

Effects of pH, ionic strength and a fulvic acid on size distribution and surface charge of colloidal quartz and hematite

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Abstract—Size distribution of colloidal quartz and hematite (initial diameter 140–190 nm and 70–360 nm, respectively) were determined by Photon Correlation Spectroscopy (PCS) in well-defined laboratory systems. Effects on the mean diameter and the size distribution were measured at various values of pH (2–12) and ionic strength (0.001–0.7 mol/l) in an inert medium (NaClO₄). The effect of an aquatic fulvic acid on the stability of the colloids was included in the study. In the absence of fulvic acid the colloids flocculate at a pH close to pH_{zpc} of the respective mineral. This increase in mean diameter is due to electrostatic interactions. Hematite colloids are also destabilised at a pH much below pH_{zpc} . The quartz colloids are stabilised in the presence of fulvic acid. The hematite/fulvic acid systems are stable at high pH, but flocculate at low pH. Increasing ionic strength induces agglomeration of the quartz colloids at 0.1 mol/l, independently of the presence of fulvic acid (2 mg/l). Hematite is destabilised at 0.02 mg/l in the absence of fulvic acid, while in the presence of fulvic acid the colloids aggregate at ionic strength >0.07 mol/l.

INTRODUCTION

THE MOBILITY and redistribution of naturally occurring as well as anthropogenic trace metals in the aquatic environment are highly dependent on interactions with suspended solids and colloidal matter (see e.g. SALOMONS and FÖRSTNER, 1984; O'MELIA, 1989). From field studies it has been shown that both transition and rare-earth elements as well as actinides are, to a significant extent, associated with particulate matter of colloidal size range in fresh waters (see e.g. HOFFMANN *et al.*, 1981; ORLANDINI *et al.*, 1990; MIEKELEY *et al.*, 1991; VILKS and DEGUELDRE, 1991). The predominant redistribution processes are exerted by adsorption reactions rather than by precipitation, because the concentrations of most trace metals are below saturation in open water bodies under oxidising conditions.

Natural colloidal and suspended solids have compositions reflecting the geology as well as the hydrochemical conditions of the watershed. Oxides and hydroxides of Al, Fe, Mn and Si can be important constituents, as well as carbonates and clay minerals. In spite of the heterogeneous mineralogical composition, some common features have been reported for colloidal suspended matter. Surface coatings of hydrous oxides of Fe and Mn as well as organic matter are known modifiers of their adsorption properties (TIPPING and COOKE, 1982). General hydrochemical parameters (notably pH and ionic strength) influence the trace metal distribution process due to the effects on surface properties of the solid phases as well as on the chemical forms of the dissolved species which interact with the surfaces.

Flocculation in the salt gradient of estuaries is widely recognised and can be explained by processes at the solid/solution interface (SHOLKOVITZ, 1976).

However, the seasonality of hydrochemical conditions in fresh waters in temperate areas can also have an impact on the stability, and thereby size distribution of solid precipitates that can act as trace element carriers in the aqueous phase. For instance, it has been shown in laboratory experiments that relatively small changes in the Ca²⁺ concentration may alter the stability of particles isolated from lake water (ALI *et al.*, 1984). Thus, transport properties and accumulation of metals in the aquatic environment are influenced by changes of size and charge of the solid suspended phase related to the hydrochemical conditions, as well as by adsorption processes at the solid/solution interface.

Natural quartz and hematite in the colloidal size range were used as model systems in a study of trace element redistribution and transport by colloidal carriers in natural aquatic systems. In the present part of the study the impact of pH, the ionic strength and the presence of an aquatic fulvic acid on the size distributions of suspended matter was investigated.

MATERIALS AND METHODS

Sample preparation and composition

Natural specimens of crystalline quartz and hematite from Olden and Kiruna, Sweden, were ground in Milli-Q water to colloidal size in a vibration mill. The suspensions were allowed to settle and equilibrate with the aqueous phase in a sedimentation funnel for a minimum of 4 weeks (in the dark, at 8°C). These solutions contained colloidal fractions (size ranges of 70–360 nm and 140–190 nm for hematite and quartz, respectively; see below) at concentrations of 1–2 g/l.

Phase composition and crystallinity of the colloids were determined by powder X-ray diffractometry (XRD) and infrared spectroscopy (FTIR). Qualitative information on

possible surface coatings (e.g. by organics) was obtained with the latter technique. Samples for XRD analysis were taken from the sedimented phase at the bottom of the sedimentation funnels. Recordings of FTIR spectra were performed using KBr-pellets or by a diffuse reflectance technique. In these studies colloids and fulvic acid were equilibrated for 24 h in NaClO_4 (0.01 mol/l) at pH values above and below the pH of zero point of charge (pH_{zpc}) (i.e. at pH 2.6 and 5.1 for quartz, and at pH 6.6 and 10.6 for hematite). The colloid concentrations were 1 g/l for both quartz and hematite and the fulvic acid concentration was 2 mg/l. The samples were collected on membrane filters (polycarbonate, Nuclepore, 0.015 μm) and dried in a Lamin-air flow bench before measurements by FTIR. Additional samples prepared were the fulvic acid which was merely mixed with the colloidal matter through grinding (dry) in an agate mortar, in order to confirm that the fulvic acid was actually adsorbed to the colloidal surfaces instead of, for example, coprecipitation during the filtration.

A potentiometric titration procedure was applied to determine the pH_{zpc} according to EPHRAIM *et al.* (1989). The solutions were purged with N_2 during the titrations.

Size distribution studies

Variations in the size distribution were studied in batch experiments (~500 mg/l and 100 mg/l of hematite and quartz, respectively, in polypropylene vessels). Individual experiments were performed with batches of colloids with slightly different initial mean diameters (quartz 140 and 190 nm; hematite 70, 150, 200 and 360 nm). The ionic medium consisted of NaClO_4 . The systems were equilibrated, usually for 24 h, in contact with the atmosphere.

The size distribution of the colloidal phase was determined by photon correlation spectroscopy (PCS) (cf. CHU, 1974; BERNE and PECORA, 1976), using a Brookhaven Instrument Corporation B190 equipped with a Lexel 2W Ar-laser, operated at 700 mW and at a wavelength of 488 nm. Measurements were performed with six replicates. Size distribution calculations were conducted by the B190 correlation software. The geometric forms of the solids were examined by scanning electron microscopy (SEM; Cambridge 250) and transmission electron microscopy (TEM; Cambridge 400T). Colloid samples, for SEM studies were prepared by filtration of ~1 ml colloid solution (without NaClO_4) through polycarbonate membrane filters (Nuclepore, 0.015 μm) mounted in a Swinnex (Millipore) filter holder. The filters were dried in a Lamin-air flow bench and covered with gold (10 nm). For the TEM examinations, grids with a plastic film were immersed into the colloid solutions and dried in a Lamin-air flow bench before assembling into the TEM. The elemental composition was routinely recorded by a Link Analytical AN10000 X-ray analyser connected to the SEM. SEM micrographs were also used to validate the size measurements conducted with PCS by counting the frequencies of different size classes. The kinetics of the flocculation were followed by PCS recordings with equilibration times of 30 min, 1 h, 1 d and 7 d, respectively. A fairly invariant size distribution (at each investigated pH and ionic strength) was reached after 30 min and remained stable during at least the 7 d-period of the experiments.

When the impact of ionic strength was studied (at a pH in each series of pH 5–7) NaClO_4 (1.0 mol/l) was added to give a final concentration in the range of 0.001–0.7 mol/l. Effects of pH were studied at a constant ionic strength of 0.01 M by adding NaOH or HClO_4 to the desired pH (2–11). In order to elucidate possible interferences from sample handling (e.g. dilution, shaking, exposure to light or biological activities) an untreated reference sample was present in each series.

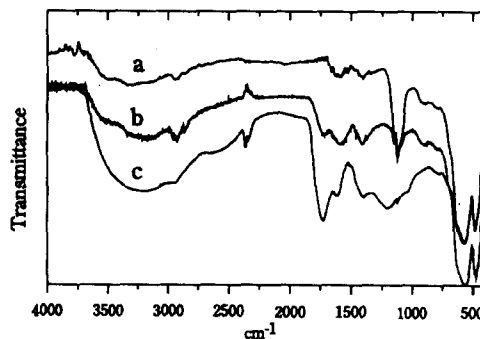


FIG. 1. FTIR spectra of hematite colloids: a. Fe_2O_3 , pH 10.8, no fulvic acid; b. Fe_2O_3 and fulvic acid, pH 10.8; c. synthetic mixture of dry Fe_2O_3 and fulvic acid (1:1).

The fulvic acid, which was added to the system in some series, was isolated from a surface water and purified according to the procedure by PETERSSON *et al.* (1989). The total acid capacity (carboxylic groups) was 4.60 meq/g and the molecular weights were 1750 (number) and 2650 (weight). All chemicals used in the experiments were of analytical grade or better. Sample preparations were made in a Lamin-air flow bench to minimise contamination. Experiments with hematite and fulvic acid were conducted in the dark to avoid photo induced oxidation/reduction reactions (cf. SIFFERT and SULZBERGER, 1991). However, the possible production of aqueous Fe(II) due to such processes was also measured (with the 1,10-phenantroline method; in the presence of F^-).

Concentrations of aqueous Fe and Si, in equilibrium with the colloidal hematite and quartz, respectively, were determined by graphite furnace atomic absorption spectrophotometry (in solution, filtered through 0.015 μm polycarbonate membranes). Solubilities of the minerals were calculated assuming equilibrium with the aqueous phase and using data compiled in LINDSAY (1979) and STUMM and MORGAN (1981).

RESULTS AND DISCUSSION

Composition of the colloids

Analyses with powder X-ray diffractometry indicated that the colloidal solids consisted of ordered crystals without any detectable impurities. Complementary analyses with FTIR showed surface properties typical of the minerals. Some measurements performed with TEM indicated a less ordered structure at the solid/solution interface, particularly of the hematite colloids. Although it was not possible with the present methods to distinguish adsorbed carbonate or hydrated mineral phases, it is likely that the original oxide surfaces were altered to some depth. The fulvic acid was adsorbed to the hematite surfaces as indicated by the FTIR-spectra (Fig. 1). It was not possible, however, to detect any adsorbed fulvic acid on the quartz colloids with this method.

Size distribution measurements

Size distribution measurements performed by PCS indicated a monomodal size distribution of the col-

loids within a relatively small size range. Some typical size distribution histograms are presented in Fig. 2. Inspection with SEM confirmed the sizes indicated from the PCS measurements and showed also that hematite colloids had a flake-like form while the quartz colloids were spherical. The corresponding surface areas of the solids at pH 6–8 were $\sim 16 \text{ m}^2/\text{g}$ and $40 \text{ m}^2/\text{g}$ for quartz and hematite, respectively, calculated from mean diameters and size distributions and considering the geometrical shape of the colloids.

Surface charge development

The surface charge of quartz and hematite as a function of pH is illustrated in Fig. 3 (calculated from potentiometric titrations; see EPHRAIM *et al.*, 1989). A charge reversal occurs at pH of 2.5 and 10.3, for quartz and hematite, respectively. These observations are quite close to similar measurements reported for carbonate-free systems (LYKLEMA, 1989), in spite of the possible contamination with $\text{CO}_2/\text{CO}_3^{2-}$ during the sample preparation. The observed surface charge of the fulvic acid (cf. Fig. 3) is supported by values reported by PETERSSON *et al.* (1989) (negative charge of the molecule at pH > 3.5).

Impact of pH on the size distribution

Quartz. Flocculation of quartz colloids, corresponding to an increase in the mean diameter from 190 to 360 nm, was observed at pH < 3.5 (at $I = 0.01$

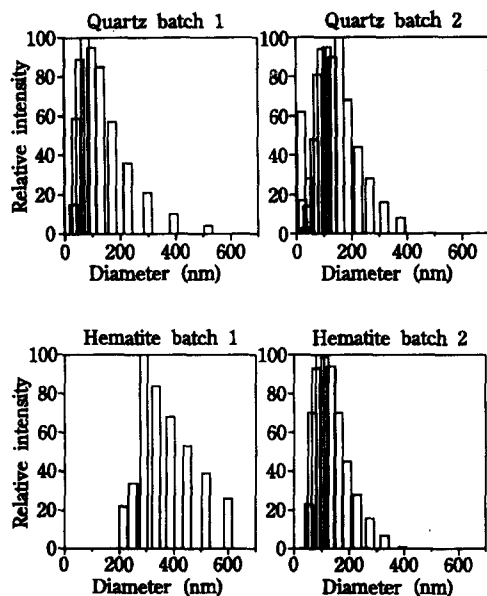


FIG. 2. Typical size distribution histograms for two different batches of quartz and hematite, respectively. Quartz: batch 1, mean diameter 140 nm; batch 2, mean diameter 190 nm. Hematite: batch 1, mean diameter 360 nm; batch 2, mean diameter 150 nm.

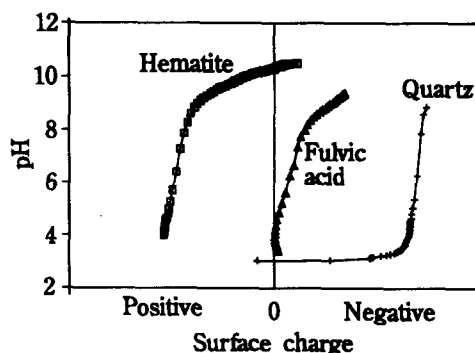


FIG. 3. The pH-dependent surface charge (relative scale) of quartz and hematite colloids and fulvic acid, according to potentiometric titrations.

and in the absence of fulvic acid). This is evidently related to the surface charge because it coincides with the pH_{zpc} (Fig. 4). The electrostatic repulsion seems to be the major process that controls the stability of the quartz system in the colloidal state. This conclusion is further supported by the rapid kinetics of the flocculation. No significant differences in mean size were observed after 30 min of equilibration. Thus, flocculation would occur at a pH close to the pH_{zpc} which, however, has been reported to be related to surface area/mass ratios (ZELTNER and ANDERSSON, 1989).

In the presence of fulvic acid (2 and 20 mg/l) the quartz colloids were stable over the studied pH range (pH 2–10). At pH < pH_{zpc} the fulvic acid could be expected to adsorb on the quartz surfaces (although it has not been shown in the present study), because a positive surface charge of the quartz would attract the partly deprotonized fulvic acid. The adsorbed fulvic acid appears to repel adjacent colloids with a similar coating under these pH conditions and thereby stabilise the system. At pH > pH_{zpc} any adsorption of fulvic acid would have to take place against a net negative charge of both constituents and is therefore not likely.

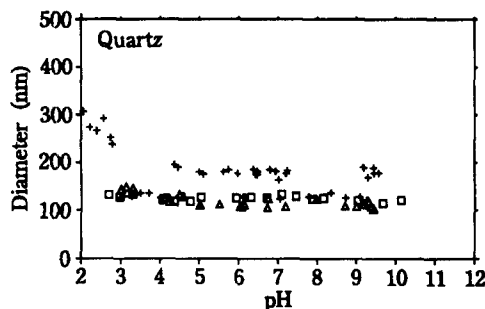


FIG. 4. Mean diameter (nm) of quartz colloids, at different fulvic acid concentrations, as a function of pH. The different mean sizes between samples with and without fulvic acid at pH > 5 are due to differences between the batches used; initial diameters were 190 and 140 nm, respectively ($I = 0.01 \text{ mol/l}$); + [fulvic acid] = 0 mg/l, \square [fulvic acid] = 2 mg/l, Δ [fulvic acid] = 20 mg/l.

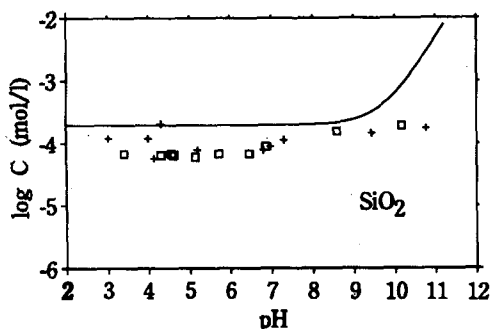


FIG. 5. Estimated solubility of quartz (solid line) as a function of pH, and measurements of aqueous Si concentrations after filtration through 0.015 μm polycarbonate membranes ($I = 0.01$ mol/l); + [fulvic acid] = 0 mg/l, \square [fulvic acid] = 2 mg/l.

Saturation estimates and measurements of dissolved Si show a fair agreement, considering the uncertainty in published stability constants. Consequently, fulvic acid at a concentration up to 20 mg/l does not significantly influence the solubility of quartz over the investigated pH-range and within the time used for equilibration (Fig. 5).

From an environmental point of view these findings suggest that quartz colloids would be rather stable under natural pH conditions, at least in environments with a minimum concentration of fulvic acid of 2 mg/l. However, in waters with lower concentrations of fulvic acid, flocculation could be induced at a pH close to the pH_{zpc} .

Hematite. Hematite flocculation was observed at high pH (at $I = 0.01$ and in systems without fulvic acid, Fig. 6). This flocculation is apparently due to mainly physical forces of attraction related to the surface charge of the colloids, just as for quartz. In the present study it corresponds to an increase in mean diameter from 200 nm to a maximum of 900 nm at pH close to pH_{zpc} (pH 10.3). At $\text{pH} > \text{pH}_{\text{zpc}}$ there was possibly a tendency of reduced mean diameter.

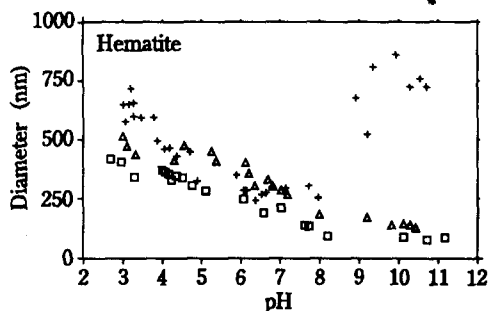


FIG. 6. Mean diameter (nm) of hematite colloids, at different fulvic acid concentrations, as a function of pH. The different mean sizes between samples with and without fulvic acid at pH 7–8 are due to differences between the batches used; initial diameters were 200 and 70 nm, respectively ($I = 0.01$ mol/l); + [fulvic acid] = 0 mg/l, \square [fulvic acid] = 2 mg/l, Δ [fulvic acid] = 20 mg/l.

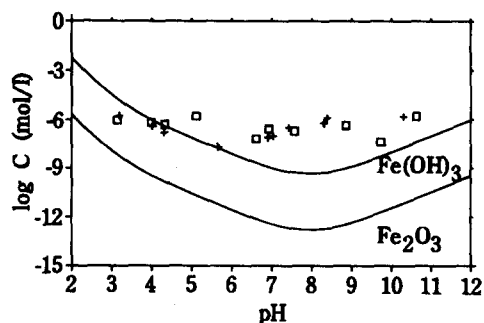


FIG. 7. Estimated solubility of hematite and amorphous Fe(III)-hydroxide (solid line) as a function of pH, and measurements of aqueous Fe concentrations after filtration through 0.015 μm polycarbonate membranes ($I = 0.01$ mol/l); + [fulvic acid] = 0 mg/l, \square [fulvic acid] = 2 mg/l.

In the presence of fulvic acid (2 mg/l and 20 mg/l), the flocculation at $\text{pH} > 8$ was inhibited. Hematite would be positively charged in this pH range (see Fig. 3), in contrast to quartz, which allows for electrostatic attraction of fulvic acid, and possibly also binding to specific groups on the colloid surface. Obviously, the forces of attraction between hematite colloids and fulvic acid are sufficiently strong to prevent desorption of fulvic acid, also when the pH of the aqueous phase is close to or above the pH_{zpc} of the hematite. This is further confirmed in the FTIR measurements (Fig. 1), which showed that fulvic acid is adsorbed to the hematite colloids both above and below pH_{zpc} . At $\text{pH} > 8$ the acidic groups on the adsorbed fulvic acid are almost completely deprotonized and the molecule reaches its highest negative charge density, and consequently, the negatively charged groups on the adsorbed fulvic acid molecules stabilise the colloids by electrostatic repulsion. At $\text{pH} < 6$ the colloids are destabilised and form aggregates, both in the absence and in the presence of fulvic acid.

The impact of organic molecules (e.g. acids) on the reductive dissolution of Fe(III)-oxides has been demonstrated and reported from both field observations and laboratory experiments (see e.g. SKOGERBOE and WILSON, 1981; WAITE and MOREL, 1984; WEHRLI *et al.*, 1989). This reaction, which is enhanced by light, seems to be at an optimum at pH close to 3 (cf. MCKNIGHT *et al.*, 1988). Possibly, the flocculation of hematite observed in the present study can be related to a fulvic acid mediated dissolution by a reductive mechanism. A production of Fe(II) (aq) in the systems with fulvic acid present correlates with the pH where flocculation is initiated, and there is an apparent over-all oversaturation with respect to hematite as well as amorphous ferric hydroxides (Fig. 7). It must be pointed out, however, that photo-induced reduction does not necessarily occur spontaneously in the present systems because the samples were handled in the dark, and that the concentrations of Fe(II) were $< 10 \mu\text{g/l}$, according to the measurements. During the PCS measurements these are, however, exposed to laser irradiation

(wavelength 488 nm) of high intensity, and consequently a reduction process might be induced under those conditions. It seems to be of limited importance on the size distribution because repeated size measurements and subsequent irradiation did not significantly alter the mean diameter. It has also been reported that reduction is predominantly induced by light with wavelengths in the UV region (SIFPERT and SULZBERGER, 1991).

Thus, flocculation of hematite at low pH both in the presence and in the absence of fulvic acid could possibly be related to processes other than merely electrostatic interactions related to the surface charge. This is also supported by the observations that even the purely inorganic systems are oversaturated with respect to hematite as well as amorphous ferric hydroxides (although the solubility of a precipitated amorphous Fe(III)-hydroxide may have been underestimated in the calculations). A plausible reaction would be a combined dissolution/precipitation at the surfaces similar to the autocatalytic dissolution of hematite that has been previously reported (WEHRLI *et al.*, 1989). Experiments performed with amorphous ferric hydroxide have showed a formation of extremely large aggregates ($>2 \mu\text{m}$), when pH was <6 , independently of the presence of fulvic acid (to be reported elsewhere).

The stabilisation of colloidal hematite by fulvic acid in the high pH range, i.e. close to the pH_{zpc} of the mineral, could be of particular importance for environmental systems. The observed flocculation properties at low pH infer that hematite particles would more easily be subjected to sedimentation with decreasing pH (<5) in the aquatic environment and thereby be less mobile. It is also noteworthy that flocculation at low pH occurs even in the absence of fulvic acid. The mechanisms are not fully understood and need further investigation. Thus, the reaction pattern of Fe(III)-systems is more complicated than the quartz system with significant effects of variations in charge density, presence of fulvic acid and possibly redox reactions within the environmental pH-range.

Impact of ionic strength on size distribution

Quartz. The impact of ionic strength on the stability of quartz colloids was studied at $\text{pH } 6.1 \pm 0.4$ and 5.5 ± 0.8 (absence and presence of fulvic acid, respectively; Fig. 8). Quartz colloids were destabilised from their original mean diameter of 140 nm when the ionic strength was $>0.1 \text{ mol/l}$ and a maximum of 1150 nm was reached at 0.7 mol/l . No significant differences were observed in measurements conducted between 30 min and 7 d after salt additions.

The results illustrate that flocculation can occur at salt concentrations representative of estuaries ($>0.1 \text{ mol/l}$), and thereby possibly also at confined release points of industrial waste water or drainage from

decomposing solid waste. The presence of fulvic acid in the system did not significantly alter the ionic strength impact at salt concentrations $<0.3 \text{ mol/l}$.

Hematite. In the absence of fulvic acid ($\text{pH } 6.7 \pm 0.3$) the flocculation of hematite was initiated at an ionic strength of $\sim 0.02 \text{ mol/l}$ (Fig. 9), which can be encountered in fresh waters. The largest diameter was found at an ionic strength of 0.1 mol/l comparable to estuarine conditions. The salt induced agglomeration was hindered in the presence of fulvic acid ($\text{pH } 5.1 \pm 0.1$). This behaviour indicates that fulvic acid binds to the surfaces and thereby stabilises the colloidal hematite. Consequently, flocculation of negatively charged colloids, due to adsorption of organic matter, is not merely a function of ionic strength.

CONCLUSIONS

From experiments, where the changes in mean size and size distribution of quartz and hematite colloidal particles were followed as a response to changes of pH and ionic strength, the following qualitative conclusions can be drawn:

A maximum mean diameter was found at pH close to pH_{zpc} for both the quartz and hematite colloids in the absence of fulvic acid. Hematite also showed increasing mean diameter at $\text{pH} \ll \text{pH}_{\text{zpc}}$. This flocculation of hematite was attributed to chemical reactions on the colloidal surfaces. In the presence of fulvic acid (2 mg/l and 20 mg/l) the quartz colloids were stable in the whole pH range 2–10. Hematite colloids were stabilised at high pH, whereas flocculation was induced at low pH.

Increasing concentrations of NaClO_4 induced flocculation of quartz at 0.1 mol/l ($\text{pH } 6.1 \pm 0.4$ and 5.5 ± 0.8 , absence and presence of fulvic acid, respectively) and were independent of the presence of fulvic acid (at $I < 0.3 \text{ mol/l}$). For hematite ($\text{pH } 6.7 \pm 0.3$ and 5.1 ± 0.1 , absence and presence of fulvic acid, respect-

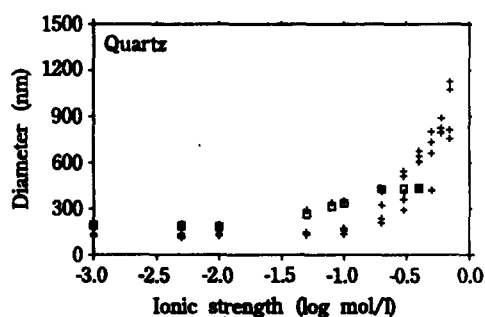


Fig. 8. Mean diameter (nm) of quartz colloids as a function of ionic strength (NaClO_4). The different original mean diameters at low ionic strength are due to differences between the batches used; initial diameters were 140 and 190 nm, respectively; + $\text{pH} = 6.1 \pm 0.4$, [fulvic acid] = 0 mg/l; □ $\text{pH} = 5.5 \pm 0.8$, [fulvic acid] = 2 mg/l.

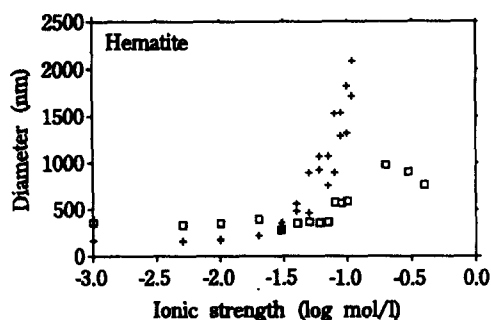


Fig. 9. Mean diameter (nm) of hematite colloids as a function of ionic strength (NaClO_4). The different original mean diameters at low ionic strength are due to differences between the batches used; initial diameters were 360 and 150 nm, respectively; + pH = 6.7 ± 0.3 , [fulvic acid] = 0 mg/l; □ pH = 5.1 ± 0.1 , [fulvic acid] = 2 mg/l.

ively) flocculation occurred at 0.02 mol/l in the absence of fulvic acid and at 0.07 mol/l when fulvic acid was present.

Natural variations in pH and/or ionic strength would be enough to change, substantially, the stability of quartz and particularly hematite colloids in many freshwater and brackish water systems. Fulvic acid, at concentrations within the natural range of fresh waters, will, to some extent, moderate these effects, but not totally cancel them out. It is not possible, from these results however, to predict fully, the behaviour of quartz and hematite colloids in the environment, because the experiments were performed with variations (separately) of only two key parameters (pH and ionic strength). Combined effects of pH and ionic strength as well as the importance of anion and cation distribution (e.g. presence of Ca^{2+} etc.) will be studied in a subsequent phase of the project.

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