

Coupled CO₂ and oxygen change over the last 100 Myr

Curious12

Biogeochemical Cycles

IAP2-19-095

Overview

The cycles of carbon and oxygen are intimately linked, and have both fluctuated over Earth's history. These fluctuations are in-turn thought to have driven major shifts in Earth's environment and the life it supports. However until recently methods of reconstructing past oxygen and CO₂ levels in the ocean and the atmosphere were largely qualitative. Thanks to recent developments in geochemistry, rapid progress is now being made on more quantitative tracers of planetary redox and CO₂ conditions, and these methods are now primed to provide new insights into major events in the geological record of environmental change.

This project will use novel trace element ratios and isotope systems in marine carbonates to reconstruct changes in ocean/atmosphere CO₂ and ocean redox conditions in key intervals of the last 100 Million years.

CO₂ reconstructions will be based on the boron isotope composition (δ¹¹B) of foraminifera (Foster & Rae 2016; Rae 2018), which reflects water pH – and thus CO₂ chemistry. This method has provided several high profile reconstructions during this time period (e.g. Anagnostou 2016, Gutjahr 2017), but records remain limited in temporal and spatial resolution.

To reconstruct redox conditions we will measure a suite of novel trace elements in foraminifera and bulk sediments, including iodine, uranium, manganese, cerium, molybdenum, and rare earth elements (e.g. Zhou et al., 2016). This will be paired with measurements of carbon isotope gradients between different species of benthic foraminifera to reconstruct bottom water oxygen concentrations (e.g. Hoogakker et al., 2015), and may be extended in key intervals with measurements of novel isotope systems (e.g. sulphur, molybdenum, uranium).

To aid interpretation, we will also use a quantitative modelling approach, pairing sedimentary redox modelling with Earth system model output.

The results of this work will improve understanding of environmental change during major transitions of the last 100 Myr, and will also help inform the use of these methods deeper in the geological record.

Supervisory Team

Dr James Rae
University of St
Andrews

**Dr Babette
Hoogakker**
Heriot Watt
University

Dr James Barnet
University of St
Andrews

Dr Eva Stueken
University of St
Andrews

Collaborators

Dr Sandra Arndt
Universite Libre de
Bruxelles

Further Information

for informal enquiries,
contact:

Dr James Rae

jwbr@st-
andrews.ac.uk

University of St
Andrews

Key Words

- Carbon Cycle
- Oxygen
- Biogeochemistry
- Isotopes
- Redox



Fig 1: Dramatic changes in ocean redox conditions have taken place during several intervals of the last 100 Myr. Most notable are the Oceanic Anoxic Events, which are expressed as black shale layers in carbonate sequences, as shown above. Here we will develop methods to quantify oxygen levels both at times of extreme changes in redox (e.g. OAEs) and during more subtle transitions.

Methodology

Marine carbonate samples are made available from the IODP and may also be collected during dedicated fieldwork. These will be analysed for boron isotopes and trace elements in the St Andrews Isotope Geochemistry (STAiG) labs, following techniques established by Foster (2008) and Rae et al. (2011), and recently developed to improve precision on small samples. Trace elements will be measured on a new state-of-the-art triple quadrupole ICPMS, allowing removal of interferences from several key elements (e.g. REEs).

We will also take advantage of – and continue to develop – new protocols for sample preparation (including automation) that will allow faster throughput of samples and thus higher resolution records to be generated.

Controls on redox proxies will be further explored using sedimentary redox modelling, in collaboration with Dr Sandra Arndt at the Universite Libre de Bruxelles. These may also be paired with output from the GENIE Earth system model.

The project is designed to be flexible, with the opportunity to focus on approaches, time intervals, and techniques of particular interest to the student.

Project Timeline

Year 1

Sediment core sampling, fieldwork, training in clean laboratory methods and mass spectrometry, initial measurements and training, literature review

Year 2

Generate long-term records. Sediment redox modelling. First manuscript.

Year 3

Finalize data sets including higher resolution intervals, apply numerical techniques

Year 3.5

Finalise manuscripts and write thesis

Training & Skills

The student will gain specific training in mass spectrometry, fieldwork, clean lab chemistry, and geochemical modelling, as well as broader education in geochemistry, oceanography, and climate science. Over the course of the PhD the student will gain transferable skills such as scientific writing, statistics and data analysis, and problem-solving, as well as time management and working towards a long-term goal.

References & further reading

Anagnostou et al. (2016), *Nature*, 533(7603), 380
Foster (2008), *EPSL*, 271, 254-266.
Foster & Rae (2016), *AnnRev*, 44, (207-237)
Gutjahr et al. (2017), *Nature* 548.7669 (2017): 573
Hoogakker et al. (2015), *Nature Geoscience* 8.1 40
Rae et al. (2011), *EPSL*, 302, 403-413.
Rae (2018), *Boron Isotopes*, Springer, 107-143
Zachos et al. (2008), *Nature*, 451, 279-283.
Zhou et al. (2016), *Paleoceanography and Paleoclimatology*, 31(12), 1532-1546

Further Information