Electrochemical depiction of the hematite/water interface

 $J.-F.\,BOILY^{1*},K.\,SHIMIZU^2\,\text{and}\,M.\,LUCAS^1$

¹Department of Chemistry, Umeå University, Sweden

(* correspondence: jean-francois.boily@chem.umu.se)

²Physical and Theoretical Chemistry Laboratory, University of Oxford, UK.

Hematite is a common iron oxide in Earth's upper crust and plays key roles in a variety of biogeochemical processes. Interfacial charging and adsorption phenomena involving this mineral are central to its reactivity, and are now linked with important surface-to-bulk electron transfer reactions. Impure *n*doped phases open possibilities for exploring electron transfer phenomena and for addressing fundamental issues of the mineral/water interface as a molecular capacitor.

Electrochemical studies of hematite single crystal electrodes have provided key insights into plausible electric potentials developed at the mineral/water interface. In this study, we present recent efforts by our group to develop an electrochemical depiction of the entire bulk hematite to hematite/water interface. We depict this system using an equivalent electrical circuit (Fig. 1) representing various resistance and capacitance terms pertaining to charge-carrier transfer across the electric double layer and the surface/bulk interface. This circuit and its parameters were developed from Electrochemical Impedance Spectroscopy measurements of hematite single crystals. Measurements on roughened and crystallographically oriented faces contacted with aqueous solutions of various ionic strengths and background electrolytes can be readily related to our current-day molecular-level knowledge of mineral-ion interactions. These measurements also offer a considerably different view on the impact of solution and surface chemistry on electric double layer capacitance values compared to those that are indirectly extracted by surface complexation modeling. We are moving this work to spatially-resolved measurements using Scanning Electrochemical Microscopy. These efforts are underscoring the heterogeneous nature of mineral/water interfacial properties of macro-sized hematite surfaces.



Fig. 1. The hematite/water interface and its equivalent electric circuit.