

# Fe and O atom exchange on hematite and goethite surfaces after aqueous Fe(II) sorption: A NanoSIMS investigation

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Fe(III) oxides are well known to sorb aqueous Fe(II) atoms which initiates exchange of aqueous and oxide Fe atoms as well as exchange of oxide O and H<sub>2</sub>O-O. Here, the Fe and O atom exchange process was investigated for hematite and goethite using isotope tracer experiments and NanoSIMS measurements that allowed for simultaneous Fe and O isotopic quantification at the mineral surfaces and at depth. Hematite and goethite of natural Fe and O isotope abundances were exposed to anoxic solutions of 99.3% <sup>54</sup>Fe(II) and 0.2% <sup>18</sup>O-H<sub>2</sub>O for 30 d. Partial sorption of aqueous <sup>54</sup>Fe(II) and <sup>18</sup>O and release of oxide <sup>NA</sup>Fe and <sup>NA</sup>O was observed. Fe and O atom exchange extents showed variation with oxide particle sizes. Reactions of synthesized nanosized hematite and nanosized goethite to the <sup>54</sup>Fe(II) solutions produced surfaces enriched in <sup>54</sup>Fe/<sup>56</sup>Fe compared to the bulk Fe(III) oxide, but less than aqueous <sup>54</sup>Fe/<sup>56</sup>Fe. Surfaces were also enriched in <sup>18</sup>O/<sup>16</sup>O compared to bulk values, but O atom exchange occurred to less extent than Fe exchange. A synthesized micron-sized hexagonal hematite became enriched in <sup>54</sup>Fe/<sup>56</sup>Fe at the basal surface, but to less extent than that of nanosized hematite. No <sup>18</sup>O/<sup>16</sup>O enrichment, though, was observed at this basal surface. The results at both particle sizes show that surface Fe reorganization does not directly reflect the aqueous Fe isotopic composition. A <sup>54</sup>Fe/<sup>56</sup>Fe depth profile on a centimeter-sized natural hematite specimen (Figure 1) revealed the sorbed <sup>54</sup>Fe can migrate deeper into the oxide structure well beyond a few layers of Fe. The <sup>54</sup>Fe/<sup>56</sup>Fe values appear to follow Fickian diffusion, but only if different diffusivities are assumed for the near-surface environment and bulk oxide. <sup>18</sup>O-H<sub>2</sub>O was exchanged only at the near-surface for this specimen. The results support the notion that exchanged Fe and O atoms are distributed rather inhomogeneously at hematite and goethite surfaces and that deeper migration of adsorbed Fe atoms is likely.

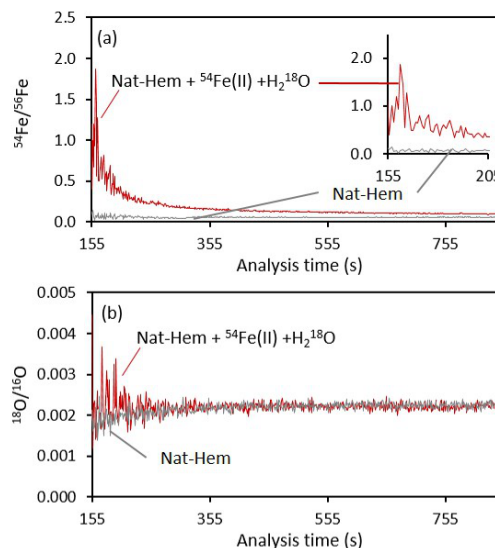


Figure 1: Single spot nanoSIMS depth profiles for Fe (a) and O (b) for reacted and unreacted <sup>NA</sup>hematite specimens.