Concentrations and chemical forms of trace metals in coastal seawater in coral reefs and their relationship to coral mucus

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Coastal seawater in coral reefs near Okinawa Island in Japan, which is in oligotrophic conditions, has a diverse and unique ecosystem. It is possible that nutrient salts and trace metals, classified into nutrient type, are effectively supplied to marine phytoplankton and zooxanthellae from seawater. However, the concentrations and chemical forms of trace metals in coastal seawater in coral reefs have been scarcely reported so far. In addition, it is reported that the coral mucus plays an important role as a nutrient supply to fishes and other animals, and scavengers of suspended particles [1]. In the present study, firstly, the characteristics of the concentrations and chemical forms of trace metals in coastal seawater in coral reefs were investigated according to seasonal variation. Secondly, the relationship between concentrations of trace metals in seawater in coral reefs and in coral mucus were discussed.

A monitoring investigation of the coastal seawater in coral reefs, located near the northern part of Okinawa Island, was carried out once every month from Sep. 2010 to Aug. 2011. After the chemical species in the seawater were separated into dissolved, acid-soluble particulate, and ionic ones, an analytical method using a chelating resin disc and a disposable syringe was employed for desalination and preconcentration of trace metals. After that, trace metals in the concentrated solutions were measured by ICP-MS. On the other hand, coral mucus was sampled from *Acropora nasuta* exposed to sunlight and then analysed by ICP-MS.

As a result, 10 elements in the dissolved form of each sample could be determined. The average concentrations (unit: $\mu g\ L^{-1}$)for all samples were as follows: Mo:10.8, U: 3.2, V:1.6, Mn:0.14, Ni:0.16, Zn:0.13, Cu:0.070, Pb:0.023, Co:0.0022, Cd:0.0019. The concentrations for most trace metals were close to ones at the surface of open seawater in the North Pacific Ocean, but the concentrations of Co, Ni, Cu, Zn, and Cd, classified into nutrient type, were significantly lower than ones in other coastal seawater. These results suggest that the coastal seawater in coral reef ecosystems were in oligotrophic conditions. The most of Mo, V, and U exist in dissolved forms, while most Fe exists in acid-soluble form. 50–70 % of Cu, Zn, Pb, and Co and 21–42 % of Cd, Mn, and Ni existed in acid-soluble particles. These results suggest that some trace metals in the nutrient type exist as biogenic particulate matter. As for their relationship to coral mucus, the concentrations of Mn, Fe, Co, Ni, Zn, Cd, and Pb in coral mucus were 10-150 times larger than those dissolved in coastal seawater in coral reefs, while those of Na, Mg, K, V, and U in coral mucus were almost the same as the dissolved forms. The elements which showed high concentration for acid-soluble particles in June and January were almost the same as those in coral mucus. Therefore, the concentrations of trace metals in acid-soluble particles in June and January may be affected by coral mucus, which combined with sediment and was lifted by tidal flows.

[1] C. Wild et al, (2004), *Nature* **428**, 66-70.

Can Nd tell us about Mediterranean Outflow Water?

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Although εNd is a well established water provenance tracer for deep ocean circulation, there remains some debate over the practicability of Neodymium (Nd) isotopes at intermediate water depth on the continental-margin. Using the method of Vance and Burton (1999), we intend to answer some of the questions on how useful Nd can be for tracking Mediterranean Outflow Water (MOW), and whether or not Nd isotopes (expressed as ε_{Nd}) measured in foraminfera from this setting represent a true water-column signal, or a post-depostional one.

We have measured ε_{Nd} in 90 foraminiferal samples (each containing 400-900 individuals) and fish-remains samples in order to assess whether or not Nd extracted from these palaeo archives can elucidate on the evolution of MOW at high temporal resolution. We examined Late Quaternary samples, to make direct comparisons between our data, other Quaternary MOW reconstructions[e.g.2] (including different phases from the same samples) and modern observations[e.g.3]. We also analysed samples from the Late Miocene, 8-6 Ma, when progressive tectonic restriction of the Betic-Rif region caused Mediterranean-Atlantic water exchange to fluctuate dramatically, making the period a good test-case for MOW extremes. We further interpreted our ε_{Nd} record within the context of more finely resolved Sr and foram assemblage records, including data we obtained from the same samples as the Nd.

From these results, we propose that ε_{Nd} in foraminifera and fish teeth can tell us about MOW evolution. For example, we clearly detect changes in water provenance, indicative of marine shallowing events and corridor 'closure'. Furthermore, our data suggest that foraminfera-hosted Nd is not diagenetic and thus our planktic Nd indeed appears to be a 'true' water-column signal. However, questions remain over whether or not boundary exchange[4] and localised riverine inputs have confused the extracted ε_{Nd} signal, and although our Sr and benthic assemblage data do present some clues to the answers, these are by no means exhaustive tests. In short, there remain significant challenges in fully understanding this continental-margin ε_{Nd} record, and we advise that although Nd can provide valuable information about changes in MOW, a multi-proxy approach is essential for making robust interpretations of the data.

[1] Vance & Burton (1999) *EPSL* **173 (4)**, 365-379. [2] Stumpf *et al.* (2010) *Quaternary Science Reviews* **29 (19-20)**, 2462-2472. [3] Spivack & Wasserburg (1988) *Geochim. Cosmochim. Acta* **52,** 2762–2773. [4] Lacan & Jeandel (2005) *EPSL* **232 (3-4)**, 245-257.