

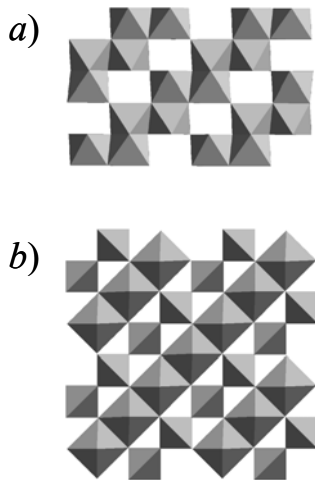
On charge transport in iron oxides

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Surfaces of iron oxide minerals are known participants or catalysts in a wide range of redox processes in natural environments. Examples include reductive dissolution of Fe^{III}-bearing oxides such as hematite by dissimilatory metal reducing bacteria, and the reduction of chromium or uranium by Fe^{II}-bearing oxides such as magnetite. A common aspect of these processes is the valence interconversion of structural iron through electron transfer. With progressive reduction of Fe^{III} or oxidation of Fe^{II} in the iron oxide surface, the lifetime of the electron transfer products becomes an important issue. Mounting experimental evidence suggests facile electron hopping through the solid outpaces surface transformation to more stable phases. This notion comes in contrast to the traditional view that electron transfer products are fixed in their initial location in the surface. Hence, the issue of electron mobility through the solid bears directly on the task of bridging time and length scales in these systems.

In this address, we will discuss what is currently known about electron mobilities in hematite and magnetite. We will also illustrate computational approaches for the transport of electrons through the lattices of hematite and magnetite, and present calculated rates of electron hopping. Rates for an electron or hole in hematite range from 10⁷-10¹⁰ s⁻¹ depending on crystallographic direction, whereas the rate for magnetite is 10¹¹ s⁻¹. These rates lead to electron mobilities in good agreement with experiment, both in terms of magnitude and directionality.



Zone views of the *a*) hematite structure down [110] and *b*) magnetite structure down [100].

The role of Si—O bonds in dissolution of silicate glasses: Inferences for rate-limiting step

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The dissolution kinetics of 5 chemically complex and 2 chemically simple borosilicate glass compositions (Na-B±Al-Si) were tested with a single-pass flow-through (SPFT) apparatus. The chemically complex glasses are representative of prospective vitreous waste forms and are characterized by relatively high molar Si/(Si+Al) and Na/(Al+B) ratios (>0.7 and >1.0, respectively). X-ray absorption spectroscopy (XAS) indicate that ratios of ^{IV}B to ^{III}B vary between values of 40 to 55% for all specimens. MAS-NMR data yield ²⁹Si peak shift values that are virtually identical (-94 to -84 ppm), indicating a similar polymerization state for the glasses, despite differences in bulk chemistry. Forward rates of reaction are identical within error for all the samples tested (avg. log₁₀ rate = -1.9 g/m²·d at pH 9, T = 40°C). Compared to other borosilicate, synthetic silica, albite, jadeite, and nepheline, and natural basalt and rhyolite glasses, the forward rates of Na-B±Al-Si glasses are equal or only slightly (≤10X) faster, implying a similar rate-governing mechanism. In contrast, relatively de-polymerized soda-lime glasses dissolve at faster (>50X) rates. It appears, therefore, that glasses with similar polymerization states dissolve at like rates. Thus, these data support a model of transition-state theory (TST), in which rates are dependent only on the rate of the slowest elementary reaction, which is hydrolysis and rupture of Si—O bonds.