ANNUAL REPORT ON GEOTRACES ACTIVITIES IN FRANCE

May 1st, 2022 to April 30th, 2023

New GEOTRACES or GEOTRACES relevant scientific results

- The unaccounted dissolved iron (II) sink: insights from dFe(II) concentrations in the deep Atlantic Ocean.

Hydrothermal vent sites found along mid-ocean ridges are sources of numerous reduced chemical species and trace elements. To establish dissolved iron (II) (dFe(II)) variability along the Mid Atlantic Ridge (between 39.5°N and 26°N, GA13 UK GEOTRACES section), dFe(II) concentrations were measured above six hydrothermal vent sites, as well as at stations with no active hydrothermal activity. The dFe(II) concentrations ranged from 0.00 to 0.12 nmol L^{-1} (detection limit = 0.02 ± 0.02 nmol L−1) in non-hydrothermally affected regions to values as high as 12.8 nmol L^{-1} within hydrothermal plumes. Iron (II) in seawater is oxidised over a period of minutes to hours, which is on average two times faster than the time required to collect the sample from the deep ocean and its analysis in the onboard laboratory. A multiparametric equation was used to estimate the original dFe(II) concentration in the deep ocean. The in-situ temperature, pH, salinity and delay between sample collection and its analysis were considered. The results showed that dFe(II) plays a more significant role in the iron pool than previously accounted for, constituting a fraction >20 % of the dissolved iron pool, in contrast to <10 % of the iron pool formerly reported. This discrepancy is caused by Fe(II) loss during sampling when between 35 and 90 % of the dFe(II) gets oxidised. In-situ dFe(II) concentrations are therefore significantly higher than values reported in sedimentary and hydrothermal settings where Fe is added to the ocean in its reduced form. Consequently, the high dynamism of dFe(II) in hydrothermal environments masks the magnitude of dFe(II) sourced within the deep ocean (González Santana et al., 2023, Science of the Total Environment).

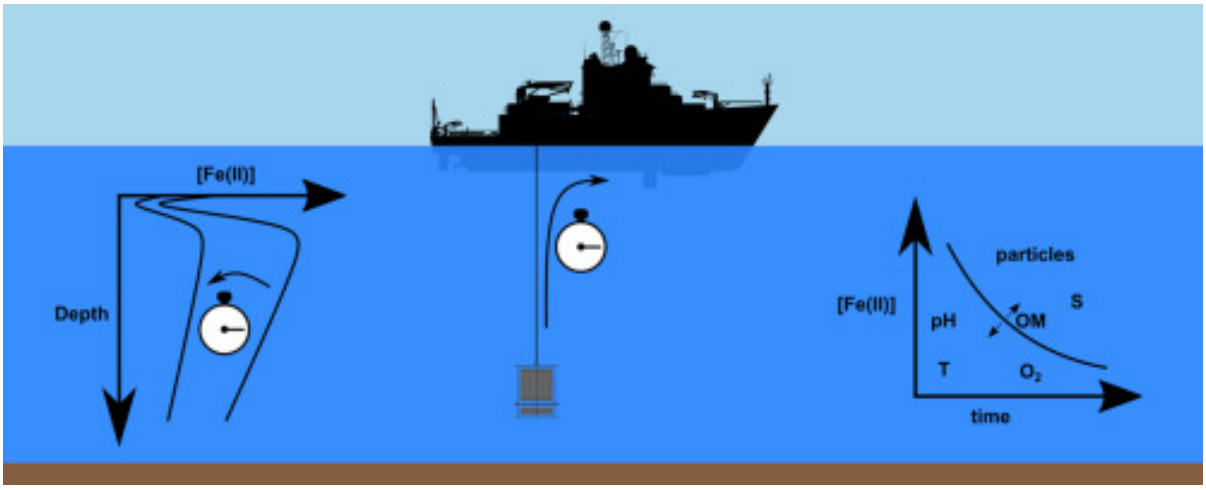

Figure FR-1: *Sources and physicochemical conditions which modulate the dFe(II) profile. Over the whole water column, the oxidation of Fe(II) is a limiting factor, with measured dFe(II) concentrations only accounting for 10 to 65 % of the computed original Fe(II) concentrations. The factors involved in the oxidation vary with ocean depths: high seawater temperature above 15 °C, high pH and highly oxic waters in the surface layer; in the central waters, where the minimum oxygen zone is produced as a result of organic matter remineralization, the conditions allow for a slower oxidation rate, where measured dFe(II) concentrations increase; in the deep ocean, hydrothermal activity acts as a source of Fe(II), whose concentrations will depend on the vent site, the distance from the vent to the sampling point and the oxidation rate (González-Santana et al., 2023).*

- Natural iron fertilization by shallow hydrothermal sources fuels diazotroph blooms in the ocean

The objective of the TONGA project and campaign (GEOTRACES GPpr14) was to study the control of ocean productivity and carbon sequestration by micronutrients of shallow hydrothermal origin. It was shown that along the west to east zonal transect, total chlorophyll-a (Chla) and particulate organic nitrogen stocks peaked in the naturally Fe-fertilized waters. N_2 fixation rates and *Trichodesmium* abundances increased by a factor of 10 and 90, respectively in these Fe-fertilized waters compared to adjacent waters. Carbon sequestration efficiency by hydrothermal Fe is much higher than those from artificial mesoscale Fe-addition experiments and in the range of values measured in well-recognized shelf driven natural fertilizations occurring in the Southern Ocean around Kerguelen and Crozet Islands, confirming that natural Fe fertilizations are more efficient. It is necessary to pay attention in future studies to the timescale of delivery of this newly-recognized mode of Fe supply through shallow hydrothermalism, especially in biogeochemical models (Bonnet, Guieu et al., 2023, Science).

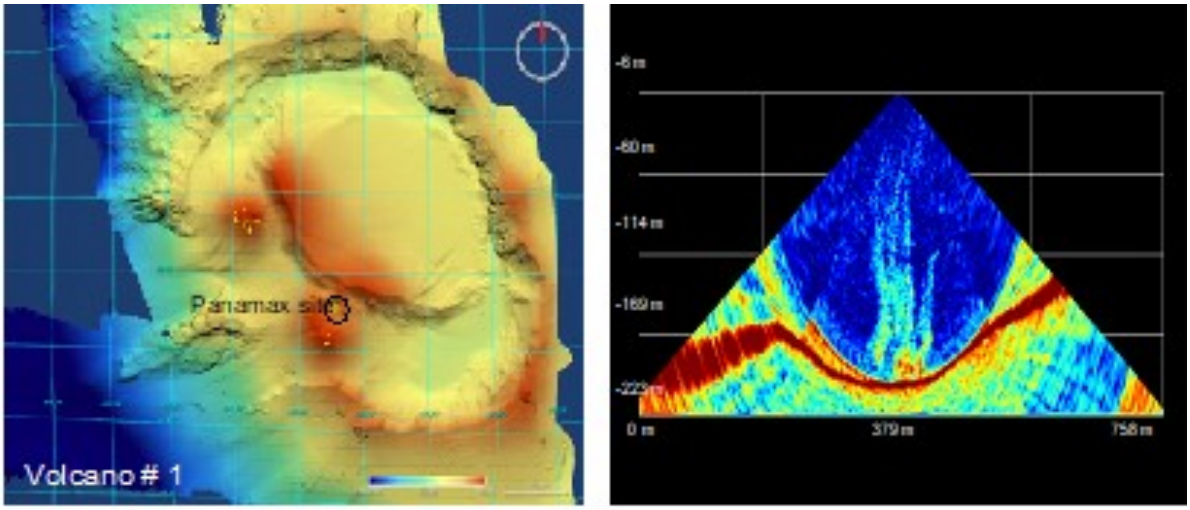

Figure FR-2: *Bathymetry of one of the explored volcanoes performed during TONGA (left). Multibeam echo sounder image showing hydrothermal gas and fluid emissions from the seafloor (~ 200 m) rising up to ~10 m below the surface (right) (Bonnet, Guieu et al., 2023).*

- Influence of shallow hydrothermal fluid release on the functioning of phytoplankton communities

The mechanisms behind iron fertilization by shallow hydrothermal sources was explored in details through novel trace metal clean mixing experiments in minicosms. Hydrothermal fluids had an initial toxic effect and some phytoplankton detoxified the environment through the production of ligands, making the toxic metals in the fluids less available; after this initial period, a strong stimulation of primary production was observed with N_2 fixation and increase in carbon export rates, in line with in-situ observations (Tilliette et al., 2023).

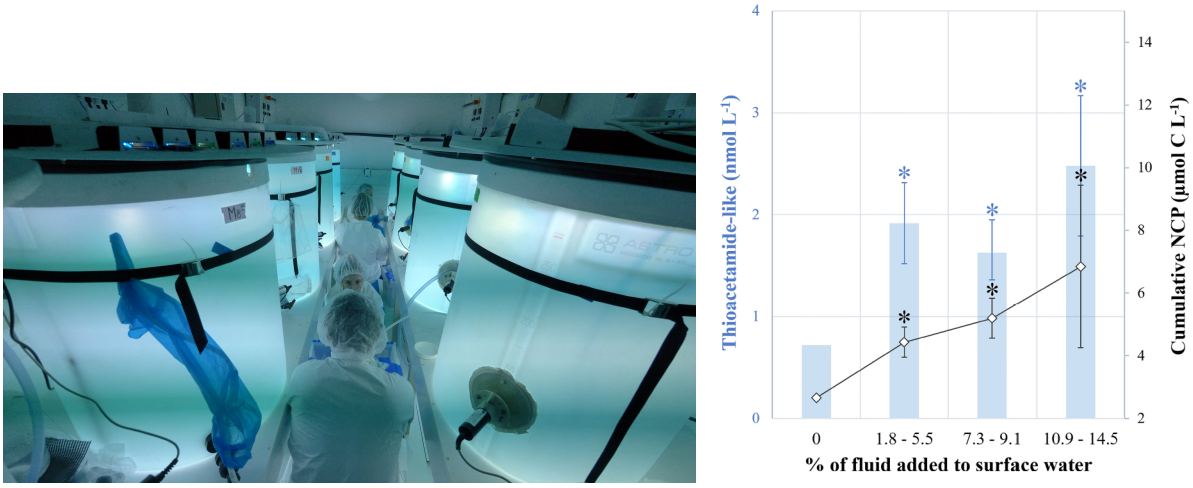

Figure FR-3: *(Left) The sampling team during the mixing experiment, inside the clean container, on-board R/V Atalante. (Right) Summary diagram. (1) in blue, the ratio of thioacetamide-like compound concentrations measured 12 h after the mixing versus at the end of the experiment (D0.5:D9) and, (2) in black, the ratio of cumulative 13C-net community production rates measured at the end versus at the start of experiment (D9:D0.5). Treatments were grouped: no addition (0, control), low (+1.8-5.5%), medium (+7.3-9.1%) and high (+10.9-14.5%) fluid addition. Asterisks represent the significance of each group relative to control (unpaired Student test, $p < 0.01$) (Tilliette et al., 2023).*

- <u>Solid-solution distribution of the cosmogenic beryllium-7 in the water column</u>

The cosmogenic radionuclide ^{7}Be has been applied as a tracer of dynamical processes in the upper ocean and of atmospheric deposition of trace elements at the sea surface. These applications usually assume that ^{7}Be is entirely in the dissolved form, and that scavenging and downward export of ^{7}Be by settling particles can be neglected. This work questions the validity and limits of this hypothesis. The ^{7}Be activity in suspended particles collected in and below the mixed layer in oceanic regions as different as the Mediterranean Sea, the Southern Ocean and the subpolar Atlantic (section GEOVIDE/GEOTRACES-GA01). While the particulate ^{7}Be ($^{7}Be_{p}$) activity generally monotonically decreases with depth below the mixed layer, they reveal that, at least in some oceanic regions, the removal of ^{7}Be by marine particles may be significant. The $^{7}Be_{p}$ fraction ranges from 2% to 32% of the total activity ($^{7}Be_{tot}$) along the GEOVIDE section in the North Atlantic. In the Labrador Sea, the comparison of the $^{7}Be_{p}$ inventories with the dry ^{7}Be deposition fluxes estimated from aerosol samples collected during GEOVIDE suggest that a significant portion of $^{7}Be_{p}$ may be removed by sinking particles. Future research should focus on quantifying the downward export of $^{7}Be_{p}$ to deep waters, and on assessing its temporal and spatial variability. For this objective, both seawater and particulate samples should be collected at the same locations, at the same depths, and at the same time (Grenier et al., 2023).

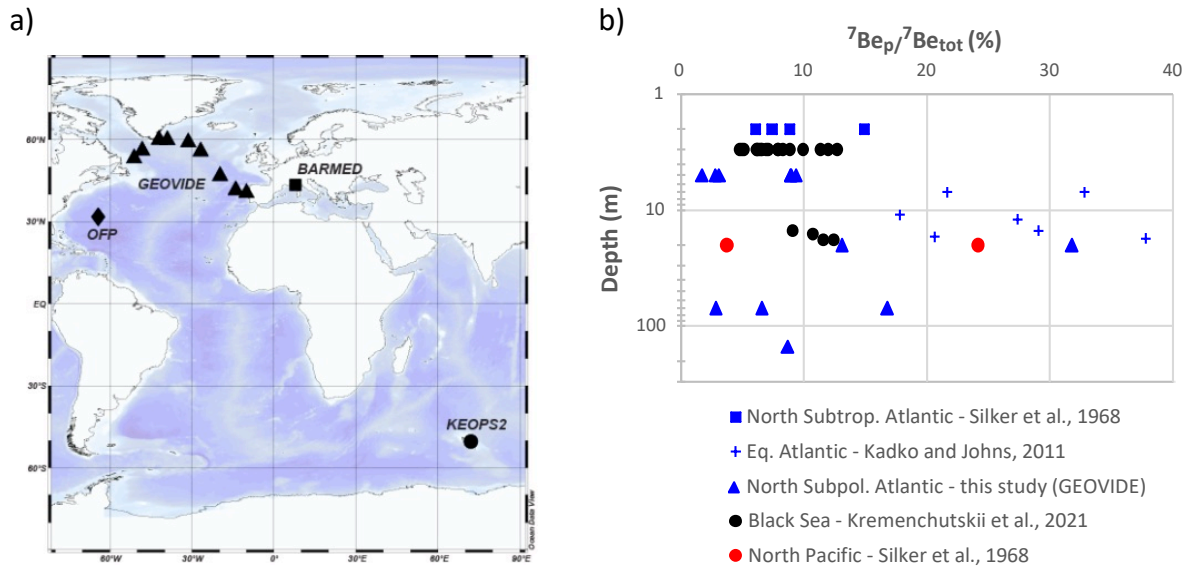

Figure FR-4: *a) Sampling stations: OFP (Sargasso Sea), BARMED (Mediterranean Sea), KEOPS2 (Southern Ocean), and GEOVIDE/GA01 (North Atlantic). b) Compilation of estimates of the $^{7}Be_{p}/^{7}Be_{tot}$ activity ratio in the open ocean (in %, linear scale) as a function of depth (in m, log scale). The particulate ^{7}Be fraction of the GEOVIDE samples accounts for 2-9% of the total ^{7}Be activity at a water depth of 5 m (n = 6) and 13-32% at 20 m (n = 2). These ranges are consistent with the existing published data (Grenier et al., 2023).*

GEOTRACES or GEOTRACES relevant cruises

- In 2023: 2 cruises were conducted at the DYFAMED station in the framework of the BE-7-FLUX project (LEFE-INSU; PIs: Pieter van Beek and Mélanie Grenier) in March and April/May to study the vertical distributions of dissolved and particulate 7Be. 7Be has been used as a tracer to study vertical mixing in the upper water column and to quantify TE atmospheric fluxes.

New projects and/or funding

- **ANR AWESOME-SWINGS**: A Water mass analysis and Exploration of linkS betweenmarine Organisms and trace MEtals along the South West INdian GEOTRACES Section. Principal Investigator: Hélène Planquette (LEMAR, Plouzané), Co-PI: Catherine Jeandel (LEGOS, Toulouse). 48 months, **481 380 €.**
- **BE-7-FLUX** (LEFE-INSU 2022-23; PIs: Pieter van Beek and Mélanie Grenier): Toward a better understanding of the 7Be cycle in the ocean.
- **IsoMargin** (EU-MSCA 2022-2024; PIs: Nolwenn Lemaitre and François Lacan): Isotopes of micronutrients to trace margin sediment fluxes

GEOTRACES workshops and meetings organized

- Hosting the S&I committee in LEMAR, Plouzané, 7-9 September, 2022

Outreach activities conducted

- ***N. Lemaitre in March 2023.*** Presentation of the research profession to students of a primary school (Blagnac) as part of the International Days of Women and Girls in Science (2h).
- ***N. Lemaitre in May 2022.*** Article in the online journal 'Connected Oceans': Nolwenn Lemaitre, Winner of a European Fellowship
- ***N. Lemaitre in May 2022.*** Phone conference with a visual impaired audience (Les Chemins Buissonniers)
- ***N. Lemaitre in March 2022.*** Online TV report (TV Trégor): Dans le sillage de Nolwenn Lemaître
- ***M. Lagarde in February 2023.*** Presentation of research careers and oceanographic cruises to high school students, lycée Berthelot, Toulouse

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

** marks the results highlighted in this report*

- Blain, S., Planquette, H., Obernosterer, I., Gueneugues, A., 2022. Contrasted export dynamics of 15 trace elements explained by their attribution to lithogenic and biogenic vectors in the Southern Ocean. *Global Biogeochemical Cycles, 36(5), e2022GB007371,* http://dx.doi.org/10.1029/2022GB007371.
- *Bonnet, S., Guieu, C., Taillandier, V., Boulart, C., Bouruet-Aubertot, P., Gazeau, F., Scalabrin, C., Bressac, M., Knapp, A. N., Cuypers, Y., González-Santana, D., Forrer, H. J., Grisoni, J.-M., Grosso, O., Habasque, J., Jardin-Camps, M., Leblond, N., Le Moigne, F. A. C., Lebourges-Dhaussy, A., Lory, C., Nunige, S., Pulido-Villena, E., Rizzo, A. L., Sarthou, G., and Tilliette, C., 2023. Natural iron fertilization by shallow hydrothermal sources fuels diazotroph blooms in the ocean. *Science* **380**, 812-817, 10.1126/science.abq4654.
- Dulaquais, G. Fourrier, P., Guieu, C., Mahieu, L., Riso, R., Salaun, P., Tilliette, C. and Whitby, H. (Accepted) The role of humic-type ligands in the bioavailability and stabilization of dissolved iron in the Western Tropical South Pacific Ocea. *Accepted for publication in Frontiers in Marine Science, Marine Biogeochemistry.*
- Fourrier, P., Dulaquais, G., Guigue, C., Giamarchi, P., Sarthou, G., Whitby, H., & Riso, R., 2022. Characterization of the vertical size distribution, composition and chemical properties of dissolved organic matter in the (ultra) oligotrophic Pacific Ocean through a multi-detection approach. *Marine Chemistry*, *240*, 104068. https://doi.org/10.1016/j.marenvres.2022.105754. P. Fourrier was a PhD student at LEMAR
- Fourrier, P., Dulaquais, G., & Riso, R., 2022. Influence of the conservation mode of seawater for dissolved organic carbon analysis. *Marine Environmental Research*, *181*, 105754. P. Fourrier was a PhD student at LEMAR
- *González Santana, D., Lough, A.J., Planquette, H., Sarthou, G., Tagliabue, A., Lohan, M.C., 2023. The unaccounted dissolved iron (II) sink: insights from dFe(II) concentrations in the deep Atlantic Ocean. *Science of the total environment, 862, 16117,* https://doi.org/10.1016/j.scitotenv.2022.161179. D. González Santana was a PhD student at LEMAR.
- *Grenier M., van Beek P., Lerner P., Sanial V., Souhaut M., Lagarde M., Marchal O., Reyss J.L., 2023. New insights on the ^{7}Be cycle in the ocean. *Deep-Sea Research I*, 194 doi.org/10.1016/j.dsr.2023.103967
- Le Roy E., van Beek P., Lacan F., Souhaut M., Sanial V., Charette M., Henderson P., Deng F., 2023. The distribution of 227Ac along the GA01 section in the North Atlantic. *Marine Chemistry* 248, pp.104207. ⟨10.1016/j.marchem.2023.104207⟩. ⟨hal-03959500⟩.

- Lemaitre N., Du J., de Souza G., Archer C., Vance D., 2022. The essential bioactive role of nickel in the oceans: Evidence from nickel isotopes. *Earth and Planetary Science Letters*, 584, 117513. https://doi.org/10.1016/j.epsl.2022.117513.
- Liang, Z., McCabe, K., Fawcett, S.E., Forrer, H.J., Jeandel, C., Marconi, D**.,** Planquette, H., Saito, M.A., Sohm, J.A., Thomas, R.K., Letscher, R.T., and Knapp, A.N. A global ocean dissolved organic phosphorus (DOP) concentration database (DOPv2021). *Scientific Data, Nature 9* (1), 772. https://doi.org/10.1038/s41597-022-01873-7
- Liao W.-H., Planquette H., Moriceau, B., Lambert, C., Desprez de Gesincourt, F., Laurenceau-Cornec, E., Bucciarelli, E., Sarthou, G., Gorgues, T. The effect of temperature on the non-reductive iron dissolution from resuspended sediments: mechanisms and Fe isotope fractionation. *Geochimica et Cosmochimica Acta,* https://doi.org/10.1016/j.gca.2023.04.014 W.-H. Liao was a Postdoc at LEMAR at the time.
- *Tilliette, C., Gazeau, F., Portlock, G., Benavides, M., Bonnet, S., Guigue, C., Leblond, N., Lory, C., Marie, D., Montanes, M., Pulido-Villena, E., Sarthou, G., Tedetti, M., Vorrath, M.-E., Whitby, H., and Guieu, C., 2023. Influence of shallow hydrothermal fluid release on the functioning of phytoplankton communities. *Frontiers in Marine Science* **10**, https://www.frontiersin.org/articles/10.3389/fmars.2023.1082077. C. Tilliette was a PhD student at LOV.

Completed GEOTRACES PhD or Master theses

- Pierre FOURRIER**.** Biogéochimie de la Matière Organique Dissoute dans l'Océan Pacifique. Biogeochemistry of dissolved organic matter in the Pacific Ocean. https://www.theses.fr/2022BRES0082

GEOTRACES presentations in international conferences

Goldschmidt, Hawaii, 2022:

- Baudet, C., Planquette, H., Bucciarelli, E., Sarthou, G., Pelleter, E., Gayet, N., Germain Y., Jeandel, C. Trace metal distributions in the South West Indian Ocean (SWINGS cruise): a focus on iron and manganese. C. Baudet is a PhD student at LEMAR

- Belhadj Senini, M., Jeandel, C., Lagarde, M., Planquette H., Baudet C. Dissolved and particulate REE distributions in the tropical and subtropical Indian Ocean (SWINGS cruise).

- Cloete, R., Loock, J., van Horsten, N., Samanta, S., Mtshali, T., Fietz, S., Planquette H., Roychoudhury A. Winter Copper and Nickel distributions from the Indian sector of the Southern Ocean. R. Cloete is now a postdoc at LEMAR.

- Lagarde, M., Pham, V., Belhadj, M., Lherminier, P., and Jeandel, C.: Rare Earth Element partition coefficients in the North Atlantic (GEOVIDE cruise, GEOTRACES GA01).

- Lemaitre, N., Planquette, H., Jeandel, C., Ellwood, M., Hassler C., Vance, D. Nickel and zinc cycling in the Southern Ocean: insights from isotopes.

- Léon, M., van Beek, P., Sanial, V., Souhaut, M. Jeandel C., Planquette H. Radium isotopes to emphasize a hydrothermal plume in the South West Indian Ridge region.

Challenger society, 2022:

- Mahieu, L., Whitby, H., Dulaquais, G., Tilliette, C., Bressac, M., Arnone, V., González-Santana, D., Sarthou, G., Planquette, H., Guieu, C., Bonnet, S., Salaün, P. Iron-binding ligands in the Western South Tropical Pacific. GPpr14 – TONGA cruise 2019

- Goddard-Dwyer M., Ryan-Keogh T., Hamelin B., Liao W., González-Santana D., Baudet C., Vorrath M., Lemaitre N., LoMonaco C., Barut G., Fin J., Mignon C., Vivier F., Kestenare E., Eldin G., Clerc C., Izard L., Sergi S., Planquette H., Jeandel C., Tagliabue A., Whitby H. Biogeochemical Cycling of Iron Binding Humic Ligands in the South-West Indian Sector of the Southern Ocean.

12th International Symposium Geochemistry of the Earth's Surface 2022:

- Lemaitre, N., Ellwood, M., Hassler, C., Jeandel, C., Planquette, H., Vance, D. Nickel and zinc cycling in the Southern Ocean: insights from isotopes.

Submitted by Kazuyo Tachikawa (kazuyo@cerege.fr).