

**Cold-water corals: exploring chromium isotopes as archives of
intermediate water oxygenation**

Edward Allen Boyle

2020-2021 Seed Project Report

MIT Portugal Partnership 2030

MIT Portugal

1. PROJECT TEAM

- **MIT-** Ed Boyle, Professor; Rick Kayser, Lab Manager; Tianyi Huang, postdoc
- **Collaborators in Portugal-** Lélia Matos, IPMA (with consultation with Fatima Abrantes and Angie Voelker, also of IPMA)
- **Other collaborators-** none

2. **SUMMARY-** Ocean oxygen depletion is one of the most significant impacts of climate change that will affect most marine biota including commercially important fish stocks. It is believed that between 1970-2010, oxygen loss occurred at a rate of 0.5 to 3.3% from the ocean surface to 1000m [1]. In order to mitigate oxygen loss consequences we need to better document and understand them. Although long-term ocean monitoring programs and mooring systems provide the study of physical and chemical water parameters for the most recent decades, we need paleoceanographic records for time periods exceeding a half-century.

The impact of oxygen loss is higher at intermediate depths of the ocean (200-1500m), especially in areas where dissolved oxygen content is already low (<2 $\mu\text{mol/kg}$) due to natural causes, called Oxygen Deficient Zones (ODZs). Intermediate depths have been less frequently studied in spite of being involved in important ocean physical and chemical processes, such as mode water formation, upwelling, mixing and stratification. These intermediate depths are also home of the diverse ecosystems engineered by calcifying cold-water corals. Cold water corals are also important geological archives for evaluating past ocean conditions. Their strong thick structures are less prone to recrystallization and diagenesis on the seafloor, and their aragonitic skeletons are datable with high accuracy by ^{14}C and uranium-thorium methods. It is also possible to use them to perform elemental analyses documenting several physical and chemical conditions (like temperature, carbonate chemistry, water mass tracing, ventilation, pollutants) within the same colony.

Chromium and chromium isotopes in the ocean are a new geochemical tracer (just beginning to be investigated by geochemists during the past decade). Cr enters the oceans from continental weathering via rivers, and departs via sedimentation, with a residence time of about 40,000 years. Four main processes influence the distribution of Cr and Cr isotopes in the ocean:

(1) Marine biota extract dissolved Cr from seawater to support essential biochemical processes (Cr enzymes. This results in the depletion of Cr in surface waters (down to 1.2 nmol/kg) and the enrichment of Cr in old deep waters (up to 6 nmol/kg). that have accumulated Cr from the microbial decay of sinking biological matter. This decay also results in proportionate oxygen depletion.

(2) Biological uptake is accompanied by a -0.8‰ depletion of ^{53}Cr relative to ^{52}Cr , leading to a linear $\delta^{53}\text{Cr}$ vs $\log [\text{Cr}]$ relationship (negative slope) throughout most of the open ocean (figure 1).

(3) In intermediate-water regions of the ocean where oxygen is very low (ODZs), Cr is partially reduced from its oxidized form [Cr(VI), CrO_4^{2-}] from its reduced form [Cr(III), Cr^{3+} hydrated cation]. $\delta^{53}\text{Cr}$ of this Cr(III) is depleted by -1.5‰ relative to the Cr(VI) source (figure 2).

(4) Cr(III) is “particle-reactive”, meaning that it attached to sinking particles and is partially removed from the water column into ocean seafloor sediments. This removal of the light Cr(III) leaves the residual dissolved Cr significantly heavier than the nearby oxic source waters.

In this project we will investigate whether cold water corals record the chromium concentrations and/or the chromium isotope ratios of the water they grow in. These corals have been demonstrated to faithfully record many seawater properties (Lead (Pb) concentrations and Pb isotope ratios, ^{14}C , Nd isotope ratios, Sr isotope ratios, etc.). As oxygen-respiring animals, corals live in oxic waters where Cr is predominantly in the oxidized CrO_4^{2-} form, and we anticipate that they will incorporate Cr into their divalent CO_3^{2-} lattice sites (as they do for SO_4^{2-}). One question we will determine is if the Cr concentration of the skeleton is proportional to the Cr concentration of the water they grow in (as is seen for Pb). Whether or not they reflect the Cr concentration, do they still reflect the chromium isotope composition of the seawater (as they do for Pb and neodymium, Nd). If so, then corals from regions in high-oxygen and low-oxygen (but not too low) regions will reflect past changes in the dissolved oxygen content of the intermediate-water ocean

From areas where water Cr concentration data exist (but not stable isotopes which have a much more limited database), we will use the existing linear relationship between $\delta^{53}\text{Cr}$ and $\log[\text{Cr}]$ to estimate $\delta^{53}\text{Cr}$. Where we can acquire water samples from the growth site, we will analyze $\delta^{53}\text{Cr}$ in these seawater samples. If the Cr and Cr isotope proxy is validated, we will perform preliminary investigation of its paleo applicability by analyzing Mid-Holocene and glacial maximum coral samples (which are in the MIT sample archive) contrasted with living samples.

The Portuguese team (from CCMAR and IPMA) is composed by: Lélia Matos, an expert in cold-water coral biogeochemistry and ecology who will be running the project; Fatima Abrantes, an experienced paleoceanographer working with productivity proxies; and Marcos Fontela, an early career chemical oceanographer with experience in tracer transport and carbon burial, who will compile water Cr concentration datasets and estimate water Cr isotopes. This collaboration will serve to the ongoing project between Drs. Boyle and Matos studying Pb pollution entrainment into the thermocline. If successful, this new project will serve as a new proxy to reconstruct the intermediate depth oxygenation state, which could improve the scientific community's ability to understand and predict the location and behavior of oxygen deficient zones.

3. OUTCOMES & ACHIEVEMENTS

Covid restrictions have slowed the pace of this work and we continue to work on this project despite expiration of the seed funding. As this report is written, we have achieved the following results. Our measurements are done by multiple-collector magnetic sector plasma mass spectrometry, which requires highly purified samples for accurate results.

(1) Initial analysis of three 0.2-0.6 gram cold water coral samples showed that the Cr concentration is very low, less than a few tenths of a part per million. At this concentration level it is difficult to make accurate Cr isotope measurements. Cr isotope ratio analysis of the slightly larger 0.6 gram sample gave a $\delta^{53}\text{Cr}$ of $-0.3 \pm 0.3\%$. In order to make more precise measurements, larger samples (at least a factor of five, preferably a factor of 10) are required.

(2) A second attempt to analyze three ~2.5 gram samples confirmed the sub-ppm deep coral Cr concentrations (0.01-0.03 parts per million) with more accurate data. However, this experiment revealed a sample processing problem in our analytical procedure: in the first step of our analytical purification procedure, we use ammonium persulfate to oxidize Cr from cationic Cr(III) to anionic Cr(VI) to separate Cr from major cations such as calcium. However, the oxidation process converts persulfate to sulfate ion, and given the high concentrations of calcium in these dissolved coral samples, calcium sulfate precipitated, carrying 95% of the divalent anionic CrO_4^{2-} in the precipitate substituting for divalent anionic SO_4^{2-} . Although the residual 5% of Cr was sufficient to make a high-quality isotope dilution concentration measurement, for all but one ten-second cycle of one of the samples the Cr signal was too low to get precise Cr isotope measurements. That one cycle gave a $\delta^{53}\text{Cr}$ value of -0.42 , confirming the original lower-precision Cr isotope measurement on a smaller sample.

(3) Now our challenge is to develop a way to remove the Cr from the Ca so that we can engage in our ion exchange purification and get a strong signal yielding a precise Cr isotope data. Prof. Matos notes that Bonnand et al. (2010, EPL 382: 10-20) utilized a cation exchange method to purify Cr from Ca solutions. We had dismissed this procedure in our original analytical development because cation exchangers use sulfonic acid groups for their negative charges – and sulfonic acid slowly leaks out of the cation exchange column, which is a problem for us because of ICPMS mass interferences introduced by polyatomic sulfur species in the cooling plasma. However, since that time, we have developed a purification method consisting of three anion exchange columns that purify Cr of sulfate and iron, hence we can use the cation exchange method to separate Cr from Ca, then use the anion exchange steps to remove sulfate from our analyte. We anticipate that this method is likely to work.

(4) Work scheduled for the next two months will confirm that this new procedure gives us precise chromium isotope data on coral samples >2.5 grams. We will then be ready to analyze new samples that Prof. Matos is sending us and we anticipate submitting another seed grant proposal to complete this work demonstrating that cold water corals are an accurate recorder of present and past Cr isotope concentrations in the ocean, and we will then proceed to analyze samples just outside of the Namibian Margin low-oxygen zone.

Figure 1: Left: deep sea camera frame with captured corals. Right deep sea coral LM5



4. Attachments

- Poster (MIT-Portugal Annual Conference October, 2021)

Cold-water corals: exploring chromium isotopes as a tracer of intermediate water oxygenation

Prof. Ed Boyle, MIT

Dr. Lélia Matos, IPMA

Tianyi Huang, MIT

Abstract: Ocean oxygen has been decreasing for the past 50 years and ocean models suggest that it will continue to decrease into the future. In order to better understand the processes that control oxygenation of the ocean, we need to have longer records, which can only be obtained from geological proxies such as corals and sediments. Cr and Cr isotopes are sensitive to ocean oxygenation levels, particularly near very low oxygen zones (ODZs). We are undertaking the first tests of the fidelity of cold water corals as recorders of past intermediate-water Cr and Cr isotope ratios to evaluate how well coral Cr and Cr isotope records can constrain ocean oxygenation levels from the past.

As we began this work, the Cr geochemistry of cold-water corals was largely unknown: although a few geologists had measured Cr isotopes in uncleaned corals and carbonate sediments, our previous work on coral and foraminiferal trace elements (TE) showed that most of the TE measured in uncleaned samples is derived from ferromanganese oxides and detrital silicates and *not* securely held within the calcium carbonate crystal lattice substituting for Ca^{2+} and CO_3^{2-} ions. So our strategy has been to clean coral samples chemically under ultrasonic conditions to remove the contaminants.

As this work began, Covid-19 restrictions delayed much of the work until just recently, and a major multicollector plasma mass spectrometer malfunction delayed analyses of samples in hand until just this week (more samples will be analyzed now that the mass spectrometer is repaired). So here we are only reporting on the first few analyses of cleaned cold water corals for Cr and Cr isotopes.

We analyzed two polyps of a live-collected cold-water coral from the Iberian margin and two polyps from a glacial maximum age coral. The sample size was ~0.5 grams. We found that indeed as suspected the Cr/Ca ratio of the coral was much lower for these cleaned samples compared to previous reports for uncleaned samples, with a large part of our final Cr analyses due to the processing blank. The coral samples had $\text{Cr/Ca} \leq 0.3 \mu\text{mol/mol}$. The $\delta^{53}\text{Cr}$ was $-0.3 \pm 0.3\text{‰}$. This data shows that if we are to measure Cr and Cr isotope ratios in deep sea corals, much larger samples would have to be utilized, preferably >5 grams. This should be possible as typical specimens are about 100 grams.

