MATTHEW DRUCE

Zinc, Isotopes and Ocean Sediment: What's the Link to Earth's Future Climate?

Oceans and climate are intimately coupled. Today the amount of carbon dioxide in the atmosphere is rapidly rising as a result of anthropogenic (human) activities.[1] Increasing atmospheric carbon dioxide can influence global climate, producing changes to the global temperature, sea level and changes in the chemistry of the oceans. In turn, these changes can impact on the efficiency of the oceans in modulating climate change.[2]

During the Earth's history, similar periods of rapid climate change have taken place and are recorded in ocean sediments that archive these analogous time periods. In a circular way, the oceans can provide a means for us to resolve the uncertainties surrounding the Earth's future.

Climate is the measure of how the atmosphere behaves over relatively long periods of time, while weather relates to atmospheric conditions over much shorter timescales. Carbon dioxide in the atmosphere absorbs infrared radiation that is emitted from the Earth's surface after solar radiation comes into contact with it. This absorbed energy is then re-emitted from the carbon dioxide molecules in all directions, and some of this energy will return to Earth. Through this mechanism, increasing carbon dioxide in the atmosphere causes the average global temperature to rise.

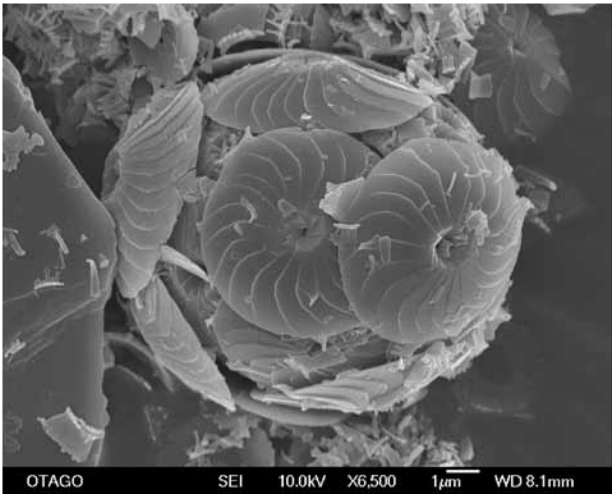

Figure 1. Scanning-electron microscope image of a fossilised phytoplankton at high magnification. The outer plates are constructed of calcium carbonate and deposited into sediment as it expires. This specimen was isolated from a sediment sample originating from the coast of New Zealand.

At the ocean–atmosphere boundary, carbon dioxide dissolves into seawater. Phytoplankton (Figure 1), microscopic plant-like organisms that exist in the very surface oceans, make use of this dissolved carbon dioxide during photosynthesis. This process of taking carbon dioxide into their cell and then utilising it effectively 'fixes' the carbon. As the phytoplankton expire, a large proportion of the 'fixed' carbon is permanently removed from the atmosphere and preserved in ocean sediments.[3]

Phytoplankton require sunlight, carbon dioxide and nutrients in order to photosynthesise and produce the energy needed to remain healthy. Typically, in the surface oceans phytoplankton growth is limited by the availability of one or more nutrients. Some nutrients are required in larger quantities, such as phosphate and nitrate, and these are termed macro-nutrients. However, those available in very low amounts (micro-nutrients) are also fundamental to phytoplankton growth. For example, it is well known that the availability of one micro-nutrient, iron, impacts phytoplankton productivity in many regions of the world's oceans.[4] However, much less is known about the role of other trace metals, such as zinc.

Zinc is essential to many biological processes, and is used in numerous enzymes. One example is the role of zinc in photosynthesis through its use in the enzyme Carbonic Anhydrase.[5] Carbon dioxide from the atmosphere dissolves in seawater and rapidly reacts to form a more soluble species, bicarbonate. Carbon dioxide and bicarbonate are not the same chemically, which means that the amount of carbon dioxide available to phytoplankton during photosynthesis can be low. However, the enzyme Carbonic Anhydrase is used to provide an additional reaction pathway with a lower energy requirement for the conversion of this dissolved bicarbonate back to dissolved carbon dioxide. Zinc acts as a metal centre (co-factor) that binds to a specific site on the enzyme, which activates it. By using zinc in this enzyme, phytoplankton can utilise the much larger 'pool' of bicarbonate to readily generate carbon dioxide and photosynthesise more efficiently.

Modern advances in technology and increased understanding of key techniques have paved the way to deconvolve the role of micro-nutrients in modulating climate change via carbon dioxide removal by the biological pump. One such advancement is the study of isotopes systems. Isotopes are atoms that contain a different number of neutrons and, as such, carry a slightly different atomic mass (i.e., heavier or lighter). However, it is important to note that isotopes are the same chemical element. For example, zinc exists in nature with five different masses; while chemically they are identical, some processes have a preference for particular isotopes. This can generate an isotopic fingerprint that can be used to understand what processes are taking place in specific environments.

In the surface waters of the modern oceans, light zinc isotopes are generally preferred by phytoplankton.[6] This results in the removal of light zinc isotopes from the surface by phytoplankton, leaving the residual seawater enriched in heavier zinc isotopes. This enriched seawater signature is recorded in the biogenic calcium carbonate secreted by phytoplankton.[7] Consequently, the chemistry of the past ocean is recorded, and as the phytoplankton expire this record is archived into the ocean sediments.

Ocean sediments accumulated over the Earth's history preserve key information about the chemical, biological and physical conditions in the oceans. These records can be used to investigate how past oceanic conditions reflect changes in the Earth's climate. Our research shows that the zinc isotope signature from the calcium carbonate excreted by phytoplankton represents a similar composition to the seawater signature at the time of deposition. This enables the zinc isotope system to be used to explore changes in circulation, nutrient availability and uptake, making it an exceptionally powerful tool in the reconstruction of past climate events. Zinc, as well as other micro-nutrients and their respective isotope systems, are emerging as key tracers that describe how phytoplankton can regulate the Earth's climate. While their potential is still being understood in the modern oceans – and in the Earth's history through sedimentary archives – these systems provide key parameters that can be used in climate models to predict the capability of the oceans in regulating climate.

Rapid climate change will have devastating consequences for life on Earth.[8] For humans, there is increased likelihood of severe weather events, from droughts to floods and wildfires, food shortages, lack of clean drinking water, increased famine, migration and conflict over natural resources. Furthermore, rapid change will endanger a vast range of fauna and flora that have been co-existing alongside humans for thousands of years, because most species will not be able to adapt to changing conditions fast enough. It is therefore imperative that we prepare for climate change, using sediment archives as an essential resource. The utilisation of these powerful oceanic isotope proxies will help make climate models more robust and accurate when used alongside conventional proxies. In turn, they can be used to set critical climate boundary parameters, as well as targets for governments to follow in the hope of mitigating disaster.

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1. P Friedlingstein et al., "Uncertainties in CMIP5 Climate Projections Due to Carbon Cycle Feedbacks," *J. Clim.*, 27 (2014), 511-26.
2. DM Sigman, MP Hain and GH Haug, "The Polar Ocean and Glacial Cycles in Atmospheric CO_2 Concentration," *Nature*, 466 (2010), 47.
3. MP Hain, DM Sigman and GH Haug, "The Biological Pump in the Past," in *Treatise on Geochemistry (Second Edition). Volume 8: The Oceans and Marine Geochemistry* (Amsterdam: Elsevier, 2014), 485-517.
4. MJ Behrenfeld, AJ Bale, ZS Kolber, J Aiken and PG Falkowski, "Confirmation of Iron Limitation of Phytoplankton Photosynthesis in the Equatorial Pacific Ocean," *Nature*, 383 (1996), 508-11.
5. MR Badger and GD Price, "The Role of Carbonic Anhydrase in Photosynthesis," *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 45 (1994), 369-92.
6. SG John, RW Geis, MA Saito and EA Boyle, "Zinc Isotope Fractionation during High-affinity and Low-affinity Zinc Transport by the Marine Diatom Thalassiosira oceanica," *Limnol. Oceanogr.*, 52 (2007), 2710-14.
7. GM Henderson, "New Oceanic Proxies for Paleoclimate," *Earth Planet. Sci. Lett.*, 203 (2002), 1-13.
8. IPCC Working Group II, *Climate Change 2014: Impacts, Adaptation, and Vulnerability. IPCC Fifth Assessment Report*, 2014, doi:10.1016/j.renene.2009.11.012.

RUTH NAPPER

From Ocean Sediment and Hidden Knowledge to the Wearing of Jewellery – A Reminder of Individual Responsibility

It all began with chatter and an underlying tension. A room filled with scientists and expectant artists, all waiting to see if they would be chosen – or would there be someone they wanted to choose?

Initially, I was captivated by the images of phytoplankton found in the ocean sediment samples that Matt Druce was working on. My mind wandered from the importance of micronutrients and the role of zinc isotopes to pondering how ocean acidification might alter the structure of these organisms, and how such changes could be portrayed using metal forming and melting methods used in jewellery fabrication. However, from my first meeting with Matt and from some papers he sent me, it was clear that his scientific endeavours were concerned with the distribution of different isotopes along the depth of the sediment – and thus with time – and could be used to inform on the ocean's productivity in the past.

This knowledge could then be combined with known temperature records over hundreds of thousands of years and be used to inform models of how the oceans may change as climate change continues. For his part, Matt saw my completed artwork as speaking honestly to the scientific knowledge that the core sample of sediment contained.

Although I am a maker of jewellery, I am also a scientist, and so being ‘true to the science’ was also an essential element I wanted to incorporate into the artwork. Sharing a range of enamel samples, stripes of pale greys, with added metal filings and salt to create sand-like textures and bright colours for a little ‘omph,’ it became clear that Matt also wanted to be true to the character of sediment, to its colours and textures. A visual representation of sediment that acts as a jewellery component to symbolise value also needs to have an inherent beauty. Was this possible with beige and browns? This was a challenge that I think has been resolved by using shades of sandy-toned enamels, with added texture and sandblasting to create a sand-like visual layering that also refers to the antiquity of the sediment sample.

I have used the shape of the core sample, its stratified nature and the colours of the sediment as key elements in the jewellery. These represent the scientific knowledge resident in the sediment. Words have been added to make it obvious that the message of ‘science as valuable’ cannot be missed. Additional words suggest that the wearer and the viewer should both ACT to combat climate change and halt, then reverse, the changes occurring in the ocean.

Both the selection and the wearing of jewellery can be intensely personal. Wearing this jewellery is both a reminder of climate change and a commitment to combat its effects on the ocean. The words “make an effort,” here displayed on a pendant, is what we all need to do.

Wearing an item of jewellery as a daily reminder that our actions matter may just work.

Ruth Napper is an artist and maker of contemporary jewellery. Photographs: Pam McKinlay.