

Electrochemical Impedance Spectroscopic Study of the Hematite/Water Interface

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Hematite is one of the most abundant and stable iron minerals in Earth's upper crust, and thus inevitably plays an important role in various bio-geochemical processes, including mass transport, pollutant migration, and microbial metabolism. This mineral is also a promising material in the search for renewable forms of energy, such as in Li-ion batteries and water splitting. The intrinsic activity of hematite surfaces notably concerns interactions with water and electrolyte ions. Recent cryogenic X-ray photoelectron spectroscopy (XPS) work in our group have addressed such issues by monitoring electrolyte ion loadings and binding mechanisms at nano-sized hematite particle surfaces.[1,2,3]

In an effort to further our understanding of reactions taking place at the hematite/water interface, we used electrochemical impedance spectroscopy (EIS) to extract interfacial properties such as adsorption resistance and electric double layer capacitance using a specially constructed set-up to study surfaces of single body semi-conductive hematite specimens.[4] EIS measurements of crystallographically oriented electrode surfaces contacted with electrolyte solutions (0.1 M NaCl, NaCl/Na₂CO₃, and NH₄Cl) were carried out both in the absence and presence of light in the 4-12 pH range. The resulting spectra were thereafter analyzed using an equivalent electrical circuit model accounting for solution, interface and bulk hematite electrochemical processes. These efforts showed, for instance, that double layer capacitances of the basal (001) plane are insensitive to solution pH and electrolyte type whereas those of the (012) are considerably affected by them. This can be attributed to differences in amphoteric attributes of these two planes. Results revealed that the ammonium ion has a greater influence on charge development than the bicarbonate ion. This finding is consistent with a cryogenic XPS study from our group [3] pointing to hydrogen-bonded interactions between ammonium and hematite surface hydroxo groups.

Photo-irradiation decreased open circuit potentials relative to dark conditions on both (001) and (012) surfaces due to photo-reduction reactions. Impedance spectra show that the (012) is affected more indicating the greater photo-reactivity of this plane. Results also show that the charge transfer resistance within bulk hematite crystal was lower through the (012) plane than on the (001) plane, as can be expected from the anisotropic nature of this mineral.

[1] Shimizu, Shchukarev, Kozin & Boily (2012), *Surf. Sci.* 66, 1005.[2] Shimizu, Shchukarev, Kozin & Boily (2013), *Langmuir* 29, 2623.[3] Shimizu, Shchukarev & Boily (2011), *J. Phys. Chem. C* 115, 6796.[4] Shimizu, Lasia & Boily (2012), *Langmuir*. 28, 7914.

Volatile behavior in an immature subduction zone inferred from boninitic melt inclusions in Cr-spinel

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Recent studies suggest that boninites formed at the immature stage of subduction zone, whereas related arc tholeiites erupted 0-7 Myrs after boninites at Izu-Bonin-Mariana Arc (e.g. Ishizuka *et al.*, 2011, EPSL), indicating significant changes in conditions of subduction within this period. We have analysed volatile contents and sulfur isotopic compositions of melt inclusions (MIs) in Cr-spinel from beach sands of fore-arc volcanic islands of boninite (Muko, Chichi) and tholeiite (Mukoo and Guam), using secondary ion mass spectrometry (ims-1280). Major element compositions of MIs fully cover compositional ranges of whole-rocks. Some boninitic MIs have MgO higher than 20 wt%, showing that they are very primitive magmas. H₂O and CO₂ contents of MIs are contrasting between boninites and tholeiites, with boninitic MIs are high (up to 4 wt%) in H₂O and low (< 50 ppm) in CO₂, whereas tholeiitic MIs are lower (H₂O ~1-2 wt%) and higher (CO₂ up to ~1300ppm) than boninitic MIs. Except for H₂O, volatiles of boninitic MIs (Cl <500ppm; S ~150ppm) are considerably lower than those in tholeiite MIs (Cl and S up to 3000ppm). $\delta^{34}\text{S}_{\text{VCDT}}$ of boninitic MIs are low (-10 to 0 ‰), whereas those of tholeiite MIs ($\delta^{34}\text{S}_{\text{VCDT}} = +2$ to $+7$ ‰) are comparable to reported arc tholeiite data. The results suggest that different sources for S were involved in the formation of boninitic and tholeiitic magmas.