

# Mechanistic links between metal-substituted goethite redox properties and structural changes due to metal incorporation

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Iron oxides such as goethite are commonly found in soils, sediments, and ore bodies with a multitude of metal-for-Fe substitutions, including trace nutrients such as zinc and technologically critical elements such as nickel. Little is known about whether the redox properties of iron oxides change with metal substitution. Here, we measured the redox properties of Ni- and Zn-substituted goethite (~2% substitution) and link these properties with structural information from X-ray pair distribution function analysis (PDF), x-ray spectroscopy (EXAFS), and *ab initio* molecular dynamics (AIMD) simulations. Using mediated electrochemical potential measurements of the goethite|Fe(II) redox couple we observed higher redox potentials of Ni-goethite (i.e., more oxidizing,  $\Delta E_H^0 = +100$  mv) and suggest that the Ni-goethite structure is less stable than Zn-goethite and unsubstituted goethite. Such differences in redox stability may provide a driving force for release of metals during redox-catalyzed iron mineral recrystallization.

Analysis of structural information from EXAFS and X-ray PDF indicate that both elements distort the goethite lattice in different manners: Zn causes expansion in a and b directions, but contraction along the c, and Ni causes lattice expansion in all directions. The difference in strain energy amounts to -7.0 kJ/mol between Ni- and Zn-goethites, in agreement with the difference in free energy of -8.4 kJ/mol from the redox measurements. PDF measurements suggest this difference is due to the element-specific short-range order around the impurity. In Zn-goethite, there is evidence for iron vacancies that prevent propagation of strain, which are not present for Ni. Using synthetic standards derived from AIMD to understand the local coordination environment confirmed Zn required ~30% protonated Fe vacancies close to the impurity. In contrast, the best fit for Ni-goethite does not include nearest-neighbor protonated Fe vacancies (consistent with PDF analysis). We hypothesize that the lack of vacancies contributed to Ni destabilizing goethite relative to Zn. Results from this study underline the crucial role defects can play in stabilizing the host lattice and imply metal incorporation can greatly alter the reactivity of common minerals, such as goethite.