately filtered through $0.22\text{ }\mu\text{m}$ PES filters. The same volume and concentration of NH_4Cl was then added to the adsorbent and the process was repeated three times to maximise the extraction of reversibly adsorbed barium, whilst minimising the barium blank from the reagent. The treated adsorbents were washed in ultrapure water three times to remove any remaining NH_4Cl .

4.2 Mineral–Water Reactions

Waters were added to mineral adsorbents in polypropylene centrifuge tubes. Several procedures were employed to ensure that the adsorbent and the water remained thoroughly mixed for the duration of the experiment.

For experiment durations less than 40 min, only manual shaking was performed to allow sufficient time for centrifugation. For experiment durations greater than 40 min, centrifuge tubes were first ultra-sonicated in a bath of ultrapure water for 20 min, before being placed on a shaker table for the remainder of the reaction. The supernatant and adsorbent were separated via centrifugation at 3100 g for 30 min, followed by immediate filtration through 0.22 μm PES membrane filters. The termination of the reaction was determined from the time of physical separation between the water and the adsorbent. Reacted waters were transferred to clean polypropylene centrifuge tubes.

4.3 Extraction of the Adsorbed Phase

The displacement of adsorbed barium cations from adsorbent surfaces was achieved following a method identical to the initial cleaning procedure used in section 4.1. This occurred immediately following the separation of the water and the adsorbent. All water and leachates were refrigerated at 5 $^{\circ}\text{C}$ prior to analyses.

4.4 Determination of Element Concentrations

Element concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an Agilent 5100 at the Department of Earth Sciences (University of Cambridge). Synthetic calibration lines, produced with certified standards, were used to calibrate element concentrations. Samples, external standards and calibration lines were matrix-matched prior to analyses. Pressure-drift during measurement sessions was prevented by using an argon gas humidifier and by diluting 1.0 M NH_4Cl samples to a concentration of 0.04 M NH_4Cl . Barium concentrations were independently determined via isotope dilution from thermal ionisation mass spectrometry (TIMS) measurements using a barium double spike [Rudge et al., 2009]. Repeated measurements of external standards (SPS-SW2 and SLRS-6 surface water standards) provided an uncertainty of 7% (2σ) for barium concentrations determined by ICP-OES and 2% (2σ) for TIMS (TIMS external standards: NIST 3104a—a barium carbonate standard reference material from the National Institute of Standards and Technology (NIST), and NBS 127—a barite standard reference material).

4.5 Barium Isotope Measurements

The barium isotopic composition of the dissolved and adsorbed phases were determined via TIMS on a Thermo Fischer Scientific TRITON Plus instrument at the Department of Earth Sciences, University of Cambridge. An aliquot of each sample was transferred to a clean polytetrafluoroethylene (PTFE) beaker containing ca. 200 ng. A known quantity of double spike solution (enriched in the ^{130}Ba and ^{135}Ba isotopes) was added to each sample to correct for the mass-dependent fractionation of barium isotopes during the chemical purification and instrument analysis stages. The samples were then shaken, before being refluxed on a hot plate at 80 $^{\circ}\text{C}$ for 24 hr to allow the sample-spike mixture to equilibrate. Co-precipitation with CaCO_3 (induced by the addition of a 1.0 M Na_2CO_3 solution) was necessary for seawater samples to increase the ratio of barium to high-concentration elements (Na, Mg, K) prior to column elution chromatography [Foster et al., 2004]. All samples were treated to remove NH_4Cl which can interfere with the ionisation and evaporation during TIMS measurements. The samples were initially evaporated before the addition of 1 mL of aqua regia. Refluxing of samples was then performed on a hot plate at 140 $^{\circ}\text{C}$ for 24 hr, before being evaporated to dry salts on a hot plate at 80 $^{\circ}\text{C}$. This process was repeated three times. Single-distilled 3.0 M HCl (1 mL) was then used to re-dissolve the samples. A two-stage ion exchange chromatography column, adapted from Hsieh and Henderson [2017], was performed to separate barium from other matrix cations. Following ion elution chromatography, the samples were evaporated and re-dissolved in ultrapure 9.8 M H_2O_2 (99.9999% trace metal basis; Sigma Aldrich) to oxidise any organic matter, before being dried and loaded onto zone-refined Re filaments (99.999% purity zone refined; H CROSS). The combined ion exchange chromatography and TIMS procedural blank was 0.07 ± 0.06 ng ($\mu \pm 2\sigma$, $n = 6$), which is $<1\%$ of the processed sample mass. The measured 1.0 M NH_4Cl blank was 3.23 ± 0.02 ng mL $^{-1}$ ($\mu \pm 2SE$) resulting in a maximum blank contribution of 4%. Two standard reference materials (NIST 3104a and NBS 127) were measured repeatedly during each analysis session over a period of three years to determine the long-term accuracy and precision of the method. This provided a minimum uncertainty of 0.03 ‰ for all isotopic measurements.

5 Details of Data Structure

Two separate files comma separated value (csv) are included in the repository. Balsoexperimentdata.csv contains the experiment data, whereas BaIsoNepalRivers.csv contains the field data. Fields which are not applicable are labelled NA. Samples or data which are available but not measured are labelled NM.

5.1 Laboratory Data

Column Name	Description	Unit
ID	ID of the individual experiment	N/A
Series	The experiment series	N/A
Subseries	The experiment sub-series	N/A
Water	Water	N/A
Adsorbent	Mineral adsorbent	N/A
Adsorbent_ID	Mineral Adsorbent ID	N/A
Water_mass	Mass of water	g
Adsorbent_mass	Mass of adsorbent	mg
Reaction_duration	Reaction duration	min
Pretreatment	Pre-treatment with 1 M NH ₄ Cl	Yes/No
Ba_diss	Barium concentration, dissolved	$\mu\text{mol L}^{-1}$
Ba_ad	Barium concentration, adsorbed	$\mu\text{mol L}^{-1}$
d138Ba_diss	Barium stable isotope ratio, dissolved	‰
d138Ba_ad	Barium stable isotope ratio, adsorbed	‰

Table 2: Table parameters, abbreviations, and units for the data file BaIsoExperimentData.csv.

5.2 Field Data

Column Name	Description	Unit
ID	ID of the sample	N/A
Date	Date of sample collection	DD/MM/YYYY
River	River name	N/A
Loc	Stationary sampling location	N/A
SSC	Suspended sediment concentration	g L^{-1}
Discharge	Riverine discharge	$\text{m}^3 \text{s}^{-1}$
Ba_diss	Barium concentration, dissolved	$\mu\text{mol L}^{-1}$
Ba_ad	Barium concentration, adsorbed	$\mu\text{mol L}^{-1}$
d138Ba_diss	Barium stable isotope ratio, dissolved	‰
d138Ba_ad	Barium stable isotope ratio, adsorbed	‰

Table 3: Table parameters, abbreviations, and units for the data file BaIsoNepalRivers.csv.

References

- Deborah A Foster, Michael Staubwasser, and Gideon M Henderson. 226Ra and Ba concentrations in the Ross Sea measured with multicollector ICP mass spectrometry. *Marine Chemistry*, 87(1):59–71, June 2004. ISSN 0304-4203. doi: 10.1016/j.marchem.2004.02.003. URL <https://www.sciencedirect.com/science/article/pii/S0304420304000520>.
- Yu-Te Hsieh and Gideon M. Henderson. Barium stable isotopes in the global ocean: Tracer of Ba inputs and utilization. *Earth and Planetary Science Letters*, 473:269–278, September 2017. ISSN 0012-821X. doi: 10.1016/j.epsl.2017.06.024. URL <https://www.sciencedirect.com/science/article/pii/S0012821X17303345>.
- Alasdair Knight, Christoff Andermann, Edward Tipper, Ambika Sitaula, and Basanta Adhikari. PRESSurE River Chemistry Time Series (Nepal), 2024. URL <https://dataservices.gfz-potsdam.de/panmetaworks/showshort.php?id=046c4508-dbc9-11ee-967a-4ffbf06208e>.
- John F. Rudge, Ben C. Reynolds, and Bernard Bourdon. The double spike toolbox. *Chemical Geology*, 265(3):420–431, July 2009. ISSN 0009-2541. doi: 10.1016/j.chemgeo.2009.05.010. URL <https://www.sciencedirect.com/science/article/pii/S0009254109002319>.