The Effect of Al on Fe Oxides. XIX. Formation of Al-Substituted Hematite from Ferrihydrite at 25 ° C and pH 4 To 7

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Abstract: Iron oxides in surface environments generally form at temperatures of 25 ± 10 ° C, but synthesis experiments are usually done at higher temperatures to increase the rate of crystallization. To more closely simulate natural environments, the transformation of 2-line ferrihydrite to hematite and goethite at 25 ° C in the presence of different Al concentrations and at pH values from 4 to 7 was studied in a long-term (16 – 20 y) experiment. Aluminum affects the hydrolysis and charging behavior of 2-line ferrihydrite and retards crystallization. Al also promotes the formation of hematite over goethite and leads to multidomainic discoidal and framboidal crystals instead of rhombohedral crystals. The strong hematite-promoting effect of Al appears to be the result of a lower solubility of the Al-containing ferrihydrite precursor relative to pure ferrihydrite. Hematite incorporates Al into its structure, as is shown by a decrease in the *a* and *c*-cell lengths and a decrease in magnetic hyperfine fields (Mössbauer spectroscopy). With hematite formed at low-temperature, these decreases were, however, smaller for the cell length and greater for the magnetic field than for hematite produced at higher temperatures. Both phenomena are removed by heating the hematite at 200 ° C. They are attributed to structural OH and/or structural defects. The relative content of Al in the structure is lower for hematite formed at 25 ° C than for hematites synthesized at higher temperatures (80 and 500 ° C). The maximum possible substitution of one sixth of the Fe positions was not achieved, similar to soil hematites. These results show that properties of widely distributed soil Al-containing hematites can reflect formation environment.

Key Words: Al-Substituted Hematite • Formation of Fe Oxide • Hyperfine Fields • Structural OH • Synthesis of Fe Oxides • Unit-Cell Size

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