

---

# Studies of the Reactivity of the Ferrihydrite Surface by Iron Isotopic Exchange and Mössbauer Spectroscopy

Brigid A. Rea<sup>1</sup>, James A. Davis<sup>2</sup> and Glenn A. Waychunas<sup>3</sup>

<sup>1</sup> Water Resources Division, U. S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303

<sup>2</sup> Water Resources Division, U. S. Geological Survey, 345 Middlefield Rd., Menlo Park, California 94025

<sup>3</sup> Center for Materials Research, Stanford University, Stanford, California 94305

**Abstract:** Two-line ferrihydrite is an important adsorbent of many toxics in natural and anthropogenic systems; however, the specific structural sites responsible for the high adsorption capacity are not well understood. A combination of chemical and spectroscopic techniques have been employed in this study to gain further insight into the structural nature of sites at the ferrihydrite surface. The kinetics of iron isotopic exchange demonstrated that there are at least two types of iron sites in ferrihydrite. One population of sites, referred to as *labile* sites, approached iron isotopic equilibrium within 24 hr in <sup>59</sup>Fe-NTA solutions, while the second population of sites, referred to as *non-labile*, exhibited a much slower rate of isotopic exchange. Adsorbed arsenate reduced the degree of exchange by labile sites, indicating that the anion blocked or greatly inhibited the rate of exchange of these sites. Mössbauer spectra were collected from a variety of samples including <sup>56</sup>Fe-ferrihydrite samples with <sup>57</sup>Fe in labile sites, samples containing <sup>57</sup>Fe throughout the structure, and samples with <sup>57</sup>Fe in non-labile sites. The spectra showed characteristic broad doublets signifying poor structural order. Refined fits of the spectra indicated that labile sites have larger quadrupole splitting, hence more local distortion, than non-labile sites. In all cases, the spectra demonstrated some degree of asymmetry, indicating a distribution of Fe environments in ferrihydrite. Overall spectral findings, combined with recent EXAFS results (Waychunas *et al.*, 1993), indicate that labile sites likely are more reactive (with respect to iron isotopic exchange) because they have fewer neighboring Fe octahedra and are therefore bound less strongly to the ferrihydrite structure. The labile population of sites probably is composed of end sites of the dioctahedral chain structure of 2-line ferrihydrite, which is a subset of the entire population of surface sites. Mössbauer spectra of samples containing adsorbed arsenate indicated that the anion may slightly decrease the distortion of labile sites and stabilized the structure as a whole by bidentate bonding.

**Key Words:** Adsorption • Arsenate • Dissolution kinetics • Ferrihydrite • Iron octahedra • Mössbauer spectroscopy • Reactive sites • Solubility • Surface chemistry

*Clays and Clay Minerals*; February 1994 v. 42; no. 1; p. 23-34; DOI: [10.1346/CCMN.1994.0420104](https://doi.org/10.1346/CCMN.1994.0420104)

© 1994, The Clay Minerals Society

Clay Minerals Society ([www.clays.org](http://www.clays.org))

---