ANNUAL REPORT ON GEOTRACES ACTIVITIES IN UNITED KINGDOM

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

Bridgestock and co-authors investigated the transport of barium into the ocean from rivers. Combining data on barium and barium isotopes across a set of river / estuarine systems, the underlying processes and an estimate of the net barium flux is derived. Desorption of barium from particles in estuaries emerged as the major driver of the changes in barium isotope changes. This then modifies the isotope composition of net riverine dissolved Ba fluxes that reach the ocean. River dissolved loads are also systematically offset to higher barium isotope values than the major oceanic sink: via burial of BaSO4 in marine sediments, which represents an apparent imbalance in the modern marine Ba isotope budget. Accounting for modification of the $\delta^{138/134}$Ba of net riverine Ba fluxes to the ocean by estuarine processes is likely to play a key role towards balancing the modern marine Ba isotope budget and that river barium isotope values do not represent the net inputs to the ocean.

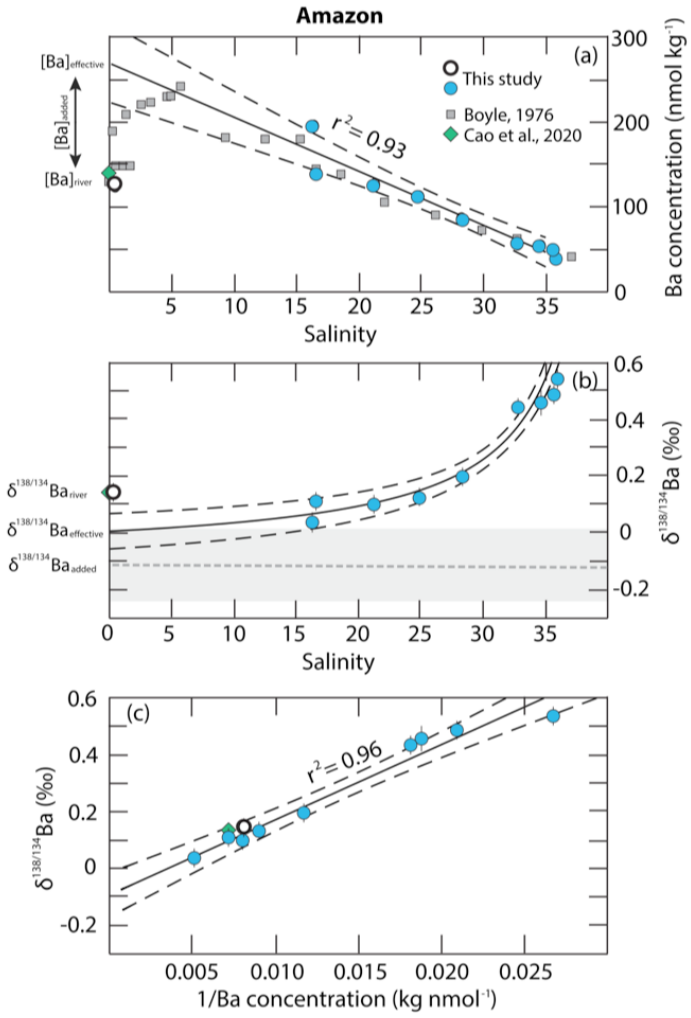

Fig. 2. Relationships between salinity, Ba concentrations and $\delta^{138/134}$Ba values in the Amazon River estuary. Solid black lines represent conservative mixing relationships, defined by linear regressions between Ba concentration and salinity (panel a) and $\delta^{138/134}$Ba and 1/Ba concentration (panel c) with dashed lines showing 95% confidence intervals. The mixing relationship in panel (b) is defined by combining the linear regressions in panels (a) and (c). Open circle denotes the Amazon River water endmember, which is omitted from regressions to define mixing relationships. Literature data are displayed by grey squares (Boyle, 1976) and the green diamond (Cao et al., 2020). In panel (b) the horizontal grey dashed lines show the $\delta^{138/134}$Ba value estimated for the Ba added to the dissolved riverine flux by estuarine processes, with uncertainties shown by the grey shaded intervals.

Paper: L. Bridgestock, Nathan, J., Paver, R., Hsieh, Y-T. Porcelli, D., Tanzil, J., Holdship, P., Carrasco, G., Annammala, K. V., Swarzenski, P. W., and Henderson, G. M., 2021, Estuarine processes modify the isotope composition of dissolved riverine barium fluxes to the ocean, *Chemical Geology*, 579, doi:10.1016/j.chemgeo.2021.120340

PhD student Daniela Koenig (supervised by Alessandro Tagliabue) published the first ever global iron isotope model in collaboration with Tim Conway, Michael Ellwood and Will Homoky. In this work, the relative contribution of external inputs and internal cycling to the distribution of iron isotopes was determined for the first time using models and observations. Overall, both distinct external source endmembers and fractionation during organic complexation and phytoplankton uptake are required to reproduce $\delta^{56}Fe_{diss}$ observations along GEOTRACES transects., with the $\delta^{56}Fe_{diss}$ distributions through the water column resulting from regional imbalances of remineralization and abiotic removal processes. $\delta^{56}Fe_{diss}$ signals from hydrothermal or sediment sources could not be reproduced by adjusting $\delta^{56}Fe$ endmember values., which highlights the importance of additional processes governing the exchange and/or speciation of Fe supplied by these sources to the ocean.

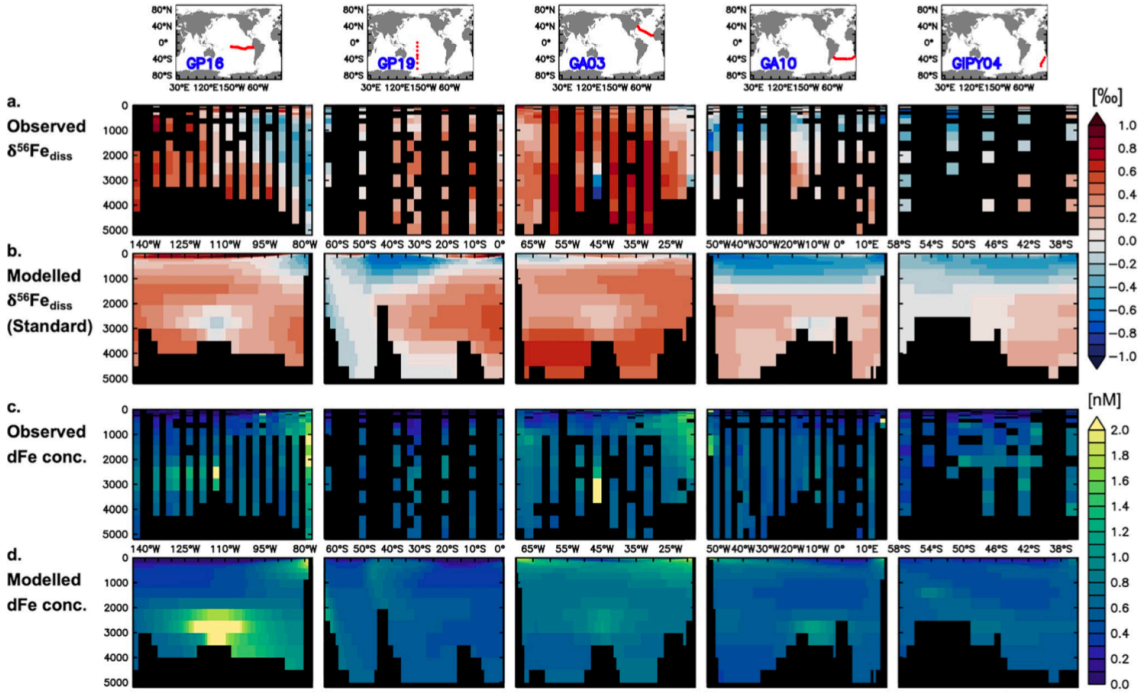

Figure 4. Observed (a, c) and standard experiment (b, d) $\delta^{56}Fe_{diss}$ (a, b; ‰) and dFe concentration (c, d; µmol m^{-3}) for five GEOTRACES sections. Data are binned at model depths; model output is extracted at the same coordinates as observations, and on interpolated coordinates in between.

Paper: König, D., T. M. Conway, M. J. Ellwood, W. B. Homoky, and A. Tagliabue, Constraints on the Cycling of Iron Isotopes From a Global Ocean Model, *Global Biogeochemical Cycles*, *35*(9), doi:10.1029/2021gb006968. 2021.

GEOTRACES or GEOTRACES relevant cruises

Homoky (Leeds) obtained new porewater and sediment samples collected for TEI analyses from RV Pelagia in July 2021 in support of the GEOTRACES process cruise, MetalGate (Lead PI R. Middag, NIOZ)

Annett (Southampton) participated (along with PhD student) in the MetalGate process study

New projects and/or funding

- Royal Society funded workshop on Marine Microbes in a Changing Climate organised by A Tagliabue, with T Mock, J Robidart and P Sanchez-Baracaldo 12-13 September 2022 with links to Biogeotraces and new BioGeoSCAPES programme
- NERC funded project: A new perspective on ocean photosynthesis (N-POP) Lohan, Bibby & Mark (Southampton)
- Annett (Southampton) obtained funding as CoI for beamtime at the European Synchrotron Research Facility to anaylyse samples from the MetalGate GEOTRACES process study

Outreach activities conducted (please list any outreach/educational material available that could be shared through the GEOTRACES web site)

Luke Bridgestock gave an online symposium talk and a tutorial on the importance of marine trace metal cycles and the GEOTRACES Program to students participating in the African Regional Graduate Network in Oceanography Academy, hosted in Namibia. The tutorial involved the students interpreting data from the GEOTRACES data product using webODV to answer questions about sources of Fe to the ocean, and human perturbation to the marine Pb cycle.

Other GEOTRACES activities

- Maeve Lohan (University of Southampton, co-chair) and Tina van de Flierdt (Imperial College London, committee member) attended 6 x virtual Standards & Intercalibration (S&I) meetings
- Maeve Lohan (University of Southampton, co-chair), Tina van de Flierdt (Imperial College London) and Alessandro Tagliabue (University of Liverpool) attended the virtual annual SSC meeting.
- Alessandro Tagliabue (University of Liverpool, co-chair) and Maeve Lohan attended 4 x virtual DMC meetings

Data Products

New iron climatology data product: Nicolas Cassar, Yibin Huang, & Alessandro Tagliabue. (2022). Data-driven modeling of dissolved iron in the global ocean., https://doi.org/10.5281/zenodo.6385044

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Gregory F.de Souza, Derek Vance, Matthias Sieber, Tim M. Conway, Susan H. Little (2022) Re-assessing the influence of particle-hosted sulphide precipitation on the marine cadmium cycle, Geochimica et Cosmochimica Acta 322, Pages 274-296
- Igor Živković, Matthew P. Humphreys, Eric P. Achterberg, Cynthia Dumousseaud, E. Malcolm S. Woodward, Natalia Bojanić, Mladen Šolić, Arne Bratkič, Jože Kotnik, Mitja Vahčič, Kristina Obu Vazner, Ermira Begu, Vesna Fajon, Yaroslav Shlyapnikov, and Milena Horvat. (2022). Enhanced mercury reduction in the South Atlantic Ocean during carbon remineralization. Marine Pollution Bulletin, Volume 178, May 2022, https://doi.org/10.1016/j.marpolbul.2022.113644.
- Sofen, L.E., Antipova, O.A., Ellwood, M.J., Gilbert, N.E., Gilbert, N.E., LeClier, G.R., Lohan, M.C., Mahaffey, C., Mann, E.L., Ohnemus, D.C., Wilhelm, S.W. & Twining

(2022) Trace metal contents of autotrophic flagellates from contrasting open-ocean ecosystems. Limnology & Oceanography Letters doi.org/10.1002/lol2.10258

- Wang, W., Lough, A., Loahn, M.C., Connelly, D.P., Cooper, M.J., Milton, A., Chavagnac, V., Castillo, A. & James, R.H (2021) Behavior of iron isotopes in hydrothermal systems: Beebe and Von Damm vent fields on the Mid-Cayman ultraslow-spreading ridge. EPSL doi.org/10.1016/j.epsl.2021.117200
- Artigue, L., Wyatt, N.J., Lacan, F., Mahaffey, C. & Lohan, M.C. (2021) The importance of water mass transport and dissolved-particulate interactions on the aluminium cycle in the subtropical North Atlantic. GBC doi.org/10.1029/2020GB006569
- Zhu, K., Birchill, A.J., Milne, A., Ussher, S., Humphreys, M.P., Carr, N., Mahaffey, C.Lohan, M.C., Achterberg, E.P. & Gledhill (20210 Equilibrium calculations of iron speciation and apparent iron solubility in the Celtic Sea at ambient seawater pH using the NICA-Donnan model. Mar. Chem 237 doi.org/10.1016/j.marchem.2021.104038
- Cerdan-Garcia, E., Baylay A., Polyviou D., Woodward E.M.S., Wrightson L., Mahaffey C., Lohan M.C., Moore C.M., Bibby T.S., Robidart J.C. (2021). Transcriptional responses of Trichodesmium to natural inverse gradients of Fe and P availability. ISME Journal. https:doi.org/10.1038/s41396-021-01151-1
- Delvigne, C., Guihou, A., Schuessler, J. A., Savage, P., Poitrasson, F., Fischer, S., ... & Basile-Doelsch, I. (2021). Silicon Isotope Analyses of Soil and Plant Reference Materials: An Inter-Comparison of Seven Laboratories. Geostandards and Geoanalytical Research, 45(3), 525-538.
- Sean Selzer, Amber L. Annett, William B. Homoky, RaDeCC Reader: Fast, accurate and automated data processing for Radium Delayed Coincidence Counting systems, Computers & Geosciences, https://doi.org/10.1016/j.cageo.2021.104699.
- Farmer, J. R., Hertzberg, J. E., Cardinal, D., Fietz, S., Hendry, K., Jaccard, S. L., ... & GEOTRACES-PAGES Biological Productivity Working Group Members. (2021). Assessment of C, N, and Si isotopes as tracers of past ocean nutrient and carbon cycling.
- Ward, J., Hendry, K., Arndt, S., Faust, J. C., Freitas, F. S., Henley, S. F., ... & Pickering, R. A. (accepted). Stable silicon isotopes uncover a mineralogical control on the benthic silicon cycle in the Arctic Barents Sea. Geochim. Cosmochim. Acta.
- Hatton, J. E., Hendry, K. R., Hawkings, J., Wadham, J. L., Benning, L. G., Blukis, R., ... & Wang, T. (2021). Physical weathering by glaciers enhances silicon mobilisation and isotopic fractionation. Geochemical Perspectives Letters, 19, 7-12.
- Cassarino, L., Curnow, P., & Hendry, K. R. (2021). A biomimetic peptide has no effect on the isotopic fractionation during in vitro silica precipitation. Scientific reports, 11(1), 1-10.
- Murphy, M. J., Hendry, K., & Opfergelt, S. (2021). Novel Isotope Systems and Biogeochemical Cycling During Cryospheric Weathering in Polar Environments. Frontiers in Earth Science, 9, 88.
- L. Bridgestock, J. Nathan,Y-T. Hsieh, P. Holdship, D. Porcelli, P. S. Andersson and G. M. Henderson, 2021, Assessing the utility of barium isotopes to trace Eurasian riverine freshwater inputs to the Arctic Ocean, Marine Chemistry, 236, doi:10.1016/j.marchem.2021.104029
- L. Bridgestock, Nathan, J., Paver, R., Hsieh, Y-T. Porcelli, D., Tanzil, J., Holdship, P., Carrasco, G., Annammala, K. V., Swarzenski, P. W., and Henderson, G. M., 2021, Estuarine processes modify the isotope composition of dissolved riverine barium fluxes to the ocean, Chemical Geology, 579, doi:10.1016/j.chemgeo.2021.120340
- Hsieh, Y.-T., R. Paver, J. T. I. Tanzil, L. Bridgestock, J. N. Lee, and G. M. Henderson (2022), Multi-colony calibration of barium isotopes between shallow-water coral

skeletons and in-situ seawater: Implications for paleo proxies, Earth and Planetary Science Letters, 580, doi:10.1016/j.epsl.2022.117369.

- Tagliabue, A, A. R. Bowie, T. Holmes, P. Latour, P. van der Merwe, M. Gault-Ringold, K. Wuttig, and J. A. Resing (2022), Constraining the Contribution of Hydrothermal Iron to Southern Ocean Export Production Using Deep Ocean Iron Observations, Frontiers in Marine Science, 9, doi:10.3389/fmars.2022.754517.
- Medieu, A., et al. (incl. A Tagliabue), Evidence that Pacific tuna mercury levels are driven by marine methylmercury production and anthropogenic inputs, Proceedings of the National Academy of Sciences of the United States of America, 119(2), doi:10.1073/pnas.2113032119. 2022
- König, D., T. M. Conway, M. J. Ellwood, W. B. Homoky, and A Tagliabue, Constraints on the Cycling of Iron Isotopes From a Global Ocean Model, Global Biogeochemical Cycles, 35(9), doi:10.1029/2021gb006968. 2021.
- Hamilton, D. S., et al. (incl. A Tagliabue), Earth, Wind, Fire, and Pollution: Aerosol Nutrient Sources and Impacts on Ocean Biogeochemistry, Annual review of marine science, doi:10.1146/annurev-marine-031921-013612. 2021
- Shaked, Y., B. S. Twining, A Tagliabue, and M. T. Maldonado, Probing the Bioavailability of Dissolved Iron to Marine Eukaryotic Phytoplankton Using In Situ Single Cell Iron Quotas, Global Biogeochemical Cycles, 35(8), doi:10.1029/2021gb006979. 2021
- Homoky, W. B., T. M. Conway, S. G. John, D. Konig, F. Deng, A Tagliabue, and R. A. Mills, Iron colloids dominate sedimentary supply to the ocean interior, Proceedings of the National Academy of Sciences of the United States of America, 118(13), doi:10.1073/pnas.2016078118. 2021
- González-Santana, D., M. González-Dávila, M. C. Lohan, L. Artigue, H. Planquette, G. Sarthou, A Tagliabue, and J. M. Santana-Casiano, Variability in iron (II) oxidation kinetics across diverse hydrothermal sites on the northern Mid Atlantic Ridge, Geochimica et Cosmochimica Acta, 297, 143-157, doi:10.1016/j.gca.2021.01.013. 2021
- Huang, Y., Tagliabue, A., & Cassar, N. (2022). Data-driven modeling of dissolved iron in the global ocean. Frontiers in Marine Science. doi:10.3389/fmars.2022.837183

Completed GEOTRACES PhD or Master theses (please include the URL link to the pdf file of the thesis, if available)

- Hollie Packman, PhD thesis, Imperial College London, “Stable isotope tracing of trace metals from anthropogenic and natural sources to the ocean”. Completed April 2022.
- Mr Sean Selzer, University of Oxford, submitted a D.Phil thesis developed from the GA13 FRidge transect, entitled "Behaviour of Radium, Barium and the Rare Earth Elements in Mid-Atlantic Ridge Hydrothermal Plumes”.

GEOTRACES presentations in international conferences

- Goldschmidt conference; keynote: The unreconciled significance of terrigenous iron supply for the ocean carbon cycle, William B. Homoky, University of Leeds
- Hoffman, C., Toner, B., Lough, A., Lohan, M.C., Lang, S., Moore, L., Monreal, P., Tagliabue, A., Resing, J., Bundy, R. (2022) Important role for microbially produced siderophores in the cycling of hydrothermal iron. Ocean Sciences
- Jones, R., Meredith, M., Lohan, M.C, Flanagan, O., Vora, M. Sourse, J., Annett, A. (2022) Tracing the impact of glacial meltwater upon fjord macronutrients at the West

Antarctic Peninsula using stable oxygen isotopes and short-lived radium isotopes. Ocean Sciences

- Twining, B., Sofen, L.E., Antipova, O.A., Ellwood, M.J., Gilbert, N.E., Gilbert, N.E., LeClier, G.R., Lohan, M.C., Mahaffey, C., Mann, E.L., Ohnemus, D.C., Wilhelm, S.W (2022). Metal contents of autotrophic flagellates from contrasting open-ocean ecosystems
- Flanagan, O., Annett, A., Sherrell, R.M., Fitzsimmons, J., Ohnemus, D.C, & Lohan, M.C. (2021) Controls on the distribution of particulate trace metals accoss the Western Antarctic Peninsula Shelf. Goldschmidt
- González-Santana, D., González-Dávila, M., Lohan, M.C., Artigue, L., Planquette, H., Sarthou, G., Tagliabue, A., Santana-Casiano J.M. (2021), Variability in iron (II) oxidation kinetics across diverse hydrothermal sites on the northern Mid Atlantic Ridge. Goldschmidt

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