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An electrokinetic study of synthetic greigite and pyrrhotite

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Abstract—The isoelectric points of synthetic greigite, Fe₃S₄, and pyrrhotite, Fe_{1-x}S, in 10⁻³–1.1 10⁻² M NaCl solution at $a_{\text{Fe}} < 10^{-4}$ and $a_{\text{S}} < 10^{-4}$ were determined to be pH 3 and 2, respectively. Below pH 2 for pyrrhotite and below pH 3 for greigite, the surfaces are positively charged; above these pH values the surfaces are negatively charged. Upon addition of sulfidic sulfur (H₂S, HS⁻), traces of terrestrial humic acids, or a combination of sulfidic sulfur and terrestrial humic acids, the surfaces are negatively charged over the entire pH range (2–11) studied. Because humic acid and sulfidic sulfur influence the zeta potential of the iron sulfide surfaces, they must be adsorbed within the shear plane of the double layer, close to the actual surface of the minerals. The isoelectric points for greigite and pyrrhotite in the absence of either sulfidic sulfur or humic acid are very close to those for natural pyrite (FeS₂) and sphalerite (ZnS), as well as synthetic ZnS, CuS, CdS, galena (PbS), chalcocopyrite (CuFeS₂), and elemental sulfur. It is plausible that the speciation of thiol surface groups ($\equiv\text{S}-\text{H}_2^+$, $\equiv\text{S}-\text{H}^0$, $\equiv\text{S}-$) dominates the surface charge on all these phases. The increase in net zeta potential upon the addition of sulfidic sulfur is, however, not well understood.

INTRODUCTION

WHILE IT IS WIDELY recognized that iron sulfides are important adsorbents in nature, our knowledge of the surface chemistry of iron sulfides is limited. Iron sulfides, the most abundant metal sulfides in the Earth's crust, form in reduced environments and provide a surface with which other, often less abundant metals may interact. This interaction may range from adsorption, surface precipitation, to coprecipitation. Through any of these processes or a combination of these processes, hereafter collectively referred to as sorption, iron sulfides may control the mobility of chalcophilic elements (e.g., Cu, Zn, As, Se, Cd, Pb, Ag) and siderophilic elements (e.g., Co, Ni, Au) in much of the world's sediment mass. Sorption of precious metals onto sulfide surfaces may also be an important depositional mechanism in epithermal ore deposits (RENDERS and SEWARD, 1989; CARDILE et al., 1993) and perhaps submarine exhalative systems (SCHOONEN et al., 1992). A better understanding of the surface chemistry of iron sulfides is also of importance to related fields such as ore beneficiation (ARBITER et al., 1975; FINKELSTEIN et al., 1975; FUERSTENAU et al., 1985) and environmental sciences (ARAKAKI and MORSE, 1993; BROWN et al., 1979; FRAMSON and LECKIE, 1978; KORNICKER and MORSE, 1991).

The main objective of this study was to determine the isoelectric point of synthetic greigite (Fe₃S₄) and pyrrhotite (Fe_{1-x}S) as a function of pH in the absence of specific sorption. The electrokinetic measurements presented in this work are the first on greigite and only the second electrokinetic study on pyrrhotite (NEY, 1973).

BACKGROUND

The charge development on divalent metal sulfides in aqueous solutions is attributed to the hydrolysis of undercoordinated metal

and sulfur atoms at the surface (e.g., PARK and HUANG, 1987; SUN et al., 1991; RÖNNGREN et al., 1991). It is assumed that the hydrolysis leads to two types of surface sites, a thiol group ($\equiv\text{SH}$) and a metal hydroxide group ($\equiv\text{Me}-\text{OH}$). The ratio between thiol groups and metal hydroxide groups on the surface is a function of the activity of aqueous Me species and S(-II) species. The activities of Me²⁺ and S(-II) are constrained by the solubility product for the metal sulfide if equilibrium is attained. The potential on the metal sulfide surface is determined by reactions involving the two types of functional groups and aqueous Me species, S(-II) species, H⁺, and OH⁻ (see e.g., NICOLAU and MENARD, 1992; and PARK and HUANG, 1987). At a fixed Me species activity, a_{Me} , and S(-II) species activity, a_{S} , the surface charge and potential are expected to vary as a function of pH due to ionization of the $\equiv\text{SH}$ and $\equiv\text{Me}-\text{OH}$ groups. Depending on the ratio of the activities of Me and S(-II) in the solution as many as three charge reversals may be observed. For example, NICOLAU and MENARD (1992) showed that for ZnS only one charge reversal at low pH (<3) is observed for suspensions with a_{Zn} and a_{S} less than 10⁻⁵, as well as for suspensions with $a_{\text{Zn}} < 10^{-5}$ but $a_{\text{S}} > 10^{-4}$. However, three charge reversals are observed for solutions with $a_{\text{S}} < 10^{-4}$ but $a_{\text{Zn}} > 10^{-4}$. The first of these three charge reversals coincides with the only charge reversal observed for suspensions with a_{Zn} and a_{S} less than 10⁻⁵, the second charge reversals occurs between pH 3.5 to 4.5, and the third charge reversal occurs at pH 5 to 7 (see Fig. 5 in NICOLAU and MENARD, 1992). In experiments where the ZnS is the only source of Zn and S in solution only one charge reversal is observed but the zeta potential curve has typically a plateau between pH 4 to 8. Figure 1 summarizes schematically how the charge is expected to change as a function of pH, a_{Me} , and a_{S} for a divalent metal sulfide.

A major problem in the study of the surface chemistry of divalent metal sulfides is oxidation. Surface spectroscopic studies show that pyrrhotite surfaces are rapidly oxidized upon exposure to air (JONES et al., 1992; PRATT et al., 1994) and water (JONES et al., 1992). Exposure of pyrrhotite to air or O₂-containing water leads to a surface precipitate of Fe(III) hydroxide overlying an Fe-deficient pyrrhotite (JONES et al., 1992). This Fe(III) hydroxide surface layer is easily removed in acid. The work by JONES et al. (1992) also shows that the surface of pyrrhotite in perchloric acid, deoxygenated solutions becomes iron deficient and that the sulfur atoms on the surface polymerize to S₂²⁻ surface species. Studies on pyrite (MYCROFT et al., 1990), zinc sulfide (WILLIAMS, 1960), cadmium sulfide (MINOURA et al., 1977; WILLIAMS, 1960), and lead sulfide (RICHARDSON and MAUST, 1976) also indicate that oxidation creates a metal-de-

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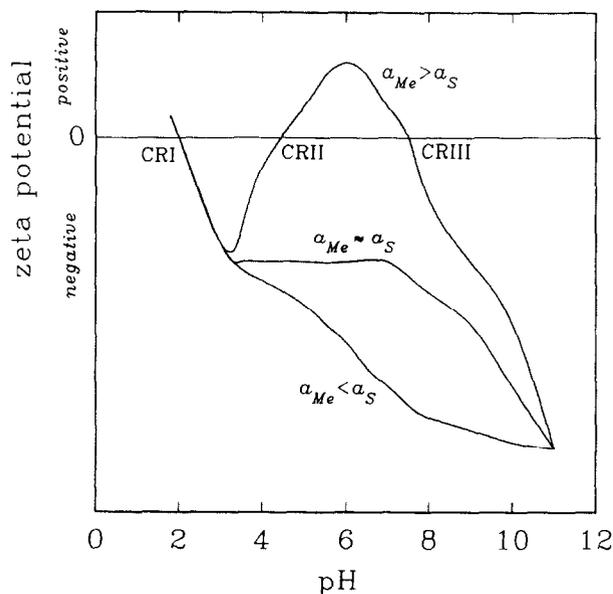


FIG. 1. Schematic diagram to show the zeta potential of metal sulfides as a function of pH, a_{Me} , and a_S . These hypothetical curves were constructed based on work by FORNASIERO et al. (1992), NICOLAU and MENARD (1992), WILLIAMS and LABIB (1985), and PUGH and TJUS (1987). Note that with $a_{Me} < a_S$ only one charge reversal is found at low pH. With increasing a_{Me} the zeta potential changes to a S-shaped curve with ultimately three charge reversal. See text for more details.

ficient, S-rich surface. The oxidation occurs even in experiments using deoxygenated solutions because in practice deoxygenation does not lead to a solution reduced enough to be in equilibrium with most metal sulfides (BUTLER et al., 1994; SATO, 1992). The important implication for the charge development on metal-sulfide surfaces is that oxidation will increase the activity of the metal ion. Most electrokinetic studies are conducted under conditions where the sulfide is the only source of S(-II) and Me in solution. The equilibrium S(-II) and Me activities are typically low because most metal sulfides have low solubilities. Therefore, it is likely that only a charge reversal at low pH will be observed if oxidation is limited (see Fig. 1). In contrast, if oxidation is significant, up to three charge reversals may be observed, or if the surface oxidation leads to an insoluble metal oxide only one charge reversal characteristic for the metal oxide will be observed. As pointed out by NICOLAU and MENARD (1992), PUGH and TJUS (1987), HEALY and MOIGNARD (1976), and FORNASIERO et al. (1992), many of the earlier electrokinetic studies on divalent metal sulfides were probably strongly affected by oxidation.

In this study, zeta potentials of synthetic greigite (Fe_3S_4) and pyrrhotite ($Fe_{1-x}S$) were determined using electrophoresis. Electrophoresis is a measurement of the mobility of colloidal particles in an applied electrical field. From the mobility measurement the potential at the shear plane, or zeta potential, is obtained. The shear plane separates a film of stationary fluid adjacent to the particle surface from the mobile solution further out (NEY, 1973; HIEMENZ, 1986). The location of the shear plane is probably within 20 to 30 Å from the actual surface (PARK and HUANG, 1987). It is generally accepted that specifically sorbed species are located within the shear plane, while all or most of the dissociated counter ions are located outside the shear plane (DAVIS and KENT, 1990; NEY, 1973; HIEMENZ, 1986). Therefore, the zeta potential is determined by the adsorption densities of PDI's and any specifically sorbed species that may be present. A reversal in zeta potential signifies a reversal in surface charge, i.e., an isoelectric point (PARKS, 1990; HIEMENZ, 1986; DAVIS and KENT, 1990). The majority of the measurements were made on suspensions in which the only source for S(-II) and Fe^{2+} was the iron sulfide itself. In addition, a few exploratory experiments were conducted to examine the influence of sulfidic sulfur (H_2S , HS^-) as well as the presence of trace amounts of humic acids on the zeta potential.

Greigite, one of the two Fe-S phases examined in this study, is a metastable iron monosulfide that is thought to form as a precursor of pyrite in marine sediments (BERNER, 1984; SCHOONEN and BARNES, 1991a,b; MORSE et al., 1987; SWEENEY and KAPLAN, 1973). It has also been found in anoxic lake sediments (SKINNER et al., 1964; HILTON, 1990; SNOWBALL, 1991) and coal seams (KRS et al., 1992). Pyrrhotite is either formed by precipitation from hydrothermal solutions (SCHOONEN and BARNES, 1991c), by crystallization from S-rich melts, and, rarely via diagenetic reactions in sediments (CLARK, 1970; REYNOLDS et al., 1990; VAN VELZEN et al., 1993). For this study, we used greigite and pyrrhotite synthesized using a new hydrothermal method with which colloidal-sized greigite and pyrrhotite can be reproducibly synthesized (SCHOONEN, 1989; SCHOONEN and BARNES, 1991c).

METHODS

Synthesis of Greigite and Pyrrhotite

Greigite and pyrrhotite were synthesized using a modified version of the high-temperature titration equipment described in previous work (see Fig. 1 in SCHOONEN and BARNES, 1991c). In short, a 0.1 M sodium sulfide solution is loaded into a 32-mL tubular, 316 stainless steel reaction vessel. The tubular reaction vessel replaces the high-temperature optical cell used in the titrator described in SCHOONEN and BARNES (1991c). The sodium sulfide solution was prepared by dissolving clear $Na_2S \cdot 9H_2O$ crystals (analytical grade, Baker). For the greigite synthesis a stoichiometric amount of pure elemental sulfur crystals is added ($S(0)/S(-II) = 1/3$). The S-containing sodium sulfide solutions were kept at temperatures in excess of 180°C for at least 2 h to allow the elemental sulfur to dissolve completely. The solution becomes yellow to red due to the formation of polysulfides. After 2 h at 180°C, the solution was cooled down to 140°C and about 6 mL of a 0.4 M Mohr's solution ($Fe(NH_4)_2(SO_4)_2$) was rapidly injected using a pump. The pyrrhotites used in this study were prepared without any elemental sulfur added. Therefore, the iron solution was injected as soon as the bomb reached the desired reaction temperature (245°C). After injection of ferrous iron, the mixture was kept at temperature for a minimum of 30 min to age the product. The products were quenched in less than 1 min, filtered over a 0.45 μ M membrane filter under nitrogen, and dried under a steady stream of nitrogen flowing from an inverted funnel. After drying under nitrogen, the run product was kept in a vacuum drying chamber for two days before storing the product in a desiccator with silica gel. The electrophoresis measurements were conducted within one month.

To minimize the amount of oxygen in the Na_2S and Mohr salt solution, all deionized water was boiled for at least 15 min and subsequently cooled in a polyethylene bottle. The water was always used within hours. Using this procedure, the dissolved oxygen concentration is less than 0.5 mg/L (BUTLER et al., 1994). The sulfide solution was kept in a stoppered glass flask and remains stable for at least one year. The Mohr's salt solution was prepared as described in SCHOONEN and BARNES (1991a) and stored in a kettle with H_2 gas slowly bubbling through the solution. The Mohr's salt solution is stable for at least 1 week. A few mL of 1 M HCl were added to the iron stock as tracer (see below).

The molar Fe/S ratio of the solution from which the iron sulfides were formed was determined by analyzing the chloride concentration (trace in the Fe solution) and sodium concentration (Na_2S solution). About 10 mL of the final solution was recovered as filtrate directly after quenching the bomb. Chloride and sodium were determined using standard Ion Chromatographic techniques (Dionex 2000i with AS4A-SC and CS10 columns). The greigite used in this study was formed from a solution with a Fe/S(-II) ratio of 0.60 and a S(0)/S(-II) ratio of 0.33 ($Fe/S_{tot} = 0.45$). The molar Fe/S(-II) ratio for the two pyrrhotites used in these electrophoresis experiments were 0.71 and 0.70, respectively.

The products were identified using X-ray diffractometry. Depending on the zerovalent sulfur content and the synthesis temperature either greigite or pyrrhotite is formed. For a S(0)/S(-II) ratio of 1/3 greigite is formed at 140°C, while at 180°C the product consisted of a mixture of pyrite and pyrrhotite. No effort was made to determine the upper temperature limit for greigite formation. In experiments without S(0) or with a S(0)/S(-II) ratio of 1/7 the synthesized pyr-

rhotite showed always a single X-ray reflection at about $44^\circ 2\theta$ using $\text{CuK}\alpha$ radiation. This may indicate that hexagonal pyrrhotite forms in hydrothermal synthesis, regardless of the S(0)/S(-II) ratio. Preliminary magnetic measurements on the same synthetic products (M. J. Dekkers and M. A. A. Schoonen, unpubl. data) suggest that an Fe-rich quenched-in lambda pyrrhotite formed (cf. SCHWARZ and VAUGHAN, 1972). The greigite particles are about 0.15 to 0.45 μm in size, while the pyrrhotite particles are 0.5 to 5 μm . These ranges in particle size are based on SEM observations of products made in this study and in earlier work using the same techniques (SCHOONEN, 1989). Addition of NaI as a mineralizer to increase the particle size (cf. HEIDER and BRYNDZIA, 1987) produced slightly sharper X-ray reflections for greigite (i.e., larger particles) but did not improve the pyrrhotite reflections. The synthesis of greigite has recently been repeated and the product analyzed with Mössbauer Spectroscopy at room temperature (I. B. Butler and M. A. A. Schoonen, unpubl. data). Given that no evidence can be found for any other Fe-S phase than greigite in the Mössbauer Spectrum or X-ray diffractogram, we estimate that the product is at least 95% pure greigite. The products of the pyrrhotite syntheses in earlier work using the same methods (SCHOONEN and BARNES, 1991c, their Table 1) as well as those in this study show no other phases in the X-ray diffractograms than pyrrhotite. No Mössbauer analysis was performed on the pyrrhotites. However, based on the X-ray diffractograms alone, we estimate a minimum purity of 95%.

Electrophoresis Measurements

The electrophoresis measurements were carried out with a Pen Kem Lazer Zee model 501 instrument in the laboratory of Dr. Talbot at the University of California at San Diego, California, USA. About 5 mg of the iron sulfides was suspended in 250 mL of a 5–10 μM NaCl solution. The pH of the suspension was subsequently raised to pH 11 by addition of NaOH (1 N). The electrophoretic mobility at pH 11 was determined after equilibrating the suspension for 15 min. Subsequent measurements at lower pH were made after addition of HCl and a 15 min equilibration period. The equilibration times were purposely held to 15 min to limit oxidation (see also HEALY and MOIGNARD, 1976). Furthermore, NaCl was used as indifferent electrolyte rather than nitrate or perchlorate salts (see NICOLAU and MENARD, 1992; JONES et al., 1992). The observed electrophoretic mobility, the average value of six determinations at each pH value, was converted to zeta potentials using the Smoluchowski equation (HIEMENZ, 1986; FUERSTENAU et al., 1985). The uncertainty in the zeta potentials is less than 3 mV; the uncertainty in the pH measurement is 0.2 pH units between pH 6 to 8, and 0.1 pH unit between 2 to 6 and 8 to 11. All measurements were conducted at 23°C. Because we used NaOH and HCl to adjust the pH of the suspension over a pH range from 11 down to 2, the ionic strength in these experiments varies from 10^{-3} to about $1.1 \cdot 10^{-2}$. The experiments with NaCl as indifferent electrolyte will hereafter be referred to as blank experiments.

In addition to the blank experiments, several experiments were conducted in which S(-II) was added to the solution, a few experiments were conducted to explore the effect of sorption of humic acids, and two experiments were conducted with seawater containing S(-II). The total humic acid concentrations (terrestrial origin; Fluka AG, Buchs SG) were typically around 50 μM in each experiment. Sulfate was removed from the seawater through precipitation with barium chloride. All synthetic solutions were prepared with 18 M Ω deionized water, and all solutions were purged for 30 min with nitrogen to remove dissolved oxygen. Purging with nitrogen for 30 min leads to a residual dissolved oxygen concentration of about 0.25 mg/L in deionized water (BUTLER et al., 1994). Unpublished results by I. B. Butler and M. A. A. Schoonen indicate that it is more difficult to remove oxygen from concentrated electrolyte solutions than from deionized water. Therefore, the residual oxygen content in the seawater may be somewhat higher than 0.25 mg/L.

As pointed out above, the charge development of the surface of a metal sulfide is a function of the activities of S(-II) and Fe^{2+} in solution. For the blank experiments, the only source of S(-II) and Fe^{2+} in solution is the iron sulfide itself. Because the iron sulfides studied here are relatively soluble metal sulfides and oxidation may take place,

we determined the iron and sulfidic sulfur concentrations in separate experiments designed to match the experimental conditions and equilibration periods employed in the electrophoresis experiments. The iron sulfides and suspensions were prepared using the same methods as described above. To resemble the conditions encountered during the electrophoresis experiments, the suspensions were kept at each pH for a minimum of 15 min before lowering the pH. After a 15 min equilibration period, a six mL aliquot was removed for Fe determination and filtered over a 0.45 μm membrane filter. The iron concentration was determined using a Beckman Spectrascan SSVB direct-current argon emission spectrometer (DCP-AES). After 15 min at pH 2, the final Fe sample was taken and then a 180 mL aliquot was taken for S(-II) determination and filtered over a 0.45 μm membrane filter. The sulfide concentration in this aliquot was determined using an iodometric titration (CLESCERI et al., 1989). In one set of experiments the a_{S} was determined at pH 6 (hence, experiment was terminated at pH 6). The detection limit for the Fe determination is 4 μM and the detection limit for the S(-II) determination is approximately 10 μM .

RESULTS

In the blank experiments for pyrrhotite and greigite only one charge reversal is observed at a pH between 2 and 3. In the blank experiments with pyrrhotite, the iron concentration is below 10 μM (i.e., $p\text{Fe} > 5.0$) over the entire pH range (2–10), while the S(-II) concentrations are always smaller than 40 μM (i.e., $p\text{S} > 4.5$). In the blank experiments with greigite, the iron concentration is <20 μM at pH >3, and 100 μM at pH 2. The S(-II) concentrations in the blank experiments with greigite are always lower than 40 μM . Greigite appears to dissolve somewhat faster than pyrrhotite in acidic solutions, but in both sets of experiments the iron and S(-II) concentrations are far lower than the equilibrium solubilities for these two Fe-S phases (see SCHOONEN and BARNES, 1991a, their Table 2). As explained above, the zeta potential is a function of pS and pFe, hence the curves reported here are only valid for the Fe^{2+} and S(-II) activities as constrained by the dissolution experiments.

There is a noticeable difference in the shape of the zeta potential curves for the two blank experiments on pyrrhotite (Fig. 2a). The experiment represented by the open circles has a plateau in its zeta potential curve between pH 4 and 8, whereas the other blank experiment (solid circles) shows a steady decrease in zeta potential over this pH range. This difference may be due to a slightly higher activity of ferrous iron in the experiment represented by the open circles (see Fig. 1). The higher a_{Fe} may be caused by slight oxidation of the pyrrhotite in this experiment. The shape of the zeta potential curve for a natural pyrrhotite reported by NEY (1973) exhibits a plateau in the zeta potential curve between 4 and 10 (see Fig. 4). The report by NEY (1973) presents no detail on the methods or composition of the solution. It is possible that the broad plateau is caused by oxidation of the pyrrhotite. Note, however, that the isoelectric point reported by NEY (1973) is in good agreement with that for the two blank experiments.

The results in the presence of sulfidic sulfur (1.1 mM) with NaCl as indifferent electrolyte shows an increase in negative zeta potential over almost the entire pH range, no charge reversal is observed, and the zeta potential becomes nearly pH independent above pH 5. Relative to the experiments in the absence of sulfidic sulfur, the increase in negative zeta potential is more pronounced for greigite than for pyrrhotite.

In the experiments with seawater containing S(-II), the effect of the sulfidic sulfur appears to be insignificant (Figs. 2c, 3c). The comparison between the experiments with S(-II)-containing seawater and the blank experiments is incomplete because the experiments with seawater could only be carried out between pH 3.5 and 8.5. (It is not possible to make measurements at the ionic strength of seawater (≈ 0.7 M) outside

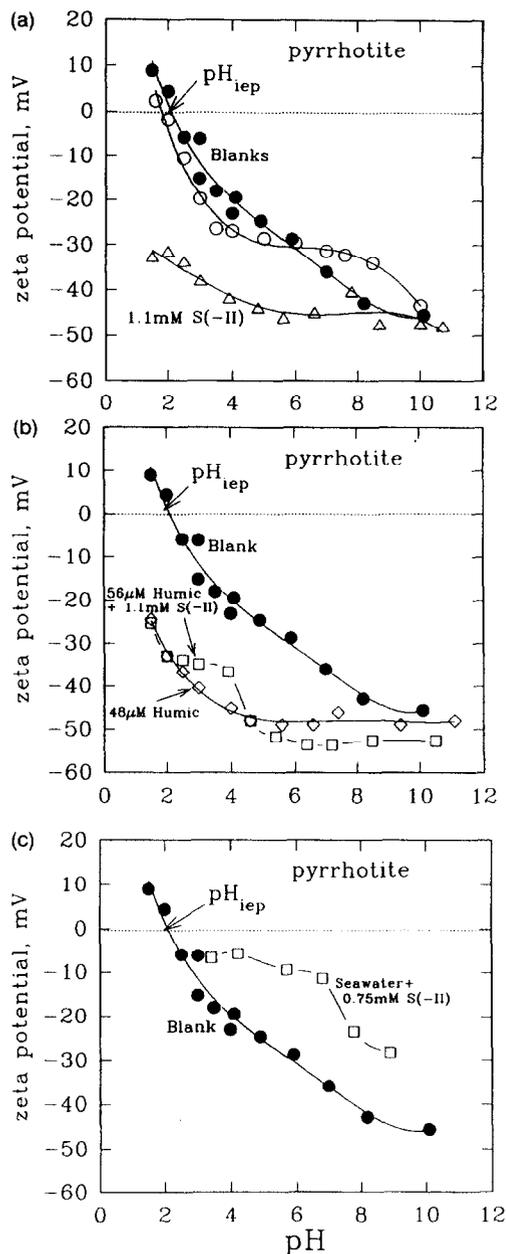


FIG. 2. Zeta potential (mV) of synthetic pyrrhotite as a function of pH and solution composition: (a) solid circles are measurements on a suspension of synthetic pyrrhotite (synthesis at 245°C) in 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl (blank), open circles for synthetic pyrrhotite (240°C) in 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl (blank), open triangles for synthetic pyrrhotite (245°C) in 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl and 1.1 mM S(-II); (b) diamonds for synthetic pyrrhotite (245°C) in 48 μ M terrestrial humic acid and 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl, squares for synthetic pyrrhotite (245°C) in 56 μ M terrestrial humic acid, 1.1 mM S(-II), and in 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl; (c) squares for synthetic pyrrhotite (245°C) in sulfate-free real seawater and 0.75 mM S(-II).

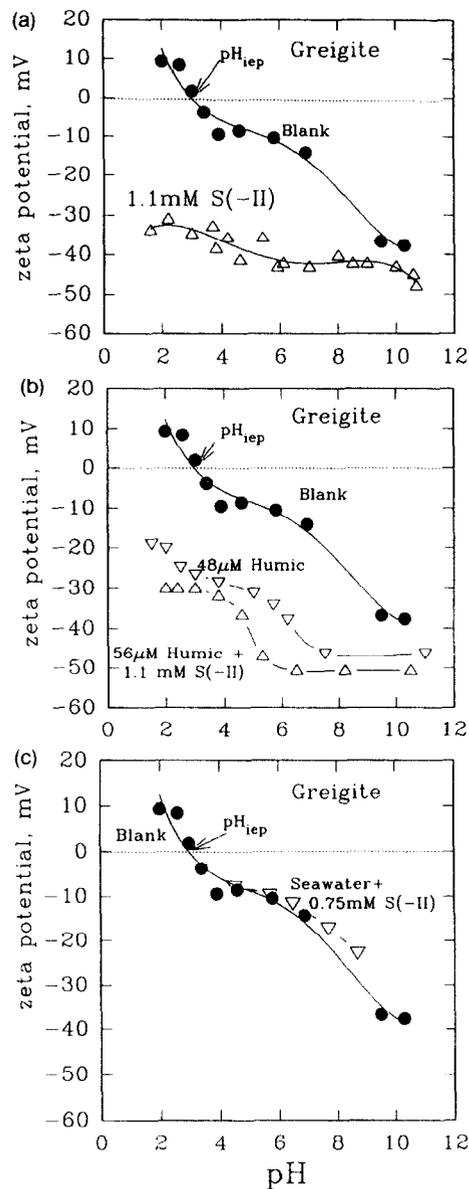


FIG. 3. Zeta potential (mV) for synthetic greigite as a function of pH and solution composition: (a) solid circles for synthetic greigite in 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl (blank), triangles for same material in 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl (blank) and 1.1 mM S(-II); (b) inverted triangles for synthetic greigite in 48 μ M terrestrial humic acid and 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl, triangles for synthetic greigite in 56 μ M terrestrial humic acid, 1.1 mM S(-II), and 10^{-3} – $1.1 \cdot 10^{-2}$ M NaCl; (c) inverted triangles for greigite in real, sulfate-free seawater and 0.75 mM S(-II).

this pH range). It is clear, however, that a large increase in net zeta potential due the presence of S(-II) is not observed in seawater.

Trace amounts of humic acid have also a considerable effect on the zeta potentials. In the presence of humic acid, the zeta potential becomes more negative over the entire pH range and no charge reversals are observed (Figs. 2b, 3b). In the presence of both humic acid and sulfidic sulfur, the zeta potential becomes as negative as in the experiments with either sulfidic sulfur or humic acid added, but in addition a sharp inflection is observed around pH 4.5 (Figs. 2b, 3b).

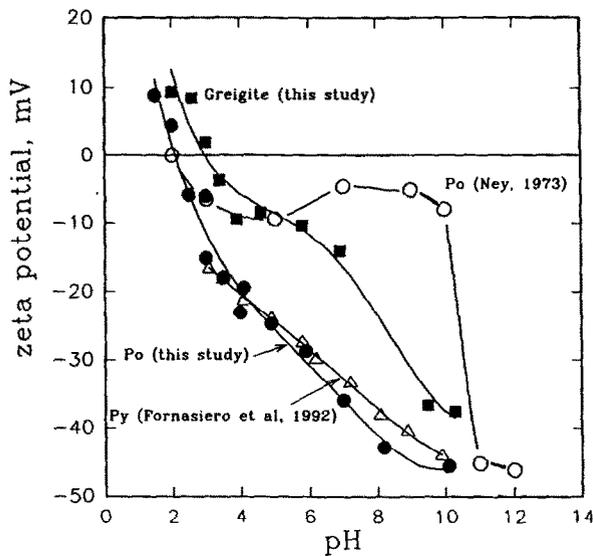


FIG. 4. Comparison of electrokinetic data for pyrite (py), pyrrhotite (po), and greigite. Note that FORNASIERO et al. (1992) report an isoelectric point for pyrite at pH 1.8, but their figures show only data down to pH 3. The ionic strength used in the electrophoresis determinations of pyrite by FORNASIERO et al. (1992) ranged from 0.005 M to 0.007 M. No details are available on the conditions of the electrophoresis measurement on pyrrhotite by NEY (1973).

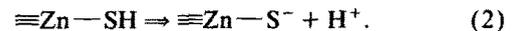
DISCUSSION

The study presented here represents the first electrokinetic study on greigite and the first well-documented study on pyrrhotite. Although limited in that it does not represent a systematic study of the zeta potential as a function of a_{Fe} and a_{S} , this study offers some important insights and the results may be compared to earlier work on pyrite (FORNASIERO et al., 1992) and other metal sulfides.

The most important result of this study is that for both iron sulfides a charge reversal is observed between pH 2 and 3.0 in experiments without added S(-II) or humic acid (i.e., blank experiments in Figs. 1 and 2). The isoelectric points observed in the blank experiments are in the same pH range as those reported for natural pyrite (FORNASIERO et al., 1992) and natural pyrrhotite (NEY, 1973), see Table 1. Furthermore, the isoelectric points in the blank experiments are in the same pH range as for many other metal monosulfides at low S(-II) activity and Me^{2+} activity, as well as elemental sulfur at low S(-II) activity (see Table 1). In comparing our results to those for other metal monosulfides, only those experiments were selected that carefully excluded oxygen or used short equilibration periods. Moreover, only those experiments were included in which the metal sulfide was the only source of dissolved sulfidic sulfur and ferrous iron (the experiment by NEY, 1973, on pyrrhotite is also included although it is unknown whether the pyrrhotite is the only source of S(-II) and Fe^{2+}). It is interesting that the identity of the metal ion appears to have little or no effect on the isoelectric point, which is radically different from the observations in metal oxide and hydroxide systems (PARKS, 1965). It is very well possible that in all these experiments, the surfaces are dominated by thiol groups (and perhaps polysulfide groups;

see JONES et al., 1992) so that the metal hydroxide groups play no significant role.

The interaction mechanism between dissolved sulfidic sulfur species (H_2S and HS^-) and the iron sulfide surface is unclear. Although examined at only one sulfidic sulfur concentration with NaCl as indifferent electrolyte, the strong effect of the addition of sulfidic sulfur on the zeta potential indicates that sulfidic sulfur is sorbed within the shear plane of the double layer. The magnitude of the increase in net zeta potential is largest below pH 7. This may be related to the sulfidic sulfur speciation. In alkaline solutions (pH > 7) where nearly all S(-II) is present as HS^- and the surface is negatively charged, Coulombic repulsion may limit the interaction between S(-II) and the surface. In addition, in alkaline solutions there may be competition between HS^- and OH^- . Below pH 7, the sulfidic sulfur is nearly all present as uncharged H_2S and the Coulombic repulsion vanishes. NICOLAU and MENARD (1992) also showed a very strong increase in negative zeta potential as a function of a_{S} . However, in contrast to our study, NICOLAU and MENARD (1992) found that the isoelectric point is not affected by the addition of $(\text{NH}_4)_2\text{S}$; hence, in all their experiments with $(\text{NH}_4)_2\text{S}$ a charge reversal was observed around pH 2. They explained the strong interaction between the S(-II) and the ZnS surface by the sulfidation of $\equiv\text{Zn}-\text{OH}$ surface groups:



In essence, a neutral $\equiv\text{Zn}-\text{OH}$ group replaces a negatively charged $\equiv\text{Zn}-\text{S}^-$ group. The fact that the isoelectric point for ZnS is not affected by the sulfidation of the $\equiv\text{Zn}-\text{OH}$ groups suggests that the newly formed $\equiv\text{Zn}-\text{SH}$ behaves identically to the $\equiv\text{S}-\text{H}$ groups. It is possible that a similar sulfidation of $\equiv\text{Fe}-\text{OH}$ groups occurs on the iron sulfide surface; however, we cannot explain why we observe no charge reversal in our experiments. This implies either that the newly formed $\equiv\text{Fe}-\text{SH}$ groups are not equivalent to the $\equiv\text{S}-\text{H}$ groups or that the interaction between S(-II) and the surface follows an entirely different mechanism. For

Table 1. Summary of isoelectric points determined for metal sulfides.

Solid	Origin of Solid	pH _{Iep} ¹	Method ²	Source
Greigite	synthetic	3.0-3.5	E	This Study
Pyrrhotite	synthetic	2.0-2.5	E	This Study
Pyrrhotite	Habachtal, Germany	2	E	Ney (1973)
Pyrite	Huanzala, Peru	0.8-1.6	E	Fornasiero et al. (1992)
Chalcopyrite	Quebec	2.2	E	Kelebek and Smith (1989)
NiS	synthetic	2.5-3.0	E	Healy and Moignard (1976)
Galena	Kansas	2.2	E	Kelebek and Smith (1989)
Galena	unknown	2.6	E	Fuerstenau et al. (1985)
Sphalerite	Sweden	3.0	E	Pugh and Tjus (1987)
Zn _{0.95} Cd _{0.05} S	synthetic	2-3	E	Williams and Labib (1985)
ZnS	synthetic	3-3.5	E	Williams and Labib (1985)
CuS	synthetic	3.0	F	Hukki et al. (1952)
Sulfur	synthetic	<2.6-3.1	F	Schoonen and Barnes (1988)
Sulfur	synthetic	<3	E	Chander et al. (1975)
Sulfur	synthetic	2.2	E	Kelebek and Smith (1989)

1: pH_{Iep} = pH at which isoelectric point occurs. Only those results were selected in which the metal sulfide is the only source for a_{Me} and a_{S} . Results were only taken from studies in which oxidation was suppressed and no other specific-sorbing species are present.

2: E = electrophoresis; F = estimated from flocculation rates

example, it is possible that the sulfidic sulfur interacts with polysulfide surface groups formed as a result of partial oxidation of the surface (JONES et al., 1992). In contrast to the blank experiments, the experiments with S(-II)-containing seawater indicate that there is no significant interaction between S(-II) and the iron sulfide surface in seawater. This may be a result of sorption of other aqueous species. For example, Ca^{2+} is known to be specifically sorbed onto pyrite (GAUDIN and CHARLES, 1953). The plateau in the experiment with pyrrhotite may be the result of specific sorption of a species such as Ca^{2+} or it may be the result of slight oxidation.

The limited electrokinetic data on the interaction between humic acids and iron sulfides presented here indicate that humic acids are specifically sorbed onto iron sulfide (see Figs. 2b and 3b). Organic macromolecules, such as the humic acids used in this study, are common in natural low-temperature aqueous systems; therefore, the interaction between organic macromolecules and iron sulfides is of great geochemical importance. For example, it is likely that in reduced marine sediments the surfaces of metal sulfides are negatively charged due to sorption of organic macromolecules (and S(-II)).

CONCLUSIONS

The isoelectric point for the two iron sulfides studied here, greigite and pyrrhotite, in solutions with low a_{Fe} and a_{S} are around pH 2 to 3. This pH range is characteristic for the isoelectric points of most divalent metal sulfides at low a_{Me} and a_{S} . This suggests that at low a_{Me} and a_{S} , the surface of metal sulfides is dominated by one and the same surface group. Surface-spectroscopic studies and electrochemical studies indicate that divalent metal sulfide surfaces readily form a metal-deficient (sulfur-rich) layer when in contact with an aqueous solution. Therefore, it is likely that at low a_{Me} and a_{S} , thiol groups dominate the surfaces of divalent metal sulfides. However, as a_{Me} increases, often as a result of oxidation, the metal-sulfide surface will become dominated by metal hydroxide functional groups. At high a_{Me} and low a_{S} , the surface may show as much as three charge reversals (see Fig. 1). Hence, the surface charge may be periodically reversed as the redox state of the system changes in environments where the redox conditions and a_{Me} and a_{S} fluctuate (e.g., in tidal flats). This may have an important effect on the sorption of aqueous species onto iron sulfides in sediments.

In the presence of bisulfide, hydrogen sulfide, and/or humic acids, the zeta potentials of the iron sulfides are negative over the entire pH range measured (2–11). This implies that in organic-rich, reducing environments, such as marine sediments, anoxic lake sediments, and landfills, the iron-sulfides are likely to be negatively charged.

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