Changes in the deglacial NW Atlantic from deep sea coral ε_{Nd}

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Carbon storage in the deep ocean during glacials and its subsequent release during deglaciation undoubtedly played a role in glacial/interglacial variation of atmospheric CO_2, with the Southern Ocean a strong candidate for both glacial storage and deglacial venting to the atmosphere. While radiocarbon records support this hypothesis [1], they cannot unambiguously identify the water masses involved. To do so requires pairing the radiocarbon data to a conservative water mass tracer, such as the Nd isotope composition (ε_{Nd}).

We describe the use of deep sea corals as an archive material providing same-sample U/Th ages, radiocarbon, and Nd isotope compositions. The majority of corals in this study are deglacial in age and span intermediate water depths of 1000 to 2600 m on the New England Seamounts (NW Atlantic), where pronounced changes in water column radiocarbon across the last glacial/interglacial cycle have already been identified [2, 3].

In the modern ocean, North Atlantic Deep Water has an offset to atmospheric radiocarbon of ~65‰ ($\Delta^{14}C$), whereas Antarctic Bottom Water has a larger offset of ~-165‰ due to longer storage time in the deep ocean. During the last glacial maximum, this storage time probably increased, leading to offsets of perhaps as much as -300‰ or greater for Southern source water [1, 4]. Circulation of these waters in the Atlantic should be identifiable from Nd isotope compositions due to their distinct compositional source regions, resulting in unradiogenic North Atlantic Deep Water (~13.5 ε_{Nd}; [5]) and more radiogenic Antarctic Bottom Water (~-9 ε_{Nd}; [6]). These are not thought to have changed significantly over the last glacial/interglacial cycle [7].

Shifts in coral radiocarbon are most pronounced between 15 and 17 ka, demonstrating incursion of radiocarbon-depleted water masses (i.e. -150 to -200‰ $\Delta^{14}C$) up to depths of ~1700 m in the NW Atlantic [3]. The corresponding Nd isotope compositions are -13 to -14.5 ε_{Nd}, typical of Northern source waters. Overlying this are comparatively well ventilated waters (-100 to -150 ‰ $\Delta^{14}C$) with ε_{Nd} compositions in the range of -11 to -12 ε_{Nd}, suggestive of mixing between Northern and Southern source waters. It is emphasised that these Nd isotope data are contrary to expectations, where shifts to more radiogenic compositions were forecast to reflect incursion of Southern source water against the less radiogenic background of the North Atlantic. These data raise several questions concerning our current understanding of ocean circulation changes during the deglaciation as well as the Nd isotope proxy as a tracer of ocean circulation, which will be discussed in this presentation.

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Chloride: the Unexpected Poison in the Growth of Crystalline Iron Oxides

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Introduction

Iron is one of the essential elements to life on Earth, existing primarily in various insoluble ferric (Fe^{III}) iron oxide and oxyhydroxide phases. These phases exhibit varying degrees of solubility and bioavailbility: the amorphous Fe-oxide and ferrihydrite being the most soluble, and hematite and goethite being the least soluble and most stable phases. Different cations and anions substitute into or interact with these phases, modifying their growth and solubility. If ligands bind strongly to the freshly precipitated iron oxide phase or ferrihydrite, they block polymerization reactions and slow the transformation to more stable Fe-oxide phases. This is expected for strongly complexing ligands, such as sulfate, phosphate, and carbonate. Ligands such as chloride are not expected to play a large role; however, this study found that chloride deters iron oxyhydroxide growth.

Freshly precipitated iron hydroxides and their transformation to crystalline phases were monitored by IR and X-ray absorption spectroscopy (XAS) methods. The structural information about Cl, S, and Fe was found using XAS techniques at the National Synchrotron Light Source (Brookhaven National Laboratory, NY, USA). Studies were conducted at room temperature and at pH values of 5.5 and 8.1.

Results & Discussion

At pH 5.5, IR spectroscopy shows that transformation from freshly prepared ferric hydroxide to goethite was found to be hindered to the greatest extent by the presence of chloride. Spectral features corresponding to goethite (bending vibrations of OH) arose out of a broad band corresponding to the amorphous iron hydroxide. Even after 250 days, chloride containing samples showed no evidence of goethite. In contrast, the sulfate containing samples showed evidence of transformation into goethite before 120 days. The XANES spectra at the chlorine K-edge exhibit a clear pre-edge feature, which is indicative of a chlorine-iron bond. Additionally, Cl-EXAFS data on these samples indicate a Cl-Fe bond, supporting the XANES observations. At pH 8.1, the spectral features of goethite start appearing after just 70 days, and the Cl-Fe pre-edge feature is missing from the Cl-XANES spectra, indicating that the Cl-Fe bonds are not forming at the higher pH and the transformation is proceeding unhindered.

These results indicate that amorphous iron hydroxides and ferrihydrite can be stable for a long time, and could be the most prevalent phase when chloride is present in reacting solutions at slightly acid pHs. Additionally, chloride's direct role in the growth of iron oxides indicates that it is not simply an inert electrolyte in these systems, and its role cannot be ignored.