MSc Project (Master 2)

Starting date and duration: January 2023, 6 months

Title: Fate of uranium during the diagenesis of green rusts

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Background: geology, (bio)geochemistry, inorganic chemistry

Abstract:
Uranium (U) isotopes signatures preserved in ancient sedimentary rocks are increasingly used as a redox proxy to reconstruct the extent of past ocean oxygenation. Indeed, the reduction of labile U^{VI} into solid U^{IV} in anoxic water columns is accompanied by significant U isotope fractionation, with the heavy isotopes preferentially incorporated into the reduced sediment.
Whereas this mechanism is well known for the reduction of U^{VI} by FeS, an ubiquitous mineral in anoxic and H_2S-rich environments, several other mechanisms are unknown, limiting our ability to quantify the extent of marine anoxia using U isotopes.

In this project, we will explore the fate of U upon reaction with green rust, a highly reactive Fe(II)/Fe(III) hydroxide, which may have been the dominant mineral phase in anoxic and Fe-rich oceans. Because of their nanocrystalline size and their mixed valence, green rusts have a great potential in adsorbing and reducing U^{VI}, respectively. Hence, they may act as a sink for U in anoxic and Fe-rich sediments. By contrast, green rust readily transforms into magnetite and siderite during early diagenesis, and whether U maintains fixed in the sediment, or, on the contrary, released back in the water column, is unknown.

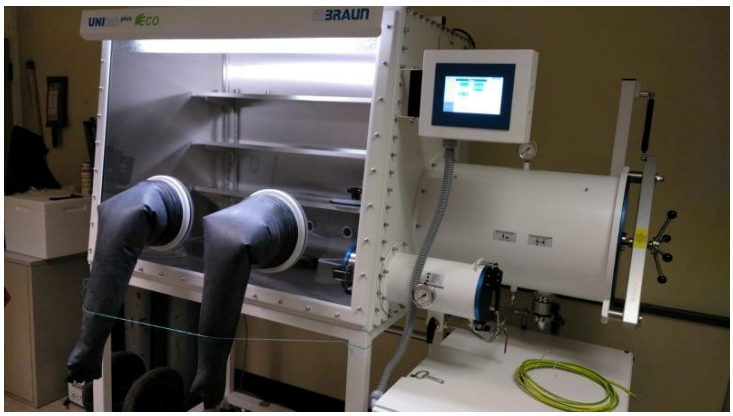

Fig. 1. Anoxic golvebox at GET.

During the project, the student will 1) synthesise green rust nanoparticles in an anoxic glove-box to maintain anoxic conditions (Fig. 1); 2) react U^{VI} with precipitated green rust; 3) characterise the solid products by XRD and analyse the solutions by ICP-MS. This will enhance their skills in experimental geochemistry, nanoparticle synthesis, anoxic environments, mineralogical and elemental analyses, all valued both in research and industry. This project will permit to prepare a large number of experimental data for further U isotope analysis.

References:

Guilbaud R., White M. L. and Poulton S. W. (2013) Surface charge and growth of sulphate and carbonate green rust in aqueous media. *Geochimica et Cosmochimica Acta* **108**, 141–153.

Halevy I., Alesker M., Schuster E., Popovitz-Biro R. and Feldman Y. (2017) A key role for green rust in the Precambrian oceans and the genesis of iron formations. *Nature Geoscience* **10**, 135–139.

O'Loughlin E. J., Kelly S. D., Cook R. E., Csencsits R. and Kemner K. M. (2003) Reduction of Uranium(VI) by Mixed Iron(II)/Iron(III) Hydroxide (Green Rust): Formation of UO2 Nanoparticles. *Environ. Sci. Technol.* **37**, 721–727.

Tostevin R., Clarkson M. O., Gangl S., Shields G. A., Wood R. A., Bowyer F., Penny A. M. and Stirling C. H. (2019) Uranium isotope evidence for an expansion of anoxia in terminal Ediacaran oceans. *Earth and Planetary Science Letters* **506**, 104–112.