

The influence of silicate content on thermal stability of 2-line ferrihydrite and properties of its transformation products

Gabriela Pieczara, Grzegorz Rzepa, Adam Gawel

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Mineralogy, Petrography and Geochemistry; al. Mickiewicza 30, 30-059 Krakow, Poland; e-mail: gabriela.pieczara@gmail.com

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Naturally occurring ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) is a poorly ordered iron (oxyhydr)oxide mineral, with non-stoichiometric composition and not fully understood structure. Because of its unique chemical and physical properties, such as low crystallinity, high surface area and surface reactivity, ferrihydrite plays significant role in e.g. inorganic weathering processes, biochemical cycling of iron and as a sorbent in various near-surface environments. Ferrihydrite is a metastable phase and transforms with time into stable oxides: goethite and/or hematite, through dissolution-reprecipitation and dehydration-rearrangement mechanisms, respectively.

Ferrihydrite structure provides numerous sorption sites and for this reason substantial amounts of admixtures are present in its chemical composition. The most common and well documented impurities include silicate, phosphate, arsenate, sulphate, calcium, aluminum and organic compounds. These ions affect ferrihydrite composition, surface molecular structure and sorption properties. Silicate, probably the most important impurity, causes decreasing crystallinity of this nanomineral, modifies magnetic ordering and solubility. Thus, natural ferrihydrite distinctly differ from synthetic pure analogue. As it was previously shown, the association of Si with ferrihydrite surface hindered thermal transformation to hematite. The implications of this observation

for the understanding of Si-ferrihydrite stability in geochemical systems are obvious. The aim of this work was determining of the influence of the Si/Fe ratio in ferrihydrites on its thermal transformation processes and the properties of the products.

Ferrihydrite samples having different Si/Fe molar ratios: 0.00, 0.05, 0.10, 0.20, 0.25, 0.50, 0.75, 1.00, and 1.50, were obtained by reaction of $\text{Fe}_2(\text{SO}_4)_3$ with NaOH in the presence of Na_2SiO_3 at pH 8.2. After four-day incubation, dialysis and freeze-drying, the precipitates were characterized using X-ray powder diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Raman spectroscopy, and scanning electron microscopy (SEM). Then thermal analyses (DTA/DTG/TG) were performed. All of the ferrihydrites were heated from 30°C to 1000°C, at 10°C min⁻¹ in flowing air, using hematite as inert material. After heating all the samples were again characterized by XRD and SEM-EDS methods.

DTA curve of pure ferrihydrite shows typical dehydration endotherm at 160°C and sharp exotherm at 350°C, attributed to hematite formation. Additional weak peaks at 550°C and 710°C were probably originated from decomposition of relic sulphate. The presence of Si in ferrihydrite appears to stabilize its structure and prevents conversion to hematite: the ferrihydrite-hematite transformation peak weakens and broadens and is shifted towards higher temperatures, up to ca. 900°C for

high-Si materials. However, no simple linear relationship between silica content in ferrihydrite and the position of this peak has been found.

X-ray diffraction patterns indicate that the main product of thermal transformation of all ferrihydrites is hematite (α -Fe₂O₃). For low-Si samples (Si/Fe < 0.20), a gradual broadening of 104, 214, 300, 110 hematite reflexes has been noticed, indicating the decrease of its crystallinity. On the other hand, for high-Si materials the broadening appears to be less distinct. Increasing Si/Fe molar ratio (≥ 0.10) in the initial material took an effect also in the appearance of a cristobalite-type oxide, the content of which increases drastically for the highest-Si samples. Additionally, the XRD pattern of the Si/Fe 0.10 sample reveals the presence of some spinel phase.

Hematite originating from the heating of Si-free ferrihydrite forms quite large (up to 1 mm in size) isometric and prismatic crystals, often

exhibiting pseudo-hexagonal shape. In contrast, the oxide particles become tenfold smaller even in the lowest-silicate material (Si/Fe = 0.05) and reveal pseudospherical morphology. In higher-silicate products (Si/Fe > 0.10) the crystallites are getting elongated and the elongation increases with increasing Si/Fe ratio.

This preliminary study demonstrates that silicate content causes the retarding of ferrihydrite (thermal) transformation to hematite and affecting crystallinity of the latter. Even small Si admixture in the precursor reduces crystal size of the product. During roasting of low-Si ferrihydrites some Si probably enter the hematite structure, but higher-Si hematites cannot form and for this reason heating of high-Si ferrihydrites produces two-phase composition.

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