ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SOUTH AFRICA

April 1st, 2020 to April 30th, 2021

New GEOTRACES or GEOTRACES relevant scientific results

New approaches to quantify the strength of iron stress: It is not possible to directly infer iron stress from observed concentrations. Manipulation experiments of natural communities provide insight regarding the role of iron addition, while proteomic techniques quantify cellular responses to in situ resource stresses. However, these existing methods cannot be easily applied at broad spatial and temporal scales across the Southern Ocean that are required to assess trends in ecosystem status linked to climate drivers. A novel approach is the in vivo quantification of the degree of nonphotochemical quenching in relation to available light (α_{NPQ}), which quantifies the strength of iron stress [Ryan-Keogh & Thomalla, 2020, Ryan-Keogh & Smith Jr., 2021]. A particular strength of this novel iron stress proxy is that it can be applied to any ocean with coincident measurements of fluorescence, photosynthetically active radiation and backscatter or beam attenuation, providing the opportunity to deliver a long term time series by taking advantage of historical measurements. The robustness of α_{NPO} as a proxy for Fe stress is supported by its ability to reproduce known gradients in Southern Ocean iron limitation, from both natural and artificial Fe fertilization. With confidence in the ability of α_{NPO} to quantify Fe stress, we used a data set of 44 BGC-Argo floats and 163 cruises comprising a total of 5683 profiles spanning 25 years, to produce the



first long term (1996 -2021) in situ assessment of Fe stress in the Southern Ocean. We find a significant positive linear trend in α_{NPO} indicative of a progressive increase in Fe stress $(5.6\% \text{ yr}^{-1})$ in the Southern Ocean. (by Dr Tommy Ryan-Keogh)

Figure 1. Robustness of α_{NPQ} as a proxy for iron stress demonstrated through natural and artificial Fe gradients and seasonal Fe depletion. (a) Mean $\alpha_{NPQ} \pm$

standard errors from BGC-Argo profiles upstream and downstream of the Kerguelen plateau and from ship-based profiles in and out of Fe-fertilized patches during SOIREE and SOFEX. Maps of α_{NPQ} based on combined BGC-Argo and ship-based profiles (1996 - 2021) for (b) Summer (DJF: December, January and - February) and (c) Spring (SON: September, October and - November) gridded to $5^{\circ} \times 5^{\circ}$. The dashed line represents the spatial extent of the Southern Ocean defined as the subpolar and ice biomes from Fay & McKinley (2014)



Figure 2• Significant long-term trend in Southern Ocean iron stress. Displayed is the seasonal and annual means, with an Ordinary Least Squares regression on the annual mean, of α_{NPQ} determined from the combined BGC-Argo and ship-based dataset (1996 -2021)

Winter distributions of dissolved cadmium (dCd) and particulate cadmium (pCd): measured for the first time in the Indian sector of the Southern Ocean thereby contributing a unique spatial and seasonal dataset. Seven depth profiles, between 41°S and 58°S, were collected along the 30°E longitude during the 2017 austral winter to investigate the biogeochemical cycling of cadmium during a period characterised by contrasting upper water column dynamics compared to summer. Our results support an important role for biological uptake during winter months albeit weaker compared to summer. Distinct, biologically driven changes in cadmium cycling across the transect were observed. For example, surface ratios of pCd to phosphorus (P; pCd:P) increased from 0.37 to 1.07 mmol mol⁻¹ between the subtropical zone (STZ) and the Antarctic zone (AAZ) reflecting increased Cd requirements for diatoms at higher latitudes which, in turn, was driven by a complex relationship between the availability of dCd and dissolved iron (dFe), zinc (dZn) and manganese (dMn). Vertical profiles (Figure 3) of pCd:P displayed near-surface maxima consistent with 1) P occurring in two phases with different labilities and the lability of Cd being somewhere in-between and 2) increasing dCd to phosphate (PO4; dCd:PO4) ratios with depth at each station. North of the Antarctic Polar Front (APF), a secondary, deeper pCd:P maximum may reflect an advective signal associated with northward subducting Antarctic Intermediate Water (AAIW). The strong southward increase in surface dCd and dCd:PO₄, from approximately 10 to 700 pmol kg⁻¹ and 40 to 400 µmol mol⁻¹ respectively, reflected the net effect of preferential uptake and regeneration of diatoms with high Cd content and the upwelling of Cd enriched water masses in the AAZ. Furthermore, distinct dCd versus PO₄ relationships were observed in each of the intermediate and deep water masses suggesting that dCd and PO₄ distributions at depth are largely the result of physical water mass mixing. (by Dr Ryan Cloete)



Figure 3. Particulate cadmium (black bars) and P (grey bars) normalised to profile maximum values (bottom axis) for the upper 1000 m in A) the AAZ, B) the PFZ, C) the SAZ and D) the STZ. The red dots are the absolute pCd:P ratios at each depth (top axis). Dashed horizontal lines represents the bottom of the euphotic zone at each station. Solid horizontal line represents the bottom of the MLD at each station. No euphotic zone data for 56°S (AAZ) due to PAR sensor failure.

Winter biogenic silica and diatom distributions in the Indian Southern Ocean: Diatoms are a major contributor to Southern Ocean particulate organic carbon (POC) production and export, and exert a strong control on Antarctic surface and Subantarctic thermocline nutrient concentrations, thus influencing the low-latitude nutrient supply. We investigated the distribution of nanophytoplankton ($\geq 3 \mu m$) and their associated biogeochemical environments along 30°E across the Indian Southern Ocean in July 2017 (Weir et al., 2020). Mixed layer-integrated biogenic silica (bSi) decreased 12-fold from the southern AZ to the STZ, resulting in a strong south-north gradient in bSi-perchl- and bSi-per-POC (Figure 4). We attribute this to a high abundance of heavilysilicified diatom species (e.g., *Fragilariopsis* spp., which dominated the AZ diatom



community) and limited a contribution of other phytoplankton to chlorophyll-a and POC to the south. While mixed-layer Si(OH)₄ concentrations decreased more than NO_3^- across the PF, likely due to preferential Si(OH)₄ consumption by iron-limited diatoms, our data imply a lower ratio of Si(OH)₄ to NO₃⁻ uptake compared to summer. This suggests that iron limitation may be less severe in the AZ in winter, at least in the west Indian sector. We conclude that AZ diatoms impact the low-latitude nutrient supply and are potentially important for carbon export in winter, despite the lower productivity of the Southern Ocean during this season. (by Dr Susanne Fietz)

Figure 4. Mixed-layer (ML) normalised to maximum value (i.e., all y-axes are scaled from 0 to 1) as a function of latitude (°S). Grey vertical lines indicates the approx. positions of the Sbdy, sACCf, PF, SAF and STF at the time of sampling. a) Average ML macronutrient concentrations (μM) , b) average ML Si* concentration (μM) , c) average upper 150 m concentrations of total chl-a (µg/L), POC, PON, and bSi (µmol/L) along with the number (nr) of diatoms (cells/mL) at the surface (~10 m), d) estimated C_{diatom} (µmol/L), contribution of C_{diatom} to total POC (%), bSi-to- C_{diatom} ratio (mol/mol) at the surface (~10 m), e) bSi-to-total chl-a ratio (mol/g), bSi-to-POC ratio (mol/mol), bSi-to-PON ratio (mol/mol), and bSiper-diatom cell (pmol/cell). Error bars denote the coefficient of variation of averages.(from Weir et al., 2020, DSR I).

GEOTRACES or GEOTRACES relevant cruises

• Dr T. Ryan-Keogh (CSIR) and Heather Forrer (UCT/FSU; Image 1) participated on the French Geotraces SWINGS cruise, looking at the effects of iron addition on photophysiology, nitrogen uptake and primary production. The cruise ran from the 10th Jan 2021 until 8th March 2021, where we departed Reunion Island and sailed via all sub-Antarctic Islands from Marion to Heard. We conducted 33 short-term iron addition experiments, 12 iron and nitrogen uptake experiments along with several other experiments measuring natural rates of primary production, nitrogen uptake and nitrification. Additionally, two international PhD students were part of Dr T. Ryan-Keogh team, 1 from University of Plymouth (Isobel Turnbull), who was studying siderophore production, and 1 student from University of Liverpool (Millie Goddard-Dwyer), who was studying microbial ligand and DOM production.

The team managed to conduct for the first-time short-term iron addition experiments to quantify the land mass effects of all sub-Antarctic islands in the Indian sector of the Southern Ocean. They found low levels of iron stress (low $\Delta(Fv/Fm)$) in close proximity to the islands, which increased as they moved further away from the islands (high $\Delta(Fv/Fm)$) (Figure 5). Co-incident with these experiments is high resolution measurements of iron speciation, from the soluble, colloidal, dissolved and particulate fractions of iron. By linking measurements of photophysiology alongside measurements of the iron fractions, we hope to begin to answer questions on what constitutes bioavailable iron. Furthermore, the team made significant progress in quantifying and characterising nitrogen cycling in this region with a particular focus on understanding how iron directly impacts uptake. This work particularly focuses on Kerguelen to determine whether nitrogen cycling in this region is dominated by nitrification.



Figure 5 (above) Results of short-term iron addition experiments from the SWINGS cruise. $\Delta(Fv/Fm)$ is calculated as the difference between the iron addition treatment Fv/Fm and control treatment Fv/Fm after 24 hours.

Image 1 (right) Miss Heather Forrer filtering samples for primary production during the SWINGS cruise.



New projects and/or funding

• Dr T. Ryan-Keogh (Early Career Researcher), National Research Foundation of South Africa (NRF; 2021-2023): "Seasonal iron speciation in the Southern Ocean, from open ocean environments to naturally fertilised sub-Antarctic Islands"

Ongoing/extended projects and/or funding

- Fietz S (2018-2020+2021) South African National Antarctic Programme (SNA170506229934) Shifts in phytoplankton and microbial community composition and functional diversity related to trace metal cycling; R914,000
- Fietz S, Lloyd J, Makhalanyane T (2018-2020+2021) South African bilateral programme, SA-Mexico (MESA170607237905) Exploiting microbes for remediation of pollution in oceans; R2,284,200
- Roychoudhury AN (2018-2020+2021) Distribution and Speciation of Bioactive Trace Elements in Southern Ocean, NRF SANAP, R1,820,000

Contributions to intl. partner projects:

• Mackey B, Roychoudhury AN, Vichi M, Findlay, K (2019 – 2022) Humpback whales in changing climate, Donor funding AUD 4,019,503

New GEOTRACES or GEOTRACES-relevant publications

SA Early Career Researcher-led publications:

- Ryan-Keogh T.J. and Thomalla, S. J., 2020. Deriving a proxy for iron limitation from chlorophyll fluorescence on buoyancy gliders. Frontiers in Marine Science, 7: 275, doi: 10.3389/fmars.2020.00275.
- Ryan-Keogh T.J. and Smith Jr., W. O., 2020 Temporal patterns of iron limitation in the Ross Sea as determined from chlorophyll fluorescence. Journal of Marine Systems, 215, doi: 10.1016/j.jmarsys.2020.103500.
- Weir I, Fawcett S, Smith S, Walker D, Bornmann T, Fietz S., 2020.Winter biogenic silica and diatom distributions in the Indian Sector of the Southern Ocean. Deep Sea Research Part I, 103421. https://doi.org/10.1016/j.dsr.2020.103421
- Ogundare MO, Fransson A, Chierici M, Joubert WR and Roychoudhury AN (2021) Variability of Sea-Air Carbon Dioxide Flux in Autumn Across the Weddell Gyre and Offshore Dronning Maud Land in the Southern Ocean. Front. Mar. Sci. 7:614263. doi: 10.3389/fmars.2020.614263
- Cloete R, Loock JC, van Horsten N, Fietz S, Mtshali TN, Planquette H, Roychoudhury AN. Winter biogeochemical cycling of dissolved and particulate cadmium in the Indian sector of the Southern Ocean (GEOTRACES GIpr07 transect). Frontiers in Marine Sciences (2021, in review, endorsed by 2 reviewers)
- Cloete R, et al. Winter dissolved and particulate zinc in the Indian Sector of the Southern Ocean: Distribution and relation to major nutrients (GEOTRACES GIpr07 transect). Marine Chemistry (2021, in revision)
- Samanta S, Menzel Barraqueta JL, de Bie J, Meynecke J-O, Roychoudhury A. Dissolved Pb and Pb isotope data in the global ocean basins: distribution and synthesis. Marine Chemistry (2021, in revision)

SA-contributions to international partner publications:

- Kauko HM, Hattermann T, Ryan-Keogh T, Singh A, et al. (2021) Phenology and Environmental Control of Phytoplankton Blooms in the Kong Håkon VII Hav in the Southern Ocean. March 2021. Front. Mar. Sci. 8:623856. doi: 10.3389/fmars.2021.623856
- Farmer J, Hertzberg J, Cardinal D, Fietz S, Hendry K, Jaccard S, Paytan A, Rafter P, Ren H, Somes C, Sutton J. (2021) Assessment of C, N and Si isotopes as tracers of past ocean nutrient and carbon cycling. Global Biogeochemical Cycles, accepted. e2020GB006775 doi: 10.1029/2020GB006775
- Shalileh F, Lloyd JR, Fietz S, Zahiri HS, Emameh RZ. Identification of novel cadmiumbinding zeta carbonic anhydrase subfamilies from marine prokaryotic and eukaryotic microorganisms (in review)

Completed GEOTRACES PhD or Master theses

PhD:

- Dr Jean Loock (04/2021): Austral Summer and Winter Trace Metal Distributions in the Southern Ocean and Antarctic Seasonal Sea Ice
- Dr Ryan Cloete (12/2020): On the distribution and biogeochemical cycling of bioactive trace metals in the Southern Ocean

MSc:

- Ms Raya Stavreva (12/2020): Constraining the suitability of barium as an indicator of paleoproductivity in different aquatic environments; https://scholar.sun.ac.za/handle/10019.1/109374
- Ms Zandria Jordaan (12/2020): Testing potential drivers for carbon isotopic signature of particulate organic carbon in the Southern Ocean; https://scholar.sun.ac.za/handle/10019.1/109335

GEOTRACES presentations at international conferences

- Samanta S, Menzel Barraqueta JL, Cloete R, Loock J, de Jongh T, Roychoudhury A. Sources and cycling of dissolved rare earth elements in the Southern Ocean: linkages to the nutrient dynamics. Goldschmidt2020. https://doi.org/10.46427/gold2020.2271
- Menzel Barraqueta J-L, Samanta S, Loock JC, Cloete R, Viljoen JJ, Mahieu L, Krisch S, Kaukurauee K, Bernhard W, Fietz S & Roychoudhury A. Winter and Spring Trace Metals at the Antarctic Marginal Sea Ice Interfaces. Goldschmidt2020. https://doi.org/10.46427/gold2020.1781
- Singh A., M. Ardelan, S. Fietz, A. Fransson, N. Sanchez, S. J. Thomalla and T. J. Ryan-Keogh. On the response of phytoplankton to iron addition in the Weddell Sea and along the Dronning Maud Land ice edge during austral autumn. p. 159. In: Ocean, Weather and Climate: Science to the Service of Society. Proceedings of the Nansen-Tutu Centre 10th Anniversary Symposium, 10-12 March 2020, Cape Town, South Africa. Editors M Rouault, JA Johannessen, A Samuelsen and B Backeberg. ISBN: 978-1-77634-359-1, 2021. https://86bba567-88e7-4f82-

90ca0152e7cb926c.filesusr.com/ugd/92b3c9_f7293264dff143539d67d12fe8d130e5.pdf

Outreach activities

- Stellenbosch TracEx Team
 - Blogs: https://southernoceanfe.wordpress.com/ https://tracexsite.wordpress.com/
 - Facebook page: https://www.facebook.com/Environmental-Geochemistry-at-Stellenbosch-University-135430226505633/
 - Twitter account: https://twitter.com/TracexS

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