

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN NEW ZEALAND

June 1st, 2015 to April 30th, 2016

New Scientific Results

- Rebecca Zitoun (PhD student supervised by Res Assoc Prof Sylvia Sander and Dr Rob Middag) participated on the German led FS Meteor 121 cruise from November 21-December 27, 2015 to study the biogeochemistry of trace elements in the southeast Atlantic Ocean. Rebecca supported the sampling team and will analyse samples for Cu-binding ligands.
- **GEOTRACES GA04N Black Sea and Mediterranean Sea Expedition.** The GEOTRACES (GA04N) expedition to the Mediterranean and Black Seas in 2013 provided an opportunity to examine the biogeochemical cycling of a suite of trace elements under low- and zero-oxygen conditions. Using multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combined with double spiking techniques, we have measured the isotopic composition of U, Fe and Cd for the entire water column and underlying sediments of the Black Sea across oxic-suboxic-anoxic-euxinic transitions. These new data help elucidate the mechanisms driving the uptake and removal of redox-sensitive metals from the dissolved phase and their export to the solid phase across a gradation of changing redox settings from oxic to anoxic and ultimately euxinic. These results form the basis of the PhD research programme of recently completed graduate student John Rolison, and were presented at the 2015 Goldschmidt Conference in the Czech Republic.

We are currently obtaining Fe and Cd isotope datasets for water samples collected during the Mediterranean legs of the GA04N expedition. The chemical preparation and isotopic analysis of surface samples is being led by Dr Nadya Teutsch from the Geological Survey of Israel, who is undertaking sabbatical research at the University of Otago. This will be followed by Zn isotope analysis of surface waters, and a combined Cd, Zn and Fe isotope investigation of water samples collected from depth profiles in the Mediterranean Sea.

- **GEOTRACES GP13 South Pacific Ocean Expedition.** Using techniques in double-spiking and MC-ICPMS, we have obtained measurements of Cd isotopic composition and Cd concentration for water column samples collected from a suite of 8 depth profiles and additional surface locations along the GEOTRACES GP13 zonal section. This cruise transect extends for 5,500 km from offshore Australia to the remote interior of the subtropical Pacific Ocean, an understudied region of the world's oceans, where Cd concentrations in the upper water column are at ultra-trace levels, and some of the lowest detected globally. These results form the basis of the PhD research of graduate student Ejin George, who is expected to submit his thesis in late 2016, and will be presented at the 2016 Goldschmidt Conference in Japan. The Cd isotope and Cd concentration datasets for the GP13 expedition have been submitted to the 2017 International Data Product.
- **Method Development.** A chemical preparation method has been devised for extracting and purifying Cd, Zn and Fe from large volume (up to 10 L) seawater samples for the purpose of double-spike Cd, Zn and Fe isotopic analysis.

Publications with NZ author or co-author

- Ellwood MJ, Hutchins DA, Lohan MC, Milne A, Nasemann P, Nodder SD, Sander SG, Strzepek R, Wilhelm SW, Boyd PW (2015) Iron stable isotopes track pelagic iron cycling during a subtropical phytoplankton bloom. *Proceedings of the National Academy of Sciences* 112 (1):E15-E20. doi:10.1073/pnas.1421576112
- Middag, R., Seferian, R., Conway, T. M., John, S. G., Bruland, K. W. & de Baar, H.J.W., 2015 Intercomparison of Dissolved Trace Elements at the Bermuda Atlantic Time Series Station. *Marine Chemistry* 177(3): 476-489.
- Middag, R., van Hulst, M.M.P., van Aken, H.M., Rijkenberg, M.J.A., Gerringa, L., Laan, P. and de Baar, H.J.W., 2015. Dissolved aluminium in the Ocean Conveyor of the West Atlantic Ocean: effects of the biological cycle, scavenging, sediment resuspension and hydrography. *Marine Chemistry* (1): 69-86.
- Rolison, J., C.H. Stirling, R. Middag and M. Rijkenberg (in review). Uranium stable isotope fractionation in the Black Sea: Modern calibration of the $^{238}\text{U}/^{235}\text{U}$ paleoredox proxy. *Geochim. Cosmochim. Acta*.
- Rolison, J., R. Middag, C.H. Stirling, M. Rijkenberg and H. de Baar (2015). Zonal distribution of dissolved aluminium in the Mediterranean Sea. *Marine Chemistry* 177, 87-100.

Presentations with NZ author or co-author

- Kleint, C., Hawkes, J.A., Sander, S.G., Koschinsky, A. Dissolved Fe and Fe binding ligand concentrations at the hydrothermal vent fields in the Coriolis Troughs, New Hebrides Island Arc. Oral presentation at the 2016 Ocean Sciences Meeting – New Orleans, 24-02-2016, USA.
- Middag, R., Alderkamp, A.-C., Arrigo, K., Limiting iron concentrations early in the season off the West Antarctic Peninsula. Oral presentation at the 2015 Antarctic Science Conference – Christchurch, 30-07-2015, NZ.
- Middag, R., Alderkamp, A.-C., Arrigo, K., van Hale, R. Limiting iron concentrations early in the season off the West Antarctic Peninsula. Poster presentation at the 2016 Ocean Sciences Meeting – New Orleans, 25-02-2016, USA.
- Middag, R., Rolison, J.M., Stirling, C.H., Van Hulst, M.M.P., Rijkenberg, M.J.A., Gerringa, L.J.A., de Baar, H.J.W. Aluminium in the West-Atlantic Ocean and Mediterranean Sea. Oral presentation at the 2015 Goldschmidt meeting – Prague, 18-08-2015, Czech Republic.
- Rolison, J.M., Stirling, C.H., George, E., Middag, R., Gault-Ringold, M., Rijkenberg, M.J.A., de Baar, H.J.W. Biogeochemical Cycling of Uranium, Iron and Cadmium Isotope Systems during Oceanic Anoxia: A case study of the Black Sea. Oral presentation at the 2015 Goldschmidt meeting – Prague, 17-08-2015, Czech Republic.
- Sander, S.G., Buck, K.N., Lohan, M.C., Turner, D.R., Clegg, S.L. Metal Speciation Analysis and Modeling – How do we Best Estimate the Bioavailable Form? Oral presentation at the 2016 Ocean Sciences Meeting – New Orleans, 24-02-2016, USA.
- Van Hulst, M.M.P., Dutay, J.-C., Roy-Barman M, Tagliabue, A., Sterl, A., Middag, R., de Baar, H.J.W. Manganese in an Ocean General Circulation Model. Oral presentation at the 2015 Goldschmidt meeting – Prague, 17-08-2015, Czech Republic.

PhD Thesis

- John Rolison – University of Otago (supervisors: Claudine Stirling and Rob Middag). Title: ‘The biogeochemical cycling of zinc and iron in the Mediterranean and Black Seas’. PhD completed: April 2016.

Funding

- Dr Middag was awarded funding under the Marsden Fast-Start scheme for a project entitled ‘The ice is melting: How do trace metals in the ocean influence the Antarctic marine ecosystem and global climate?’. This project is based on samples from the GEOTRACES process study Phantastic II in the Southern Ocean, west of the Antarctic Peninsula.

Other

- Dr Middag has been appointed Associate Editor for Marine Chemistry.

Submitted by Rob Middag (rob.middag@otago.ac.nz).