



Subject offered for a contract starting October 2019

**SUBJECT TITLE:** Solubility and bioavailability of Patagonian dust in the future Southern Ocean

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Financing: Doctoral contract with or without teaching assignment

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**Presentation of the subject**

• **Context and objectives**

The dust emitted by Patagonia is a source of trace metals essential for the growth of phytoplankton in the Southern Ocean<sup>1</sup> (SO). This ocean is indeed the largest High Nutrient-Low Chlorophyll (HNLC) province in the world's ocean where the activity of microalgae, in particular for the pumping of atmospheric carbon dioxide (CO<sub>2</sub>) by photosynthesis, largely depends on the inputs of these limiting micronutrients, especially of iron (Fe)<sup>2,3</sup>. Intensification of Fe and other bioactive metals inputs would have stimulated the biological carbon pump driven by Antarctic diatoms in the SO at the Last Glacial Maximum, during which time the atmospheric deposition was substantially greater<sup>4</sup>. More generally, the tight connection observed between high dust input to the Southern Ocean and the emergence of deep glaciations that characterize the past 1 Ma of Earth history strongly suggests that the supply of dust in this ocean has the potential to modify the global climate<sup>5</sup>.

Future projections of atmospheric deposition are still uncertain<sup>6,7</sup>, but increase in desertification<sup>8</sup> and in frequency and magnitude of storms in the Subantarctic Zone (SAZ)<sup>9</sup> should bring more wind-blown dust to this region. The biological impact of these future changes remains unclear<sup>10,11</sup>, mainly because of the low constraints of the solubility of the metals contained in the aerosols, a determining factor for estimating the bioavailability of the atmospheric input, and thus, its impact on the efficiency of the biological carbon pump in the SO. Indeed, most of the values were principally obtained under non-realistic acidic conditions<sup>12,13</sup>, which are themselves much lower than the pH predicted in the most extreme scenarios of ocean acidification<sup>14</sup>. Therefore, new experimental studies are needed to estimate realistically the solubility of trace metals contained in Patagonian dust.

In addition to dust delivery, the surface waters of the SAZ will experience other environmental changes, becoming warmer, more acidic, depleted in macronutrients, enriched in Fe, and receiving more photosynthetically active radiation (PAR)<sup>15,16,17</sup>. This range of additional stressors should also impact dissolution kinetics and biological activity, yet their cumulative effect is far from being known. One recent pioneer multi-stressors study<sup>21</sup> demonstrated

<sup>1</sup> Cassar, N. et al., 2007. The Southern Ocean biological response to aeolian iron deposition. *Science*, 317: 1067-1070.

<sup>2</sup> de Baar, H.J.W., Boyd, P.W., Coale, K.H., Landry, M.R., Tsuda, A., Assmy, P., Bakker, D.C.E., Bozec, Y., Barber, R.T., Brzezinski, M.A., Buesseler, K.O., Boye, M., et al., 2005. Synthesis of iron fertilization experiments: From the Iron Age in the Age of Enlightenment. *Journal of Geophysical Research*, 110: C09S16, doi:10.1029/2004JC002601.

<sup>3</sup> Boye M. et al., 2005. Major deviations of iron complexation during 22 days of a mesoscale iron enrichment in the open Southern Ocean. *Marine Chemistry*, 96: 257-271.

<sup>4</sup> Petit, J.R., et al., 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature*, 399: 429-436.

<sup>5</sup> Martínez-García, A. et al., 2011. Southern Ocean dust-climate coupling over the past four million years. *Nature*, 476: 312-315.

<sup>6</sup> Tegen, I., Werner, M., Harrison, S.P., Kohfeld, K.E., 2004. Relative importance of climate and land use in determining present and future global soil dust emission. *Geophys. Res. Lett.* 31 (5), L05105. doi:10.1029/2003GL019216.

<sup>7</sup> Mahowald, N., et al., 2011. Aerosol Impacts on Climate and Biogeochemistry. *Annu. Rev. Environ. Resour.*, 36, 45-74.

<sup>8</sup> Woodward, S., Roberts, D. L., and Betts, R. A., 2005. A simulation of the effect of climate change-induced desertification on mineral dust aerosol. *Geophys. Res. Lett.* 32, 2-5. doi: 10.1029/2005GL023482.

<sup>9</sup> Boyd, P.W., and Law, C.S., 2011. An Ocean Climate Change Atlas for New Zealand Waters. Technical Report 79, Wellington: NIWA.

<sup>10</sup> Tagliabue, A., Bopp, L., Aumont, O., 2008. Ocean biogeochemistry exhibits contrasting responses to a large scale reduction in dust deposition. *Biogeosciences*, 5, 11-24.

<sup>11</sup> Mahowald, N., et al., 2011. Aerosol Impacts on Climate and Biogeochemistry. *Annu. Rev. Environ. Resour.*, 36, 45-74.

<sup>12</sup> Thürröczy C.-E., M. Boye, R. Losno, 2010. Dissolution of cobalt and zinc from natural and anthropogenic dusts in seawater. *Biogeosciences*, 7: 1927-1936.

<sup>13</sup> Conway, T.M. et al., 2015. Constraints on soluble aerosol iron flux to the Southern Ocean at the Last Glacial Maximum. *Nature Communications*, 6:7850, doi:10.1038/ncomms8850.

<sup>14</sup> Bopp, L., et al., 2013. Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. *Biogeosciences*, 10 : 6225-6245.

<sup>15</sup> Moore, J. K. et al., 2013. Marine ecosystem dynamics and biogeochemical cycling in the Community Earth System Model CESM1(BGC). *J. Clim.* 26, 9291-9321.

<sup>16</sup> Boyd, P. W. et al., 2008. Climate-mediated changes to mixed-layer properties in the Southern Ocean: Assessing the phytoplankton response. *Biogeosciences* 5, 847-864.

<sup>17</sup> Boyd, P.W. et al., 2016. Physiological responses of a Southern Ocean diatom to complex future ocean conditions. *Nature Climate Change*, 6, 207-213.

biased future predictions from experimental outcomes when only a subset of multi-stressors is considered, stressing the need for new experiments.

**In this context, the PhD goal is to diagnose the net effect of multi-faceted change predicted in the SAZ for the 2100 horizon on the solubility of trace metals contained in Patagonian dust and on subantarctic diatoms.**

This necessitates to estimate the individual and interactive effects of multi-stressors change in actual and future SAZ surface water conditions.

The thesis will provide new and pioneer insights on dust solubility and bioavailability under different climatic scenarios, constituting invaluable results to accurately develop biogeochemical ocean-atmosphere coupled modelling in the past/actual/future SO.

## • Working plan

The study is based on laboratory experiments (abiotic and biotic) using batch incubations under controlled multi-stressor conditions (CO<sub>2</sub>, T, PAR, macronutrients, Patagonian dust). Actual and predicted conditions in the SAZ will be reproduced.

**Strategy:** A collapsed 2<sup>2</sup> factorial experimental design will be used to reduce the number of experiments. There, dust is the target factor and the remaining stressors constitute a combined factor. The design allows identification of effect of increased dust deposition alone, the collapsed stressors, and their interplays.

**Methods:** Dust generated from soils already harvested in Patagonia (collaboration with R. Losno, IPGP) and diatoms isolated from Subantarctic domain will be incubated in artificial seawater under ultra-cleaned and controlled conditions.

**Sampling parameters and analytical methods:** Trace metal concentrations used to estimate the dissolution rates are analyzed by High Resolution sector field ICP-MS (Element 2)<sup>18,19</sup>. Dissolved inorganic carbon and pH used to calculate the carbonate system are measured using IR-detector of CO<sub>2</sub> mounted on an AIRICA flow-injection analysis system, and a pH ultra-electrode mounted on a HQ40d multimeter. T and conductivity are analyzed using sensors mounted on the same multimeter. PAR sensor is used for irradiance. Macronutrient concentrations are analyzed using a Bran+Luebbe AAIII auto-analyzer<sup>20</sup>. Cell density and size that will serve to estimate the growth rate and morphology are determined by classical optic microscopy and using a scanning electronic microscope. Particulate carbon and nitrogen are analyzed in the suspended particles using a Carlo Erba Analyzer 1500<sup>21</sup>. Biogenic silica will also be determined in particles<sup>22</sup>.

**Statistical analysis:** The relative importance of individual and interactive effects of the stressors will be estimated by statistical analysis in a model selection context<sup>23</sup>. Partial-R<sup>2</sup> will be calculated to describe variation explained by model components (dust, other stressors, their interactions).

**Timetable:** The working plan is based on publishable results after each series of experiments. Dust dissolution experiments will be conducted during the first 1 year, followed by the experiments on physiological impact during the second year. The last year will be used to complete the analyses, to finalize publications and to write the PhD. Conference attends are disseminated over the 3 years.

## • Training and skills

- Experimental work (biotic and abiotic) in ultra-cleaned and controlled conditions
- Statistical interpretation of chemical and biological data to identify the effect of multi-stressor environmental changes
- Training on HR-ICP-MS techniques at IPGP for trace metal analyses, and on other methods
- Publications and presentations of research at national and international conferences

Applicants should have a Master degree in earth/environment sciences and a background either in biogeochemistry, geochemistry, chemistry, microbiology, oceanography and/or environmental sciences. Aptitude and/or strong interest for experimental and analytical work are necessary. Capacity to work independently and within a research team is wished.

<sup>18</sup> Boye, M., et al., 2012. Distributions of dissolved trace metals (Cd, Cu, Mn, Pb, Ag) in the southeastern Atlantic and the Southern Ocean. *Biogeosciences*, 9, 3231-3246, doi:10.5194/bg-9-3231-2012.

<sup>19</sup> Rapp, I., et al., 2017. Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry. *Anal. Chim. Acta* 976, 1–13.

<sup>20</sup> Aminot, A., and Kérouel, R., 2007. Dosage automatique des nutriments dans les eaux marines : méthodes en flux continu. Ed. Ifremer, Méthodes D'analyse en Milieu marin (188 pp).

<sup>21</sup> Le Moigne, F.A.C., et al., 2013. Description of the biogeochemical features of the subtropical southeastern Atlantic and the Southern Ocean south of South Africa during the austral summer of the International Polar Year. *Biogeosciences* 10, 281–295.

<sup>22</sup> Ragueneau, O., et al., 2005. A new method for the measurement of biogenic silica in suspended matter of coastal waters: using Si:Al ratios to correct for the mineral interference. *Cont. Shelf Res.*, 25, 697-710, doi:10.1016/j.csr.2004.09.017.

<sup>23</sup> Burnham, K. P. & Anderson, D. R., 2002. Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach 2nd ed (Springer).