

## The Story of Ocean Oxygenation Through Glacial Interglacial Cycles Revealed by Laboratory Redox Titration: a novel experimental approach

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### Context

The biosphere and geosphere are coupled via the carbon and oxygen cycles (Galvez et al., 2020). Deep ocean sediments provide valuable archives recording past changes in ocean and atmospheric oxygenation. Yet understanding the record can be complex (Jaccard et al., 2005) as physical and chemical processes can affect deep ocean oxygenation changes.

Various laboratory approaches have been developed to decipher changes in deep sea redox conditions based on the mineralogical/chemical composition of marine sediments. These proxies broadly indicate that oscillations in deep ocean oxygenation levels track fluctuations in atmospheric pCO<sub>2</sub>, yet the relation between both metrics can be non-linear and sometimes out of phase (Jaccard and Galbraith, 2012). The reason for this is likely to be complex (Jaccard et al., 2016).

Significant progress will arise from complementary tools to track changes in deep sea oxygenation based on marine sediments. A novel laboratory-based method to quantify the redox capacity of rocks and sediments (Galvez and Jaccard, 2020), independently of a knowledge of bulk sediment element or isotopic composition, may provide an orthogonal approach to reconstruct past changes in deep ocean oxygenation. This is assuming the method can be applied accurately and precisely to deep-sea sediments that are often characterized by complex matrices, including salts and various hydrous phases.

The research project will contribute to adapt the existing method to become applicable to deep-sea sediments retrieved from the North Pacific Ocean.

### Aims and Methods

The objective of the project will be to lay the ground for applying the redox titration method (Galvez and Jaccard, 2020) to deep sea sediments containing various biogenic and lithogenic phases.

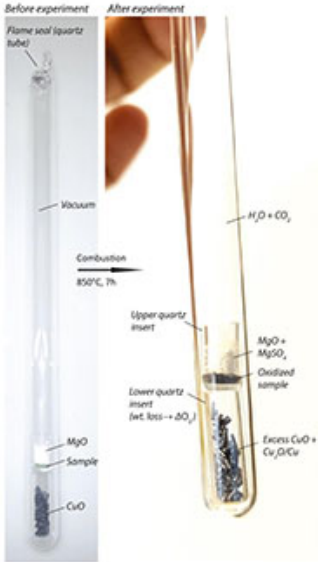
The project is methodological, and will involve extensive laboratory work, learning the basics of the method and producing the data necessary for extending its applicability to hydrous and often sulfur-rich deep-sea sediments. The work is interdisciplinary, situated at the frontier between applied chemistry, petrology and oceanography. The work will involve conditioning samples for analysis (desalination, fine crushing), and laboratory analysis (redox titration at ETH Zurich, XRD, SEM and other geochemical analyses at UNIL). In particular, the student will produce synthetic sediment samples that mimic the bulk composition of deep-sea sediments. The measured redox capacity of those synthetic samples will then be compared to theoretical predictions. This will serve to adapt, refine and optimize the experimental protocol.

As an application of this fundamental groundwork, the student will start quantifying the redox capacity of a series of deep-sea sediments drilled from the North Pacific and spanning a period of ca. 20000 years, thus covering the last deglacial transition.

Requirements for the project are a taste for rigorous and quantitative work, but previous experimental work experience is not required.

### References

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- Jaccard, S.L., Galbraith, E.D., 2011. Large climate-driven changes of oceanic oxygen concentrations during the last deglaciation. *Nature Geoscience*, 5: 151.
- Jaccard, S.L., Galbraith, E.D., Martínez-García, A., Anderson, R.F., 2016. Covariation of deep Southern Ocean oxygenation and atmospheric CO<sub>2</sub> through the last ice age. *Nature*, 530(7589): 207.

 <p>       Before experiment    After experiment     </p> <p>       Flame seal quartz tube     </p> <p>       Vacuum     </p> <p>       Combustion        850°C, 1h     </p> <p>       MgO        Sample        CuO     </p> <p>       H<sub>2</sub>O + CO<sub>2</sub> </p> <p>       Upper quartz insert        MgO + MgSO<sub>4</sub> </p> <p>       Oxidized sample     </p> <p>       Lower quartz insert        (wt. loss → ΔO<sub>2</sub>)     </p> <p>       Excess CuO + Cu<sub>2</sub>O/Cu     </p> <p>       Fig. 1. Design of experimental assembly     </p>	<p>Website</p>
<p>Prerequisite</p>	