Contrasted iron-speciation in obsidians and tektites: A spectroscopic study

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Iron has long been known to play an important role in determining the properties of natural magmatic liquids. The determination of the sites occupied by ferrous and ferric cations in volcanic glasses may provide information on the physico-chemical conditions prevailing at the magmatic stage as well as on the cooling conditions of the magma. We discuss Fe speciation in calc-alkaline rhyolitic glasses (obsidians) and tektites, using optical absorption spectroscopy (OAS) and electron paramagnetic resonance (EPR). In obsidian, OAS reveals a major contribution of Fe^{2+} in a regular octahedral site, an unusual environment in synthetic glasses and tektites where this cation is mostly 4- and 5-coordinated [1], [2].

The presence of Fe-oxide nano-clusters, suspected since a long time from previous EPR studies [3], is confirmed by variable-temperature OAS in all obsidians investigated. By contrast, tektites do not show such contribution. Specific absorption bands, assigned to Fe-Fe and Fe-Ti intervalence charge transfers (IVCT), are characterized by a spectacular intensity dependence as a function of temperature over 1000 K (1000K-10K). This thermally-activated behavior shows an activation energy similar to that observed for IVCT in various minerals. The evidence of specific Fe^{2+} sites and of IVCT processes, indicate the presence of Fe-oxide clusters. These clusters, showing a local re-arrangement around Fe, are related to the cooling history of the glass, as they are not found in the medium range structure of synthetic glasses [4]. The existence of these clusters and their nature seem to be related to the conditions of formation of the investigated obsidians and they may clarify the information brought by these glasses about its magmatic history.

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Thermodynamics and Kinetics of Fe(II)-Fe(III) Electron Transfer Across Interfaces

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Fe(II)-Fe(III) electron transfer is a key exchange in the biogeochemical cycle of iron. For most environmentally relevant conditions this exchange involves interaction between soluble ferrous iron and solid-phase iron (oxyhydr)oxides, with possible involvement of electrical conduction through the solid-state. This presentation addresses global thermodynamic limits and molecular-scale controls on the kinetics of this exchange from selected observations and simulations of Fe(II) interaction with hematite, goethite, and magnetite.

Single crystal single surface potentiometry and amperometry on hematite were used to examine the pH-dependence of surface electrical potential, the kinetics of protonation/deprotonation, and current flow from one crystallographic face to another, examining the effect of aqueous Fe(II) addition. The data reveal a pH-dependent energy band model with the iron redox couple in solution that is compatible with the magnitude and direction of face-to-face Fe(II)/Fe(III) current flow through the semiconductor bulk. Despite structural distinctions, in a similar fashion Fe(II) interaction with $Fe_{3-x}Ti_xO_4$ nanoparticles at various amounts of pre-oxidation shows a reversible topotactic Fe(II) uptake and release consistent with surface deprotonation and protonation, respectively. Synchrotron Fe L-edge x-ray absorption and magnetic circular dichroism spectroscopies are used to map Fe site occupancy and valence before and after pre-oxidation and Fe(II) recharge. Molecular simulations of Fe(II) adsorption and subsequent interfacial electron transfer with Fe(III) at hematite and goethite surfaces reveal the importance of surface net charge, the protonation state of bridging ligands, and proton coupled electron transfer to facilitate the electron exchange into the solid. Aspects covered will include thermodynamic energy requirements for bulk crystal conduction, including heat dissipation in the solid, and possible free energy sources sustaining bulk currents, Fe(II) adsorption energies and the kinetics of electron injection, and the structural dependence of Fe(II)-Fe(III) electron exchange through the crystal lattice, towards a new, more comprehensive mechanistic model for these systems.

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