

## Nucleation and growth of acicular goethite from ferric hydroxide gel under moderate temperature (30 and 70°C)

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The present study describes a simple and novel synthesis route for sub-micrometric acicular goethite ( $\alpha$ -FeOOH) using high OH/Fe molar ratio (=5) and moderate temperature (30 and 70°C). Two different alkaline sources (NaOH and Ca(OH)<sub>2</sub>) and two iron (III) sources (FeCl<sub>3</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) were investigated. FESEM, XRD, FTIR, N<sub>2</sub> sorption isotherms, colour evolution and pH monitoring have been used to determine the formation mechanism, the particle size, specific surface area, and morphology of goethite. Three pH regions were determined during goethite formation and each region was qualitatively associated to (I) the formation of ferric hydroxide gel, leading to acid conditions (pH<2.5); (II) spontaneous nucleation of goethite, leading to alkaline conditions (pH>11) and fine sedimentable particles; (III) growth of goethite in alkaline conditions (11<pH<13.5). The kinetic behaviour depends clearly on the reaction temperature; globally the nucleation-growth of goethite at 70 °C was about three times faster than at 30 °C. For example, well-crystallized goethite particles (high acicular goethite < 1µm in length with moderate specific surface area, S<sub>BET</sub>=31.2m<sup>2</sup>/g) were produced after 7h of reaction at 70 °C while about 24h of reaction are required to produce well-crystallized goethite particles (low acicular goethite < 0.5µm in length with high specific surface area, S<sub>BET</sub>=133.8m<sup>2</sup>/g) at 30 °C using in both cases iron chloride. In summary, the temperature and iron (III) source have a significant effect on the particle size, specific surface area and morphology of goethite. Herein, single-phase goethite particles were formed. When Ca(OH)<sub>2</sub> particles are used as alkaline source, a complex mineral composite with high specific surface area (87.3 m<sup>2</sup>/g) was synthesized; this powdered material was mainly composed of unreacted Ca(OH)<sub>2</sub> coated by nanosized particles (possibly amorphous iron hydroxide), calcium iron oxide chloride hydrate and calcite. The best conditions to prepare uniform goethite particles, possibly with high potential as adsorbents or pigments, have been established.

## Uncertainty assessment in quantification of silicate weathering rates in global rivers

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Chemical weathering is important for understanding landscape evolution, nutrient supply to ecosystems, and global geochemical cycles. Total silicate weathering fluxes to oceans have been quantified using compilations of catchment-wide measurements of concentration and water discharge [1-3]. Sources of chemical elements were differentiated using geochemical mass balance models (forward and inverse models) to partition the fluxes of each of the measured elements into carbonate, silicate, evaporite, and rain-water pools.

In this research, we analyze time-series of elemental concentrations and discharge from 52 global rivers provided by the GEMS/Water compilation, which together constitute a database of ~9000 data points. With these comprehensive datasets, we estimate uncertainties within silicate weathering rates in global rivers that consider the effects of infrequent sampling, covariation between river discharge and concentration, and uniqueness of attribution of weathering fluxes to the different pools. This is accomplished using a Bayesian Metropolis-Hastings algorithm to estimate the overall uncertainties within, and covariation between weathering fluxes that are attributed to the different pools based on the GEMS/Water database. Knowing the overall uncertainties in global estimates will provide information about required sampling frequencies, number of sites, and chemical elements that will help to design future catchment-scale studies.

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[3] Meybeck & Ragu (1997) UNEP Publication.