

# Ocean Sulfate and Earth's Surface Evolution.

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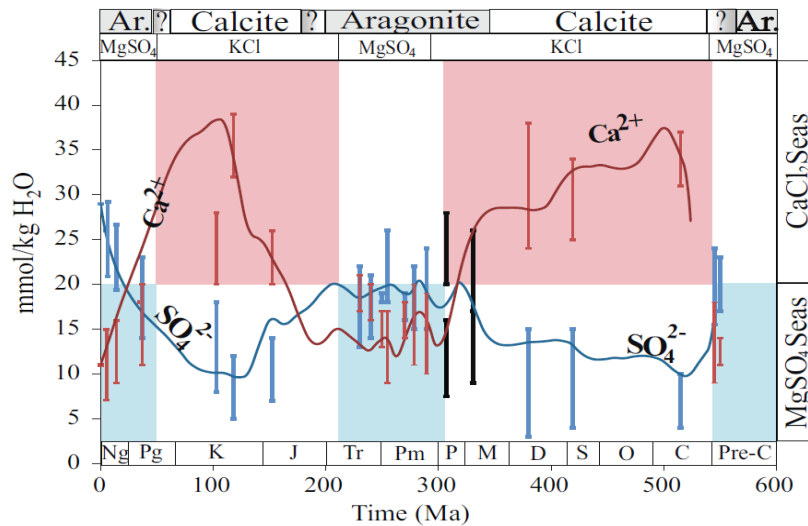
Ocean sulfate is an underappreciated control on the evolution of Earth's surface environment. Sulfate concentrations have changed a lot over the course of Earth's history (fig 1.), but the effect on the biogeochemical cycles of other elements and the links to evolutionary events has received relatively little attention. It's well known that the burial of organic carbon and pyrite controls the amount of oxygen in Earth's atmosphere. Sulfate is both the most important oxidant for organic matter in modern ocean sediments (after dissolved oxygen), and its abundance in seawater controls exerts a control on pyrite burial. It can account for up to 80% of organic matter oxidation in present day continental shelves where most organic carbon is buried, but how would this change if its concentration were 10% of modern and what feedbacks would this induce? A low sulfate ocean also promotes methane production in marine sediments, a process proposed to have important implications for the amount of oxygen in bottom waters (Hall et al, 2018). It's less well known that sulfate exerts a strong control on the primary carbonate mineralogy precipitated in the oceans and so is central to transitions between calcite and aragonite seas (Bots et al, 2011). Work at Leeds is now also connecting low ocean sulfate with several mass extinction events with profound carbon cycle perturbations, but we don't know how these observations may be connected.

We are starting to appreciate that ocean sulfate concentrations may be able to change very quickly (geologically speaking) during evaporite deposition and dissolution events (e.g. Wortmann and Paytan, 2012), but the possible effects of such rapid change are poorly understood and we have little evidence with which to test this idea. This leaves us with two linked problems which form the focus of this PhD.

- 1) How has ocean sulfate changed on both short and long timescales? Current datasets and methods are inadequate to answer this question so we need methods for determining ancient ocean sulfate concentrations that can be used at higher temporal resolutions. This project will investigate two new methods for determining marine sulfate concentrations.
- 2) What effects do changing ocean sulfate concentrations have on the operation of other biogeochemical cycles such as carbon? This project will explore these effects using biogeochemical modelling.

Initial work will focus on the time period from the start of the Jurassic to the present, with fieldwork in Bulgaria and Morocco. This time period encompasses an approximately three-fold increase in ocean sulphate and contains several interesting carbon cycle perturbations such as the early Toarcian and Palaeocene-Eocene Thermal Maximum. To understand the implications of these records the student will use various modelling approaches to explore the controls on the oceanic sulphur cycle and its effect on the marine carbon cycle and sedimentary methane production.

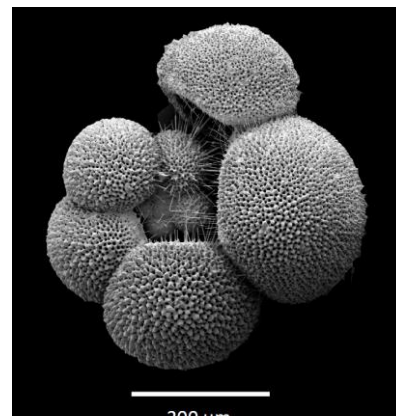
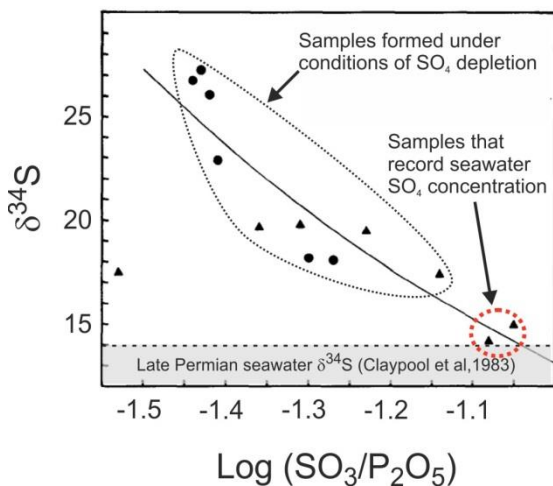
The most direct method of estimating past ocean sulphate is from the chemistry of fluid trapped in halite crystals formed in evaporitic environments (fluid inclusions), but these records are sparse, and have large error bars in both concentration and age (Figure 1; Holt et al., 2014; Horita et al., 2002) making them unsuitable for recording shorter timescale changes. To address the need for high resolution records of past-ocean sulfate, the student will explore two novel methods based on the substitution of sulphate into phosphate and carbonate minerals. Both phosphate deposits and foraminifera have a much more continuous record than evaporites and can be dated with far greater precision.



**Figure 1.** A compilation of Phanerozoic ocean concentrations of sulphate and calcium (left) derived from the chemistry of fluid inclusions. There are very few data points for such a long time interval. Black bars are new data from Carboniferous evaporite deposits. Error bars on ages are not shown but are on the order of a few million years. (Holt et al., 2014)

Sulfate substitutes into the structure of the phosphate minerals francolite or hydroxyapatite in proportion to the concentration of sulphate in the water surrounding them (McArthur, 1985). The isotopic composition of the substituted sulfate is used to correct for sulfate depletion by bacterial sulfate reduction in the sediment. This method has been shown to successfully predict sulfate concentration (Hough et al., 2006) but has not yet been widely applied. Pilot work by the lead supervisor has derived estimates for the Cretaceous that overlap those from fluid inclusion studies.

Experimental work with CASE partner Professor Liane Benning at GFZ (Potsdam, Germany) will investigate the controls of sulphate incorporation into francolite under lab conditions to explore the interpretation of this record. This will involve a placement at GFZ to precipitate francolite in the laboratory under a range of conditions indicative of ancient seawater chemistry.

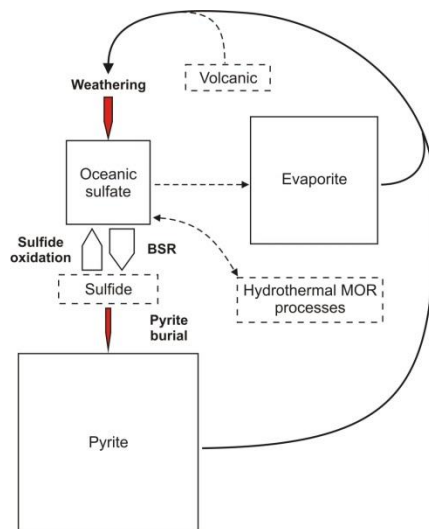


**Figure 2.** Left: Phosphorite S:P ratio plotted against the sulphur isotope composition of the sulphate substituted into the phosphorite lattice from the late Permian Phosphoria Formation (adapted from Piper and Kolodny, 1987). Where the sulphur isotope composition records seawater, the S:P ratio reflects the sulphate concentration of the ocean. Right: Scanning electron microscope image of the foraminifera *Globigerinella siphonifera* from the S.W. Indian Ocean.

Sulfate substituted into carbonate minerals is already widely employed as a proxy for the sulphur isotopic composition of ancient oceans, but the controls on the amount of sulphate contained in the mineral lattice are only understood from experimental work (e.g. Busenberg and Plummer, 1985). Recent work on cultured foraminifera suggest a clear relationship between S/Ca in the shell and dissolved sulphate concentration (Paris et al., 2014). The student will explore the controls on the sulphate concentrations in foraminiferal calcite (e.g. Figure 2) first in the Holocene, and then in the rest of the Cenozoic.

Many of the samples necessary for the project are held in collections either in Leeds or with project partners. Additional sample collections will be made to improve the time resolution of the phosphorite records during **fieldwork to Morocco and Bulgaria** where phosphorite deposits are common in the Palaeogene, and Jurassic to Cretaceous respectively.

The student will integrate the results of the analytical phases of the project with other published information by developing a box model of the marine sulphur cycle (Figure 3) and the sedimentary carbon cycle. The modelling will be based on well-established methods (see Garrels and Lerman, 1984) used to compute past seawater sulphate concentrations from variation in  $\delta^{34}\text{S}$ , and will draw on more recent approaches, which model fluxes of the major components of seawater under changing biogeochemical and tectonic processes (Arvidson et al., 2013). This will allow a quantitative appraisal of the various factors that may be influencing changes to the marine sulphur and carbon cycles on a range of time scales.



**Figure 3.** A schematic representation of the global sulphur cycle illustrating the controls on ocean sulfate concentrations. The size of the solid boxes is proportional to the size of the reservoirs. Organic carbon is consumed during bacterial sulphate reduction (BSR). Dashed boxes and lines represent variable or poorly constrained reservoirs or fluxes. MOR – mid ocean ridge (Newton, unpublished)

## Aims and Objectives:

The aims of the project will be to:

- 1) Derive a high resolution record of sulphate concentrations from the Jurassic to present
- 2) Explore the controls on the preservation and interpretation of the new proxies
- 3) Investigate the controls on marine sulphate concentrations and the implications for the sedimentary carbon and oxygen cycles across particular events and more broadly across the geological timescale.

This will be achieved by:

- 1) Analysing a suite of phosphorite samples for their S:P ratio and the  $\delta^{34}\text{S}$  of their structurally substituted sulphate. This will also entail SEM work and other techniques to constrain the presence of pyrite or other sulphur phases which may pose a risk of contamination.
- 2) Undertaking experimental work to understand the controls of sulphate incorporation into phosphorite minerals at CASE partner Institution (GFZ, Germany).
- 3) Undertaking fieldwork in Bulgaria and Morocco to supplement the pre-existing collections of phosphorite samples to improve the time resolution of the record. This work will exploit pre-existing links to help with local logistics and permissions.
- 4) Selecting and analysing a suite of foraminiferal samples for their S:Ca ratio to test a range of possible controls on sulphate incorporation e.g. a range of species, cosmopolitan species from sites with a range of temperatures, etc. Possible diagenetic controls on the preservation of pristine S/Ca ratios will also be assessed using a range of standard techniques.
- 5) Developing a box model for ocean sulphate concentrations and the marine sedimentary carbon cycle across the studied time interval constrained by the new information from 1) and 3) above and supplemented by previously published proxy records (e.g. marine sulphate isotope record).

## Potential for high impact outcome:

The project will address fundamental questions about the detailed chemical evolution of the oceans, one of the most important components of Earth's biogeochemical cycles. It also has the potential for significant impact on our understanding of the Earth's atmospheric methane budget over time, a key component of the climate system. We therefore expect the project to result in a number of significant papers in the field with at least one or more being suitable for a high impact journal.

## Training

The student will be trained in the wet chemical techniques used to measure the element ratios of interest, isotope geochemistry, foraminiferal identification and box modelling. Techniques which will form an integral part of the project are stable isotope mass spectrometry, ion chromatography, ICP-MS, ICP-OES, SEM, and XRD. All of these techniques are available in the School. In addition, the student will gain expertise in experimental geochemical approaches via the link with Professor Liane Benning at the CASE partner institution, GFZ. The supervisory group is made up of expertise on geochemistry and stable isotopes (Dr Robert Newton), micropalaeontology (Dr Tracy Aze) numerical modelling (Dr Ben Mills) and experimental geochemistry (Professor Liane Benning) providing a high level of specialist training in all aspects of the project work. The student will become part of the Earth Surface Science Institute in the School and the Cohen Geochemistry and Palaeo@Leeds research groups. This organisational framework provides a supportive environment which allows the cross fertilisation of ideas and expertise. In addition to the bespoke high level training for the PhD, the student will have access to a wide range of other training and support. Examples would include other useful scientific skills such as programming or statistics, transferable skills such as time management, writing and giving presentations, and skills specific to a PhD programme such as managing your degree and preparing for your viva (<http://www.emeskillstraining.leeds.ac.uk/>).

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