#### ANNUAL REPORT ON GEOTRACES ACTIVITIES IN UNITED KINGDOM

April 1st, 2020 to April 30th, 2021

#### New scientific results

#### • Deep sea lithogenic weathering a source of iron colloids for the ocean

Homoky and co-workers (2021, see reference below) determined the isotope composition of dissolved iron (Fe) profiles in shallow surface sediments of the South Atlantic Uruguayan margin, from shelf-top to abyssal floor. They confirmed the presence of lithogenic iron isotope compositions in the oxidising zones of sediment porewaters, and further showed that these signatures are uniquely attributed to the presence of iron colloids (20-200nm). An isotopically constrained porewater mass-balance model is used to show that reductive dissolution and oxidation cannot fully account for the production of iron colloids, whereas non-reductive weathering of lithogenic phases and the production of nano-scale Fe organo-minerals can explain these data. An exchangeable inventory of dissolved iron in porewater is compiled for the ocean depths based on all the sites currently observed and suggests that sedimentary supply to the deep ocean interior will be dominated by organo-mineral iron colloids bearing lithogenic isotope signatures.



**Figure 1:** Characterising the exchangeable source of dissolved iron in shallow porewaters beneath the open ocean. (A) Data markers correspond to measured surface (0-1 cmbsf) values compiled from sediments of the western South Atlantic (this study), the eastern South Atlantic, Cape margin<sup>1</sup>, the North Pacific, Oregon and California margins and Borderland Basins<sup>2,3</sup>, the North Atlantic, Celtic Sea<sup>4</sup>, and the Southern Ocean, Crozet Island abyss<sup>2</sup>. The measured surface inventory of porewater dFe is illustrated by the size of data symbols, and the relative abundance of colloidal iron in porewater is indicated by the colour scale – except for sites with symbols in grey, where dFe speciation was not determined (n.d.). (B) Illustrated summary of key factors attributed to colloidal Fe production, and the nature of its distribution so far observed. Additional data sources used in this figure: [1] Homoky et al. Nature Comms, 4, 2143 (2013); [2] Homoky et al. Geology 37, 751-754 (2009); [3] Severmann et al. Geochimica et Cosmochimica Acta 74, 3984-4004 (2010); [4] Klar et al. Biogeochemistry 135, 49–67 (2017).

Homoky et al. (2021), PNAS.

#### • An unknown source of reactor radionuclides in the Baltic Sea

The combinations of multi-isotope fingerprints from uranium and iodine isotope indicates a source of reactor <sup>236</sup>U in the Baltic Sea in addition to inputs from the two European reprocessing plants and global fallout. This additional reactor <sup>236</sup>U may come from unreported discharges from Swedish nuclear research facilities as supported by high <sup>236</sup>U levels in sediment nearby Studsvik, or from accidental leakages of spent nuclear fuel disposed on the Baltic seafloor.



**Figure 2:** <sup>236</sup>U/<sup>238</sup>U increases in the Baltic, demonstrating addition of reactor <sup>236</sup>U. *Qiao et al. (2021), Nature Comms.* 

# • Updated compilation of the global continental and marine lithogenic neodymium isotopic measurements

The work proposed by Robinson and co-workers (2021, see reference below) was more than



expected! Using an upto-date compilation of published terrestrial and marine sedimentary Nd isotopic measurements, they constructed a high resolution, gridded, global maps that characterise the Ndisotopic signature (ENd) of the continental and seafloor margins sediment. This ล considerable of Ndimprovement source identification compared to the seminal work of Jeandel et al. (2007,see reference below). Among others, Robinson's study provides a refined map of the seafloor sediment  $\varepsilon$ Nd, based on measurements from pore waters and deep seafloor detrital samples. Such better characterisation of global  $\varepsilon$ Nd distributions at the entire sediment-ocean interface, together with a refined description of the  $\varepsilon$ Nd signature of the fields surrounding the northern North Atlantic Ocean, is a rich resource for further modelling.

**Figure 3:** These maps display the location and  $\varepsilon$ Nd of the samples assembled in the updated compilation of over 5000 published terrestrial and marine sedimentary Nd isotopic measurements presented here, (a). From this database, we construct high resolution, gridded, global maps that characterise the Ndisotopic signature of all continental margins and seafloor sediment, e.g. (b). These maps are especially designed for investigating marine Nd cycling, particularly to aid in constraining the magnitude and  $\varepsilon$ Nd from sediment-water interaction and how this influences the distribution of marine  $\varepsilon$ Nd. Thus, the new compilation and gridded datasets offer a concrete way forward to improve the application of Nd isotopes as a useful tracer of ocean circulation.

Robinson et al. (2021), Chem. Geol.

## • Co-occurrence of Fe and P stress in natural populations of the marine diazotroph Trichodesmium

Trichodesmium's (cynaobacteria that fixes nitrogen) colonial lifestyle likely produces challenges for dissolved Fe and P acquisition, which must be compensated for by production of multiple nutrient transport systems, such as for particulate iron and organic phosphorous, at a considerable cost. Metaproteomic observations and accompanying nutrient uptake model demonstrate that Fe and P co-stress is the norm rather than the exception.



**Figure 4:** (A) Relative abundance of iron stress protein IdiA (A) and phosphate stress protein SphX (B). IdiA and SphX were among the most abundant proteins in the entire dataset. Error bars are one standard deviation on the mean when multiple samples were available. Dashed lines represent average values across the dataset. (C) Relative abundance of IdiA (orange) and SphX (blue) overlaid on the sampling locations. Held et al. (2020), Biogeosciences.

### • Tropical Pacific fisheries affected by uncertainty in phytoplankton iron uptake.

Tagliabue et al. (2020), Global Change Biol.

### **GEOTRACES or GEOTRACES relevant cruises**

• PhD student Isobel Turnbull (U Plymouth) participated in the French GEOTRACES cruise SWINGS (GS02).

### New projects and/or funding

• Gideon Henderson (U Oxford) and Alex Baker (UEA) won funding for their project 'Atmospheric fluxes of mineral dust-derived soluble trace elements to the ocean using thorium isotopes (ThorMap)'. NERC standard grant (2021-2023). Involves the measurement of a range of GEOTRACES water and aerosol samples.

### **Outreach** activities conducted

• Jade Hatton published an article in the ECO magazine about sensors. <u>http://digital.ecomagazine.com/publication/frame.php?i=674747&p=&pn=&ver=html5&v</u> iew=articleBrowser&article\_id=3771619

### **Other GEOTRACES activities**

- Maeve Lohan (NOCS, co-chair) and Tina van de Flierdt (Imperial College London, committee member) attended bi-weekly virtual Standards & Intercalibration (S&I) meetings from summer 2020 to spring 2021.
- Maeve Lohan (NOCS, S&I co-chair) and Alessandro Tagliabue (University of Liverpool, DMC co-chair) attended four virtual DMC meetings.
- Maeve Lohan (NOCS), Tina van de Flierdt (Imperial College London) and Alessandro Tagliabue (University of Liverpool) attended the virtual annual SSC meeting.

#### New GEOTRACES and GEOTRACES relevant publications (published or in press)

- Archer, C., Vance, D., Milne, A., Lohan, M.C. (2020), The oceanic biogeochemistry of nickel and its isotopes: New data from the South Atlantic and the Southern Ocean biogeochemical divide. Earth and Planetary Science Letters, 535, 116118, https://doi.org/10.1016/j.epsl.2020.116118.
- Artigue, L., Lacan, F., van Gennip, S., Lohan, M.C., Wyatt, N.J., Woodward, E.M.S., Mahaffey, C., Hopkins, J., Drillet, Y. (2020), Water mass analysis along 22°N in the subtropical North Atlantic for the JC150 cruise (GEOTRACES, GApr08). Deep Sea Research I. Volume 158, April 2020, https://doi.org/10.1016/j.dsr.2020.103230.
- Bryan, A.L., Dickson, A.J., Dowdall, F., Homoky, W.B., Porcelli, D., Henderson, G.M. (2021), Constrols on the cadmium isotope composition of modern marine sediments. Earth Planet. Sci. Lett, 565, https://doi.org/10.1016/j.epsl.2021.116946.
- Bundy, R.M., Tagliabue, A., Hawco, N.J., Morton, P.L., Twining, B.S., Hatta, M., Noble, A.E., Cape, M.R., John, S.G., Cullen, J.T., Saito, M.A. (2020), Elevated sources of cobalt

in the Arctic Ocean. Biogeosciences, 17(19), 4745-4767, https://doi.org/10.5194/bg-17-4745-2020.

- Cassarino, L., Hendry, K. R., Henley, S. F., MacDonald, E., Arndt, S., Freitas, F. S., Pike, J., Firing, Y. L. (2020), Sedimentary nutrient supply in productive hotspots off the West Antarctic Peninsula revealed by silicon isotopes. Global Biogeochemical Cycles, e2019GB006486, https://doi.org/10.1029/2019GB006486.
- Chen, L., Little, S.H., Kreissig, K., Severmann, S., McManus, J. (2021), Isotopically Light Cd in Sediments Underlying Oxygen Deficient Zones. Frontiers in Earth Science, 9: 623720, doi: 10.3389/feart.2021.623720.
- 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. Geochimica et Cosmochimica Acta, 297, 143-157, https://doi.org/10.1016/j.gca.2021.01.013.
- Griffiths, A., Packman, H., Leung, Y.L., Coles, B.J., Kreissig, K., Little, S.H., van de Flierdt, T., Rehkämper, M. (2020), Evaluation of optimized procedures for high-precision Pb isotope analyses of seawater by MC-ICP-MS. Analytical Chemistry 92(16), 11232-11241, https://doi.org/10.1021/acs.analchem.0c01780.
- Hawco, N.J., McIlvin, M.R., Bundy, R.M., Tagliabue, A., Goepfert, T.J., Moran, D., Valentin-Alvarado, L., DiTullio, G.R., Saito, M.A. (2020), Minimal cobalt metabolism in the marine cyanobacterium Prochlorococcus. Proceedings of the National Academy of Sciences, 117 (27). 15740-15747, https://doi.org/10.1073/pnas.2001393117.
- Hawkings, J. R., Linhoff, B. Wadham, J. L., Stibal, M., Lamborg, C., Carling, G., Lamarche-Gagnon, G., Kohler, T., Ward, R., Hendry, K.R., et al. (accepted/in press), Large subglacial source of mercury from the southwestern margin of the Greenland Ice Sheet. Nature Geoscience.
- Held, N.A., Webb, E.A., McIlvin, M.M., Hutchins, D., Cohen, N., Moran., D.M., Kunde, K., Lohan, M., Mahaffey, C., Woodward, E.M.S., Saito, M.A. (2020), Co-occurrence of Fe and P stress in natural populations of the marine diazotroph Trichodesmium. Biogeosciences, 17, 2537–2551, https://doi.org/10.5194/bg-17-2537-2020.
- Homoky, W. B., Conway, T. M., John, S. G., Koenig, D., Deng, F., Tagliabue, A., Mills, R.A. (2021), Iron colloids dominate sedimentary supply to the ocean interior. Proceedings of the National Academy of Sciences, 118(13), https://doi.org/10.1073/pnas.2016078118.
- Horner, T. J., Little, S.H., Conway, T.M., Farmer, J.R., Hertzberg, J.E., Janssen, D.J., Lough, A.J.M., McKay, J., Tessin, A., Galer, S.J.G., Jaccard, S.L., Lacan, F., Paytan, A., Wuttig, K., GEOTRACES–PAGES Biological Productivity Working Group Members (2021), Bioactive trace metals and their isotopes as paleoproductivity proxies: An assessment using GEOTRACES-era data. Global Biogeochemical Cycles e2020GB006814, preprint: https://doi.org/10.1002/essoar.10504252.2.
- Hsieh, Y.-T., Bridgestock, L., Schermann, P.P., Seyfried Jr., W.E., Henderson, G.M. (2021), Barium isotopes in mid-ocean ridge hydrothermal vent fluids: A source of isotopically heavy Ba to the ocean. Geochimica et Cosmochimica Acta, 292, 348-363, https://doi.org/10.1016/j.gca.2020.09.037.
- Hsieh, Y.-T., Geibert, W., Woodward, E.M.S., Wyatt, N.J., Lohan, M.C., Achterberg, E.P., Henderson, G.M. (2021), Radium-228 derived ocean mixing and trace element inputs in the South Atlantic. Biogeosciences, 18, 1645–1671, https://doi.org/10.5194/bg-18-1645-2021.

- Little, S.H., Archer, C., McManus, J., Najorka, J., Wegorzewski, A. V., Vance, D. (2020), Towards balancing the oceanic Ni budget. Earth and Planetary Science Letters, 547, 116461, https://doi.org/10.1016/j.epsl.2020.116461.
- Little, S.H., Wilson, D.J., Rehkämper, M., Adkins, J.F., Robinson, L.F., van de Flierdt, T. (2021), Cold-water corals as archives of seawater Zn and Cu isotopes. Chemical Geology, 578, 120304, https://doi.org/10.1016/j.chemgeo.2021.120304.
- Ng, H.C., Robinson, L.F., Rowland, G.H., Chen, S.S., McManus, J.F. (2020), Coupled analysis of seawater and sedimentary 231Pa/230Th in the tropical Atlantic. Marine Chemistry, 227, 103894. https://doi.org/10.1016/J.MARCHEM.2020.103894.
- Pickering, R. A., Cassarino, L., Hendry, K. R., Wang, X. L., Maiti, K., Krause, J. W. (2020), Using Stable Isotopes to Disentangle Marine Sedimentary Signals in Reactive Silicon Pools. Geophysical Research Letters, 47(15), e2020GL087877, https://doi.org/10.1029/2020GL087877.
- Pryer, H.V., Hatton, J. E., Wadham, J. L., Hawkings, J. R., Robinson, L. F., Kellerman, A. M., Marshall, M.G., Urra, A., Covey, A., Daneri, G., Häussermann, V., Hendry, K. R. (2020), The Effects of Glacial Cover on Riverine Silicon Isotope Compositions in Chilean Patagonia. Frontiers in Earth Science, https://doi.org/10.3389/feart.2020.00368.
- Pryer, H.V., Hawkings, J. R., Wadham, J. L., Robinson, L. F., Hendry, K. R., Hatton, J. E., Kellerman, A.M., Bertrand, S., Gill-Olivas, B., Marshall, M.G., Brooker, R.A., Daneri, G., Häussermann, V. (2020), The Influence of Glacial Cover on Riverine Silicon and Iron Exports in Chilean Patagonia. Global Biogeochemical Cycles, 34(12), e2020GB006611, https://doi.org/10.1029/2020GB006611.
- Qia, J., Zhang, H., Steier, P., Hain, K., Hou, X., Vartti, V.-P., Henderson, G.M., Eriksson, M., Aldahan, A., Possnert, G., Golser, R. (2021), An unknown source of reactor radionuclides in the Baltic Sea revealed by multi-isotope fingerprints. Nature Communications, 12:823, https://doi.org/10.1038/s41467-021-21059-w.
- Ratnarajah, L., Blain, S., Boyd, P.W., Fourquez, M., Obernosterer, I., Tagliabue, A. (2020), Resource colimitation drives competition between phytoplankton and bacteria in the Southern Ocean, Geophysical Research Letters, 48 (1), e2020GL088369, https://doi.org/10.1029/2020GL088369.
- Rigby, S.J., Williams, R.G., Achterberg, E.P., Tagliabue, A. (2020), Resource Availability and Entrainment Are Driven by Offsets Between Nutriclines and Winter Mixed-Layer Depth. Global Biogeochemical Cycles, 34(7), https://doi.org/10.1029/2019GB006497.
- Schmidt, K., Birchill, A.J., Tarran, G.A., Brewin, R.J.W., Padro, W., Woodward, E.M.S., Smyth, T.J., Clark, J., Widdicombe, C.E., Hickman, A.E., Johns, D.G., Milne, A., Ussher, S.J., Polimene, L., Lohan, M.C., Atkinson, A. (2020), Picocyanobacteria win under increasing iron-nitrogen starvation of temperate shelf waters. Global Change Biology 26(10) 5574-5587, https://doi.org/10.1111/gcb.15161.
- Sedwick, P.N., Bowie, A.R., Church, T.M., Cullen J.T., Johnson, R.J., Lohan, M.C. Marsay, C.M. McGillicuddy, Jr., D.J., Sohsta, B.M. Tagliabue, A. and Ussher S.J. (2020), Dissolved iron in the Bermuda region of the subtropical North Atlantic Ocean: Seasonal Dynamics, mesoscale variability and physicochemical speciation. Marine Chemistry, 219, 103748, https://doi.org/10.1016/j.marchem.2019.103748.
- Stichel, T., Kretschmer, S., Geibert, W., Lambelet, M., Plancherel, Y., Rutgers van der Loeff, van de Flierdt, T. (2020), Particle-seawater interaction of neodymium in the North

Atlantic.ACSEarthandSpaceChemistry,https://doi.org/10.1021/acsearthspacechem.0c00034.

- Tagliabue, A., Barrier, N., Du Pontavice, H., Kwiatkowski, L., Aumont, O., Bopp, L., Cheung, W. W. L., Gascuel, D., Maury, O. (2020), An iron cycle cascade governs the response of equatorial Pacific ecosystems to climate change. Global Change Biology, 26 (11), 6168-6179, https://doi.org/10.1111/gcb.15316.
- Twining, B. S., Antipova, O., Chappell, P.D., Cohen, N.R., Jacquot, J.E., Mann, E.L., Marchetti, A., Ohnemus, D.C., Rauschenberg, S., Tagliabue, A. (2020), Taxonomic and nutrient controls on phytoplankton iron quotas in the ocean. Limnology and Oceanography Letters, 6 (2), 96-106, https://doi.org/10.1002/lol2.10179.
- Wyatt, N.J., Milne, A., Achterberg, E.P., Browning, T.J., Bouman, H.A., Woodward, E.M.S., Lohan, M.C. (2020), Seasonal cycling of zinc and cobalt in the Southeast Atlantic along the GEOTRACES GA10 section. Biogeosciences, https://doi.org/10.5194/bg-2020-42.

## Completed GEOTRACES and GEOTRACES relevant PhD or Master theses

- PhD Arthur Gourain. 'Copper biogeochemical cycle and the organic complexation of dissolved copper in the North Atlantic.' University of Liverpool.
- PhD Korinna Kunde. 'Coupling Macro and micro biogeochemistry: Distribution and speciation of iron and other bioactive trace metals required for phosphorus acquisition in the sub-tropical North Atlantic.' University of Southampton.
- PhD Shaun Rigby. 'Copper biogeochemical cycle and the organic complexation of dissolved copper in the North Atlantic.' University of Liverpool.
- PhD Wenhao Wang. 'Biogeochemical cycling of iron and chromium in the North Atlantic Ocean: Insights from stable iron and chromium isotopes.' University of Southampton.
- MSc Oliver Flanagan. 'Biogeochemical controls on particulate bioactive trace metals along the Western Antarctic Peninsula Shelf.' University of Southampton.
- MSc Magali Roberts. 'Seasonality and physico-chemical speciation of iron in nepheloid layers and creation of an optical method to estimate the concentration of particulate iron'. University of Plymouth (exchange student from the University of Bretagne Occidentale Brest).

## **SELECTED GEOTRACES** presentations in international conferences

## • Virtual Goldschmidt Conference, 21-26 June 2020

- Susan Little chaired Theme 13: *Chemistry of the Oceans and the Atmosphere: now and through time.*
- Wang, W., Goring-Harford, H., Kunde, K., Lohan, M., Connelly, D., James, R. (2020), 'Biogeochemical Cycling of Chromium and Chromium Isotopes in the Sub-Tropical North Atlantic Ocean.'

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