Kinetic behavior and redox buffer capacity of pyrrhotite

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Introduction and Objectives

The redox state of the system is one of the fundamental aspects in the context of stability of waste radioactive repositories. The most realistic approach to take into account the buffering redox capacity of a system is considering the kinetic assumptions.

Despite pyrrhotite, a non-stoichiometric iron sulfide with composition $Fe_{1-x}S$ (x: 0-0.125) is the most common iron sulfide in nature after pyrite, their role in controlling redox systems is not well understood. Therefore, a better understanding of the buffer capacity of pyrrhotite is needed to improve the role of Fe/S in buffering the redox state in natural systems.

Experimental and Results

In order to determine the redox buffer capacity of pyrrhotite, two different approaches are used: the thermodynamic approach, focused on the response of the mineral to an external perturbation and the kinetic approach, focused on the determination of oxidant uptake rate.

Experiments are carried out using reactors with adjustable volume in order to avoid the presence of gas phase even during sampling. pH, ORP (Pt and Au electrodes), dissolved oxygen, iron and sulphide are monitored as a function of time.

This work is performed with grounded and sieved (100-150 μ m) natural pyrrhotite obtained from Gualba (Spain). XRD reveals the presence of small quantities of quartz and pyrite.

Preliminary results show that pyrrhotite buffers the redox state of the system without significant differences between gold and platinum electrodes. In the other hand, fast oxygen consumption by pyrrhotite has been observed in a few hours, an order of magnitude higher than mineral dissolution rate.

Flow through cleaning and sequential dissolution of planktonic foraminifera for Mg/Ca analyses

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In the last decade Mg/Ca paleothermometry on foraminifera has been developed into a powerful tool to reconstruct paleo sea water temperatures. However, several issues, like for example dissolution, lack of sufficient material, and diagenesis, can complicate the reconstruction resulting in a loss of the primary signal. Here we demonstrate the application of a Flow Through (FT) cleaning device and sequential dissolution to conducting Mg/Ca measurements on foraminifera from a range of different settings.

FT cleaning pumps water and other reagents in a constant flow over a sample to remove contaminants and then dissolves the sample calcite while other contaminants remain on the sample holding filter. We have developed a fully automatic FT cleaning device at the MARUM, University of Bremen, and the initial results obtained by coupling the device to an ICP-OES are very promising. The linear response of the element/Ca ratio of a standard solution while Ca counts vary by six orders of magnitude is remarkable and enables the element/Ca ratio of samples to be calculated very simply. The accuracy of the technique for the determination of Mg/Ca ratios is demonstrated by the repeated measurement of the limestone standard powder (ECRM 752-1) utilised in a recent foraminiferal Mg/Ca interlaboratory study (Greaves *et al.* 2008).

Two examples of initial results show that firstly, the method is able to distinguish between different calcite phases, allowing to determine the influence of diagenesis in bulk samples of *G. sacculifer* from the Pliocene (ODP Site 999). Secondly, the method allows for the analysis of single foraminifers from a sediment trap off South Java linking the Mg/Ca ratios to direct temperature measurements. Single shell analyses can then potentially be used to reconstruct paleo seasonality.