-SUPPORTING INFORMATION-

Rates and Extent of Reduction of Fe(III) Compounds and O_2 by Humic Substances

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- 5 Pages (including cover page)
- 3 Figures
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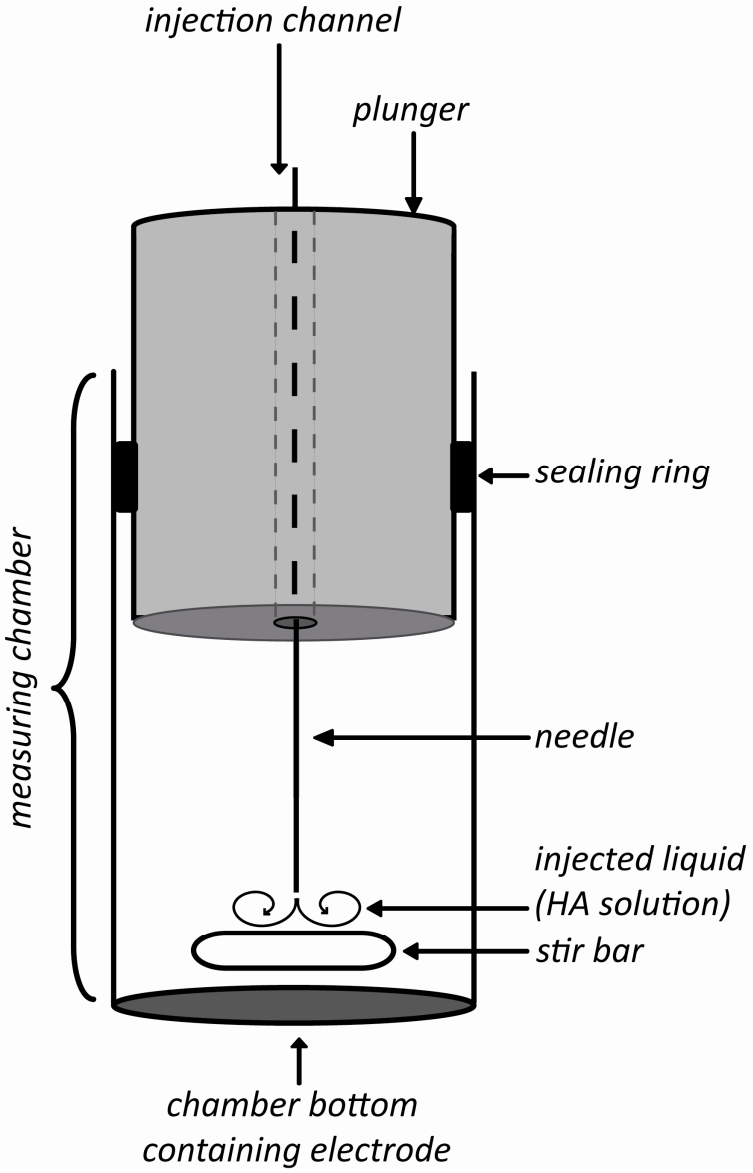

Figure S1: Schematic drawing of the measuring chamber of the O_2 electrode (OX1LP dissolved O_2 package, Qubit systems).

O_2 electrode: Experimental Setup of Quantification of O_2 Reduction by HA

The setup consists of a polarographic O_2 electrode at the bottom of a closed measuring chamber (adjustable volume of up to 6 mL, Figure S1). At the bottom of the chamber, O_2 diffuses through a Teflon membrane covering a Pt cathode, where O_2 reduction and thus quantification takes place. The cathode is in electrical continuity with an Ag-AgCl anode via a KCl electrolyte solution. HA preparations were deoxygenated and filtered. Aliquots (0.2-0.5 ml) of reduced or non-reduced HA preparations, at different concentrations, were injected through a 1 mm wide and 1.3 cm long channel from the top into the measuring chamber. Before HA injection, we adjusted the volume of the chamber to 3 mL and filled the chamber

completely with air-saturated phosphate buffer (50 mM, pH 7) or water. For injection, a 1 mL syringe (Kendall Monoject) with a long needle (Braun Sterican, 0.6 x 60 mm) was used. Thus the HA preparations could be injected into the phosphate buffer or water as close as possible to a magnetic stirring bar at the bottom of the measuring chamber to guarantee instantaneous homogeneous mixing. The increase in liquid volume in the chamber during injection caused a slight rise of fluid into the injection channel, which had no effect on the measurement. Injection of an anoxic solution into the oxic fluid in the measuring chamber led to a decrease in O_2-content due to dilution. This decrease was considered in the calculations of O_2-consumption by HA. Diffusion of O_2 into the chamber through the injection channel during the time of the measurements was negligible. Before each measurement, the system was calibrated with a two-point-calibration using air-saturated phosphate buffer or water (defined as 100% O_2) vs phosphate buffer or water which was bubbled with N_2 (defined as 0% O_2). After proper calibration the electrode was able to resolve changes of 0.1% O_2. Current air pressure and temperature were taken into account.

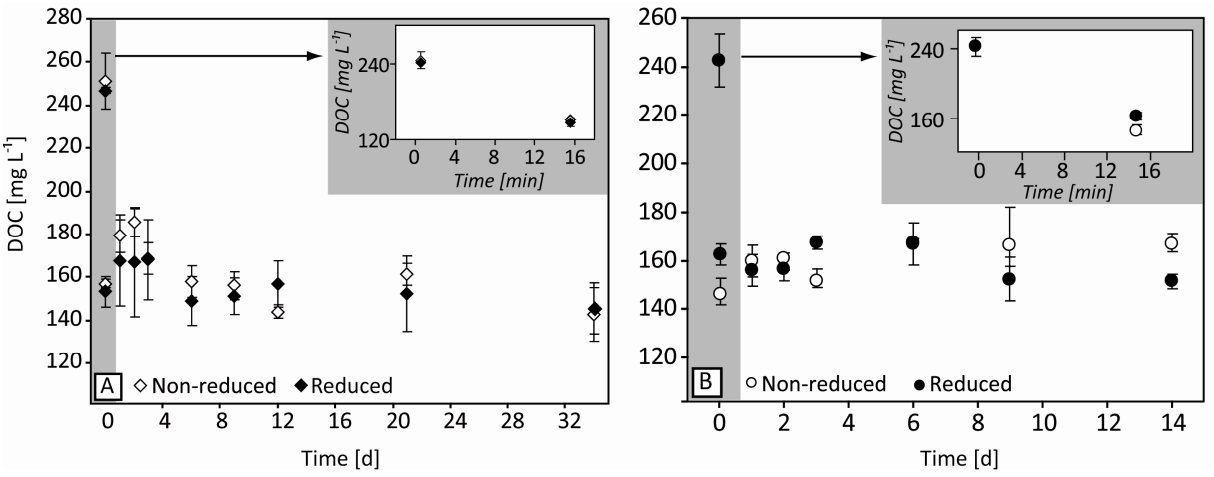

Figure S2: Amount of humic substances sorbed to goethite (A) and hematite (B) mineral surfaces during reduction by IHSS Pahokee Peat HA. Figures show dissolved organic carbon (DOC) over time. Open symbols represent non-reduced HS, closed symbols stand for reduced HS. Standard deviations were calculated from three independent parallels. Grey inserts represent an enlargement of the first two sampling points (before and 15 minutes after addition of Fe(III) minerals). Multi-point BET measurements yielded surface areas of 9.2 m^2 g^{-1} for goethite and 2.3 m^2 g^{-1} for hematite. Ferrihydrite (not shown here) had a surface area of 249 m^2 g^{-1}.

Table S1: Redox potential values of predominant Fe(III)/Fe(II) redox couples reacting with HA at pH 7. $E_h^{0'}$ values from literature as well as in-situ E_h' values are given which were calculated using equations 1-4 given below. For calculations, initial and final experimental concentrations of Fe(III)/Fe(II) were used. For Fe(III) citrate, initial concentration of Fe(II) was 5 µM due to some Fe(II) present in Fe(III) citrate solutions; for all Fe(III) minerals, an initial concentration of Fe(II) of 1 µM (detection limit of ferrozine assay) was used. Concentrations were used instead of activities for simplification.

Fe(III)/Fe(II) redox couples	**$E_h^{0'}$ [mV]**	**E_h' [mV] (initial)**	**E_h' [mV] (final)**
Fe(III) citrate/Fe(II) citrate	+ 372[b]	+ 933	+ 833
[a]$Fe(OH)_3/Fe^{2+}$	- 100 to + 100[b,c,d,e]	+ 18	- 77
α-FeOOH/Fe^{2+}	- 274[b]	- 215	- 320
Fe_2O_3/Fe^{2+}	- 287[b]	- 228	- 328

[a] for E_h' calculations, a value of $E_h^{0'}$ = 0 mV was used
[b] from [1]
[c] from [2]
[d] from [3]
[e] from [4]

(1) Fe(III) citrate + e^- → Fe(II) citrate

$$E_h' = E_h^{\,0} + 0.059 \cdot \lg \frac{[Fe(III)citrate]}{[Fe(II)citrate]}$$

(2) $Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$

(3) α-FeOOH + e^- + $3H^+$ → Fe^{2+} + $2H_2O$

(4) 0.5 Fe_2O_3 + e^- + $3H^+$ → Fe^{2+} + 1.5 H_2O

$$E_h' = E_h^{\,0} + 0.059 \cdot \lg \frac{(H^+)^3}{(Fe^{2+})}$$

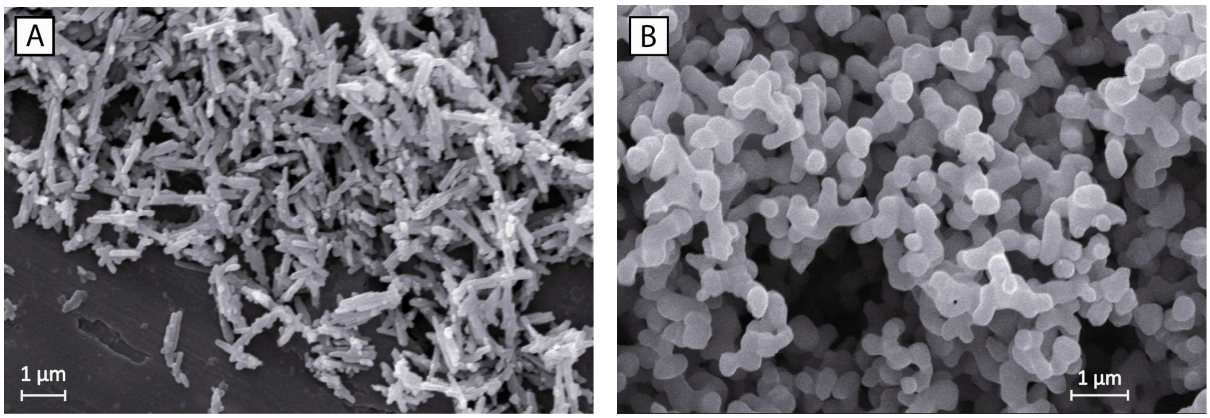

Figure S3: Scanning electron micrographs of goethite (A) and hematite (B) used in our experiments. (A) shows characteristic needle-shaped crystals of goethite with particle sizes ranging from 0.2-0.9 µm. (B) shows hematite crystals with particles of a size range of 0.1-0.3 µm (that form larger aggregates). Size bar in both images indicates a length of 1 µm.

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