AMMONIA FORMATION BY THE REDUCTION OF NITRITE/NITRATE BY FeS: AMMONIA FORMATION UNDER ACIDIC CONDITIONS

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Abstract. One issue for the origin of life under a non-reducing atmosphere is the availability of the reduced nitrogen necessary for amino acids, nucleic acids, etc. One possible source of this nitrogen is the formation of ammonia from the reduction of nitrates and nitrites produced by the shock heating of the atmosphere and subsequent chemistry. Ferrous ions will reduce these species to ammonium, but not under acidic conditions. We wish to report results on the reduction of nitrite and nitrate by another source of iron (II), ferrous sulfide, FeS. FeS reduces nitrite to ammonia at lower pHs than the corresponding reduction by aqueous Fe^{+2}. The reduction follows a first order decay, in nitrite concentration, with a half-life of about 150 min (room temperature, CO_2, pH 6.25). The highest product yield of ammonia measured was 53%. Under CO_2, the product yield decreases from pH 5.0 to pH 6.9. The increasing concentration of bicarbonate, at higher pH, interferes with the reaction. Comparing experiments under N_2 and CO_2 shows the interference of bicarbonate. The reaction proceeds well in the presence of such species as chloride, sulfate, and phosphate, though the yield drops significantly with phosphate. FeS also reduces nitrate and, unlike with Fe^{+2}, the reduction shows more reproducibility. Again, the product yield decreases with increasing pH, from 7% at pH 4.7 to 0% at pH 6.9. It appears that nitrate is much more sensitive to the presence of added species, perhaps not competing as well for binding sites on the FeS surface. This may be the cause of the lack of reproducibility of nitrate reduction by Fe^{+2} (which also can be sensitive to binding by certain species).

Keywords: ammonia, ammonium, aqueous, iron (II), iron sulfide FeS, nitrate, nitrite, nitrogen fixation, non-reducing atmosphere, prebiotic synthesis, reduction

1. Introduction

The origin of life requires the availability of reduced nitrogen for the formation of species such as amino and nucleic acids. In a strongly reducing atmosphere (CH_4, NH_3), compounds essential to the chemical evolution of life, such as amino acids, can be formed by reactions between HCN, NH_3, and carbonyl compounds produced in spark discharges, as well as by other Miller-Urey processes (Chang *et al.,* 1983; Stribling and Miller, 1987). It has also been shown experimentally that organics can be produced by mildly reducing atmospheres of CO and CO_2 (Löb, 1906, 1914).

However, current geochemical evidence points to a non-reducing atmosphere made primarily of carbon dioxide, nitrogen and water (Chang *et al.*, 1983; Holland, 1984; Mattioli and Wood, 1986; Walker, 1986; Kasting, 1987; Gregor *et al.*, 1988;

Wood and Vigo, 1989; Delano, 2001). The presence of ammonia, or other forms of reduced nitrogen, on the early Earth, or other planets with a carbon dioxide/nitrogen atmosphere, is problematic. In such an atmosphere electric discharges produced NO and CO (Yung and McElroy, 1979; Chameides and Walker, 1981; Fegley Jr. *et al.*, 1986; Kasting, 1990). How can reduced nitrogen be formed under a neutral atmosphere, and what conditions are needed for such formation to occur?

One possibility is the conversion of NO into nitric and nitrous acids (through HNO) which is then rained into the oceans (Mancinelli and McKay, 1988). The reduction of nitrite by aqueous Fe^{+2}, such as was likely to have been present on the early Earth (Holland, 1973, 1984; Walker *et al.*, 1983; Walker and Brimblecombe, 1985; Perry and Jacobsen, 1990), could then have produced ammonia (Summers and Chang, 1993).

$$6Fe^{+2} + 7H^+ + NO_2^- \rightarrow 6Fe(III) + 2H_2O + NH_3 \qquad (1)$$
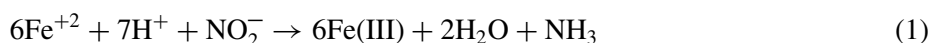
However, this reaction does not proceed at a pH less than 7.3. The pH of the early ocean is uncertain. The presence of carbon dioxide in the early atmosphere (Walker, 1977, 1986; Holland *et al.*, 1986; Kasting and Ackerman, 1986; Kasting, 1987, 1993; Gregor *et al.*, 1988) makes an acidic ocean a significant possibility.

This paper reports results on the reduction of nitrite and nitrate by another source of iron (II), FeS. It is expected that hydrothermal systems would be releasing large amounts of aqueous Fe^{+2} and H_2S. Some of the Fe^{+2} would be precipitated, by the S^{-2}, as iron sulfides (Holland, 1973; Drever, 1974; Veizer, 1978; Walker and Brimblecombe, 1985). Tectonic and/or volcanic activity was much higher on the early Earth than now (Windley, 1976; Turcotte, 1980). Additionally, if continental masses were smaller or nonexistent (Windley, 1976; Turcotte, 1980), a greater proportion of this activity would be in marine environments. Also, the geological context of the first compelling evidence of life may have been dominated by island volcanism and hydrothermal activity in a shallow marine environment (Barley *et al.*, 1979; Groves *et al.*, 1981). This indicates that iron sulfide particles suspended in water, or deposited in shallow or tidal sands, may have been relatively common on the early Earth. In fact, hydrothermal vents today discharge iron sulfides ranging from pyrrhotite to pyrite (Hannington *et al.*, 1995).

2. Results and Discussion

Since the early Earth is likely to have had a carbon dioxide rich atmosphere (Chang *et al.*, 1983; Holland, 1984; Mattioli and Wood, 1986; Walker, 1986; Kasting, 1987; Gregor *et al.*, 1988; Wood and Vigo, 1989), experiments were run under carbon dioxide (except when nitrogen was used as a control) at suitable pHs. Unlike Fe^{+2}, which precipitates as $Fe(CO_3)$ in the presence of bicarbonate, FeS is a solid and can't be precipitated as $Fe(CO_3)$. The total amount of ammonia produced

is used to calculate the percentage of the nitrite or nitrate that was converted to ammonia (the product yield). No visible change in the suspension was observed during the course of the reaction, though the solution, after filtering, would change from colorless to yellowish.

2.1. REDUCTION OF NITRITE

Shown in Figure 1 is a plot of the formation of ammonium versus time when nitrite is added to a suspension of FeS under both carbon dioxide and nitrogen. The reduction of nitrite to ammonia proceeds well in both cases. Both reactions were run at a pH of $\sim$6. Reduction of nitrite to ammonia by Fe^{+2} doesn't proceed in solutions which are acidic. This extends nitrite reduction to lower pHs than has been previously observed. The fact that the reaction proceeds at pHs where aqueous Fe^{+2} doesn't produce ammonia, and the low solubility of FeS, argues that the actual reduction takes place at the FeS surface and not via Fe^{+2} in solution. FeS also shows much more reactivity than $FeCO_3$ (which may react primarily through Fe^{+2} in solution, Summers and Chang, 1993).

Figure 2 displays a plot of ln $[NO_2^-]$ versus time. The data show a first-order rate dependence on nitrite concentration and a half-life for nitrite of 82 min. A plot of $[NO_2^-]$, or $1/[NO_2^-]$, versus time shows a poorer fit to a straight line ($r^2 = 0.955$
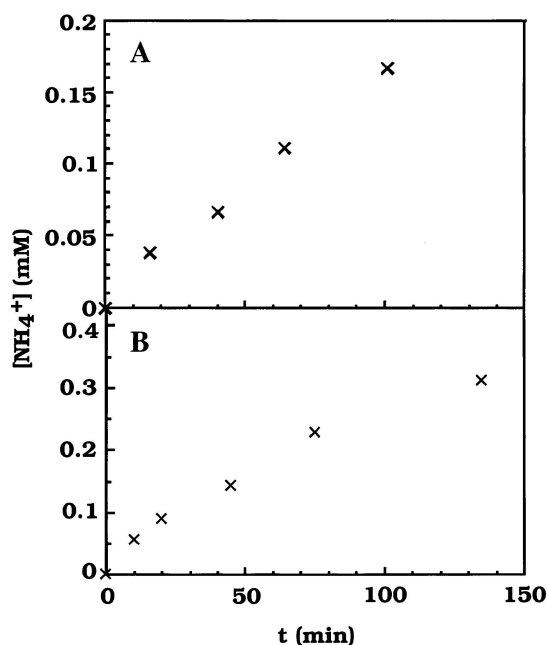

Figure 1. Plot of NH_4^+ concentration versus time in the reduction of NO_2^- by FeS under (A) N_2 (pH 5.5–6.5) and (B) CO_2 (pH 6.3). Final concentrations were (A) 0.28 mM and (B) 0.57 mM.
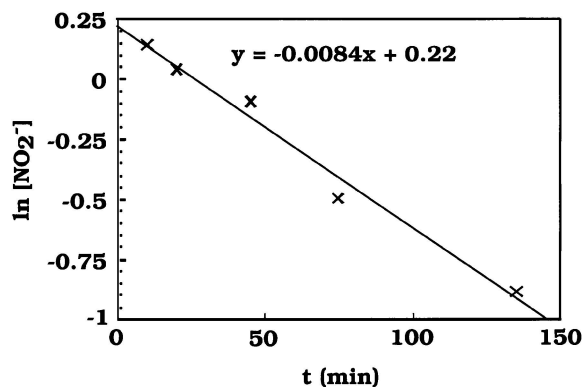
Figure 2. Plot of ln concentration versus time during reduction of NO_2^- by FeS under carbon dioxide (pH 6.3).

or 0.969 versus 0.982) and curvature. This matches the reduction of nitrite by Fe^{+2} which has been previously shown to be first order in nitrite (Summers and Chang, 1993). The slope gives a pseudo first-order rate constant of 0.0084 min^{-1}. On the basis of the weight of FeS, this would give $k = 8.9 \times 10^{-4}$ L g^{-1} min^{-1}. The product yield in this experiment was 27%.

In preparation of the suspensions, it was found that the pH would sometimes rise as an unbuffered suspension was stirred. This was presumably due to the mechanical stirring which broke up particles, exposed fresh surfaces, and increased the surface area. This pH change is much slower, and in the opposite direction, compared with the change that occurs during the course of reduction of nitrite/nitrate (Summers and Chang, 1993). A pH drop would have occurred during reactions if the solutions were not buffered by bicarbonate/phosphate or controlled by the addition of base.

In all the experiments, no correlation was seen between product yields and the amount of FeS added to the reactions.

2.2. Effects of pH variation on nitrite reduction

In order to determine how pH affects the reaction, the reduction of nitrite by FeS was run, under CO_2, from pH 4.9 to 7.2. Figure 3a and Table I show how the product yield varies with pH between pH 4.9 and 6.9. There is a smooth decrease from 53% at pH 4.9 to 18% at pH 6.9. The yield changed faster with pH under more acidic conditions. Ammonia was produced over the entire pH range.

According to the half-cell for nitrite reduction, Equation (2), the reaction should be favored by lower pH.

$$8H^+ + NO_2^- + 6e^- \rightarrow 2H_2O + NH_4^+ \tag{2}$$

TABLE I

NH_4^+ yield versus pH for the reduction of NO_2^- by FeS[a]

pH	$[NH_4^+]$ (mM)	% Yield[b]	FeS (mg/mL)
4.9	1.33	53	14
5.4	0.94	38	12
6.1	0.52	21	6.8
6.3	0.50	20	9.5
6.9	0.44	18	8.4

[a] Also Room Temperature, 2.0 mM $NaNO_2$, 9.4 mg/mL FeS, under 1 atm CO_2. Reactions ran 24 h.
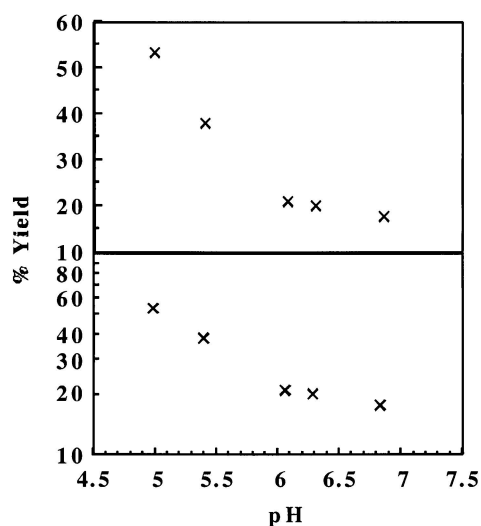[b] Based on starting amount of nitrite.

Figure 3. (A) Plot of NH_4^+ yield versus pH and (B) log plot of NH_4^+ yield versus pH for the reduction of NO_2^- by FeS under 1 atm carbon dioxide.

However, the data doesn't show the dependence on pH that this equation would lead one to expect (a plot of log yield versus pH shows curvature, as shown in Figure 3b). At higher pH, in a CO_2 saturated solution, more bicarbonate will be present. Bicarbonate does affect the yield (as described below). It is likely that the decrease in yield with pH is at least partially due to bicarbonate competition for reactive sites on the surface of FeS.

2.3. EFFECTS OF OTHER SPECIES ON NITRITE REDUCTION

As mentioned above, "spectator" species can have an effect on the reaction. This was seen in the reduction of nitrite by Fe^{+2} (Summers and Chang, 1993). The ocean

TABLE II

NH_4^+ yield under different conditions for the reduction of NO_2^- by FeS^a

Added Species	Atmosphere[b]	$[NH_4^+]$ (mM)	% Yield[c]	FeS (mg/mL)
none	CO_2	0.78	31	11
Cl^-	CO_2	0.61	24	12
SO_4^{-2}	CO_2	0.67	27	11
$H_2PO_4^-$	CO_2	0.278	11	9.6
$H_2PO_4^-$	N_2	0.50	20	12

[a]Also room temperature, 2.0 mM NaNO2, at pH 6.1. Reactions ran 24 h. $Cl^- = 0.1$ M KCl, $SO_4^{-2} = 24$ mM K_2SO_4, $H_2PO_4^- = 25$ mM $KH_2PO_4 + K_2HPO_4$.
[b]At 1 atm pressure.
[c]Based on starting amount of nitrite.

today contains large amounts of sodium chloride as well as smaller amounts of other salts. The effects of the presence of other species that may have been present in the early ocean and may have a deleterious effect on the reaction were evaluated. How these species can affect the yield of ammonia is described in Table II. There is a small, but noticeable effect when Cl^-, SO_4^{-2} are added to the reaction (compare lines 2 and 3 of the data in Table II with line 1). Presumably these species compete for Fe reaction sites on the surface of the FeS particles. The addition of HPO_4^{-2} (compare line 4 of the table with line 1) has a larger effect on ammonia production, probably because the phosphate ion can bind to the iron better and compete more effectively.

Running the reactions under CO_2 or N_2 also has an effect on ammonia formation. Reactions performed under CO_2 with a phosphate buffer produced lower yields (compare line 5 of the table with line 4) compared with those under N_2 with a phosphate buffer. This is likely due to the presence of bicarbonate and is consistent with the decrease in yield with pH (as described above).

2.4. EFFECTS OF pH ON NITRATE REDUCTION

Nitrate reduction is observed with Fe^{+2}, but the reaction is not reproducible. For example, the reaction will sometimes produce ammonia with a product yield as high as 95% and, when the reaction is run again, produce no detectable ammonia at all. FeS also reduces nitrate but, unlike Fe^{+2}, the reduction is reproducible. The reaction was run, under CO_2, from pH 4.7 to 6.9. Figure 4 and Table III show how the product yield varies with pH. As with nitrite, there is a smooth decrease in the product yield with pH. The yield is 6.7% at pH 4.7 and drops all the way to 0% at pH 6.9 (the level of ammonia produced, if any, was below the detection limit of the ion chromatograph). As with nitrite, the reaction should be favored by lower pH

TABLE III

NH_4^+ yield versus pH for the reduction of NO_3^- by FeS[a]

pH	$[NH_4^+]$ (mM)	% Yield[b]	FeS (mg/mL)
4.7	0.17	6.7	7.2
5.3	0.13	5.3	6.4
6.0	0.061	2.4	4.8
6.9	0	0	8.4

[a]Also room temperature, 2.0 mM $NaNO_3$, under 1 atm CO_2.
Reactions ran 24 h.
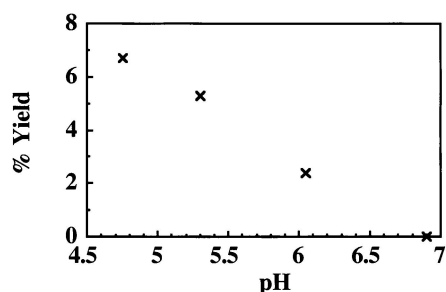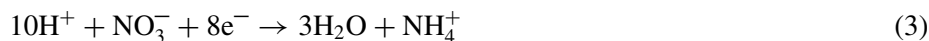[b]Based on starting amount of nitrate.

Figure 4. Plot of NH_4^+ yield versus pH for the reduction of NO_3^- by FeS under 1 atm carbon dioxide.

(Equation (3)), but doesn't show the dependence on pH one would expect.

$$10H^+ + NO_3^- + 8e^- \rightarrow 3H_2O + NH_4^+ \tag{3}$$

Here also, the drop in yield is probably due to the presence of increasing bicarbonate concentrations. However, the reduction of nitrate seems to be more sensitive to competing species than nitrite (also, see below). This may explain why the yield drops all the way to zero.

2.5. EFFECTS OF OTHER SPECIES ON NITRATE REDUCTION

The reduction of nitrate is much more sensitive to the presence of added species. Ammonia is produced under a carbon dioxide atmosphere and, hence, produced in the presence of bicarbonate (Table IV, see line 1 of the data). However, no ammonia was produced in the presence of chloride, sulfate, and phosphate under CO_2 or in a phosphate buffer under N_2 (Table IV, see lines 2–5 of the data). It appears that nitrate is much more sensitive to the presence of added species. Perhaps nitrate doesn't bind as well to Fe centers on the FeS surface as nitrite and is not able to compete as well with other ions. This may be why the yields seen from nitrate reduction are lower than those seen from nitrite reduction (nitrate is more easily displaced from the surface by bicarbonate). The lack of reproducibility of nitrate reduction

TABLE IV

NH_4^+ yield under different conditions for the reduction of NO_3^- by FeS^a

Added Species	Atmosphere	$[NH_4^+]$ (mM)	% Yield[b]	FeS (mg/mL)
none	CO_2	0.13	5.1	8.4
Cl^-	CO_2	0	0	5.2
SO_4^{-2}	CO_2	0	0	5.2
$H_2PO_4^-$	CO_2	0	0	8.0
$H_2PO_4^-$	N_2	0	0	5.6

[a]Also room temperature, 2.0 mM $NaNO_3$, under 1 atm CO_2, at pH 6.1. Reactions ran 24 h. $Cl^- = 0.1$ M KCl, $SO_4^{-2} = 24$ mM K_2SO_4, $H_2PO_4^- = 25$ mM $KH_2PO_4 + K_2HPO_4$.
[b]Based on starting amount of nitrate.

by Fe^{+2} (which also can be sensitive to binding by certain species, Summers and Chang, 1993) might also be a related phenomenon.

2.6. PRODUCTS OF IRON OXIDATION

This raises the question of, if nitrite and nitrate are reduced, what is the oxidation product? What is the iron oxidized to? To test this, 0.41 g of FeS (4.67 mmoles) was exposed, at pH 6.0 under CO_2, to 25 mL of a 25 mM NO_2^- (0.625 mmoles). Not all of the FeS is available for reaction (some of it is buried in the interior of the particles). Around 0.21 mmoles of the nitrite was able to react with the FeS, enough to react with 7–14% of the Fe(II). The product yield of ammonia was 11%.

Figure 5 shows a SEM/EDX analysis at 20 kV of the surface of the FeS after reaction. Only a trace of oxygen is seen on the surface. Furthermore, what little oxygen that was seen was matched by a carbon peak, indicating that most of the oxygen seen may be due to the presence of a trace of carbonate on the surface. Shown in Figure 6, another spectrum was run at 3.5 kV. At this energy, the beam doesn't penetrate as far into the sample ($\sim$0.25 versus 1–3 μm). Again, oxygen can be attributed to adsorbed carbonate.

An analysis at 20 kV of the surface of FeS after exposure to just water, buffered at the same pH, is shown in Figure 7 and is similar to the spectrum in Figure 5. While the comparison of peak intensities of the spectrum taken of irregular surfaces can be hazardous, these samples showed a lower S/Fe ratio, but still didn't show a large amount of oxide. Shown in Figure 8 is a spectrum, at 3.5 kV, of the FeS exposed to just water. There is a larger oxygen/sulfur peak compared with both the Fe and S peaks. The carbon peak is also larger, though this (and the other relative peak sizes) is somewhat more variable from particle to particle. (The density of particles is high enough that the carbon tape underneath is not in the field of view of the instrument and similar spectra are obtained when the electron beam is focused onto
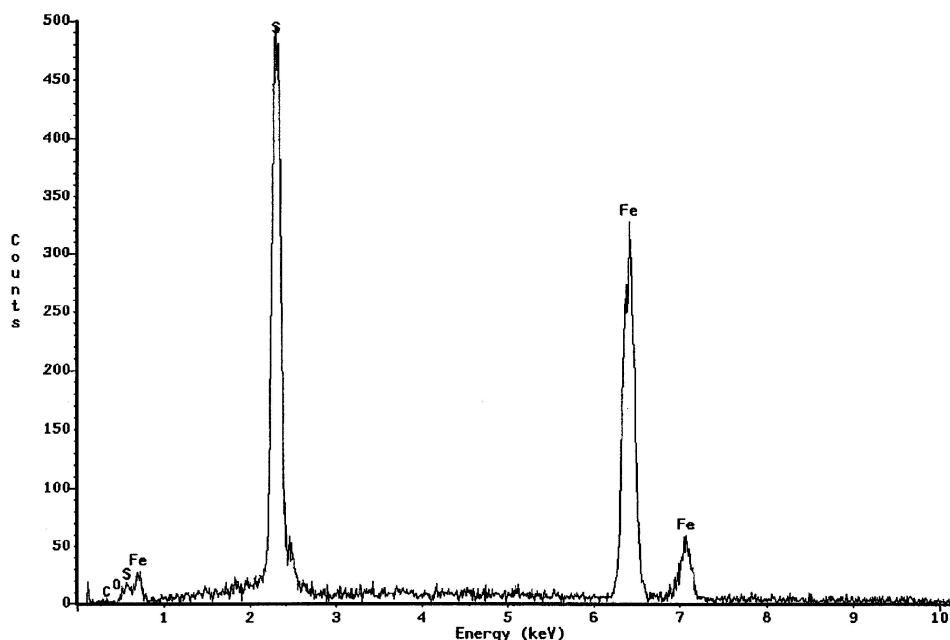
Figure 5. EDX analysis, at 20 kV, of the surface of a FeS particle after reaction with a nitrite solution.

the surface of a single particle). It may be that, for some unknown reason, more carbonate evaporates onto the surface or it may be that a thinner (compared with the changes in sulfide composition seen in the 20 kV spectra) layer of oxide forms on the surface under these conditions (this is particularly consistent with the much smaller sulfur peak).

Thus, the 20 kV spectra are consistent with the view that exposure to nitrite changes the bulk of the surface to an iron sulfide that is more sulfur-rich than exposure without the oxidizing nitrite. The 3.5 kV spectra show that exposure to water probably forms a thin oxide layer (consistent with the passivation one sees with old samples of FeS). The reaction of the surface with nitrite prevents the formation of this oxide layer by forming a relatively oxidized iron sulfide layer. If pyrite, FeS_2, was being formed, it would be less likely to form an oxide layer upon exposure to water.

Thus, the reaction would seem to be

$$2FeS \rightarrow FeS_2 + Fe^{+3} + 3e^- \tag{4}$$

The Fe(III) gains waters of aquation and is converted to Fe_2O_3. In fact, Fe_2O_3 precipitate can be seen suspended above the FeS after it settles out and the supernatant has a decidedly yellow color. A small amount of sulfate was found in solution, but not enough to account for the nitrite reduction. The amount
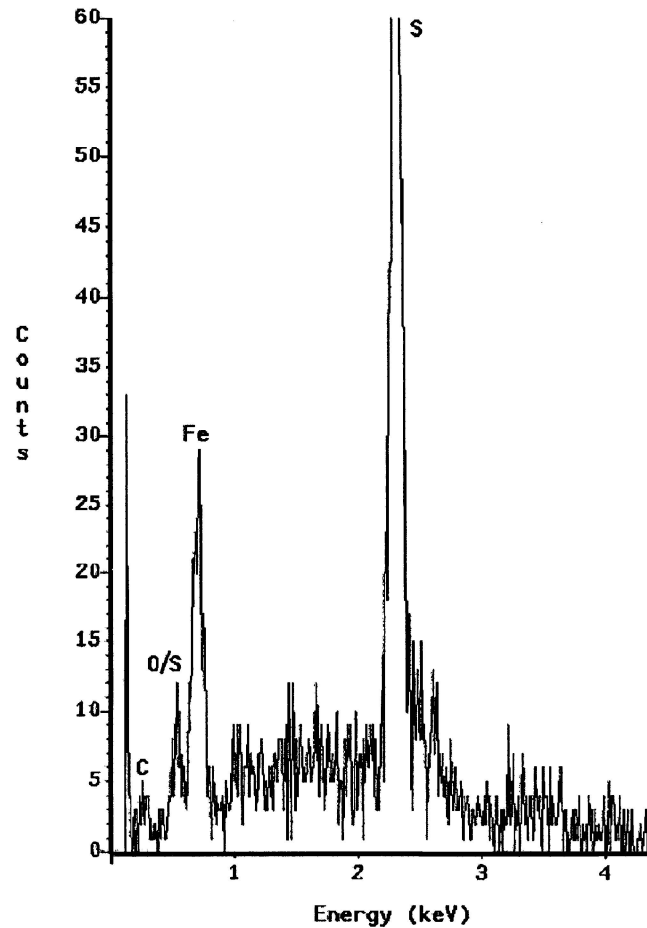
Figure 6. EDX analysis, at 3.5 kV, of the surface of a FeS particle after reaction with a nitrite solution.

could well be due to oxidation by air of sulfide during preparation for ion chromatography.

3. Conclusions

These results indicate that FeS is a good reductant for the conversion of nitrite and nitrate to ammonia. This means that the reduction of nitrite and nitrate are viable sources for ammonia, even if the early ocean was acidic. The reaction operates under pH conditions in which Fe^{+2} won't reduce nitrite to ammonia. FeS also shows greater reproducibility toward the reduction of nitrate than Fe^{+2}. The reaction, while it operates at more acidic pHs, otherwise shows many similarities. It shows similar effects of added ions and is also first order in nitrite.
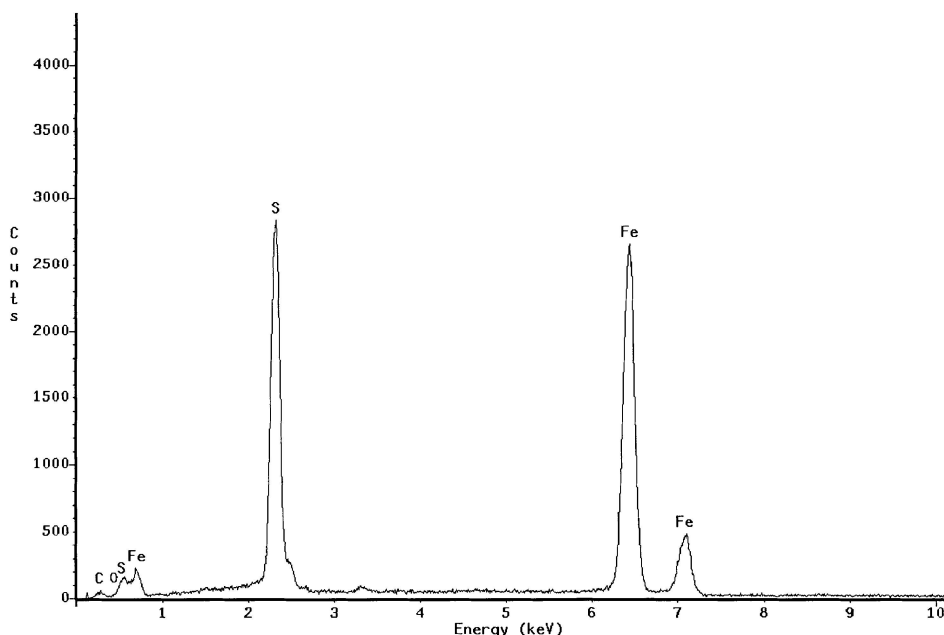
Figure 7. EDX analysis, at 20 kV, of the surface of a FeS particle after exposure to buffered water.

The reduction of nitrite tolerates the presence of many of the salts that would likely have been present in an early ocean, though some drop in yield is seen. The reduction of nitrate is more questionable in this regard. Both reactions show a higher yield at lower pH, indicating that they will be favored in an acidic early ocean. The drop is more catastrophic for nitrate and it looks like it could only have contributed to ammonia formation in a fairly acidic ocean.

4. Experimental

All water was purified (to at least 18 mega-ohm cm conductivity) using a Tech One reverse osmosis purified water system (the company has since been bought out by Zyatech). In a typical experimental setup, pH adjusted, CO_2 (or N_2) purged, water (with any added species already present) was added to a vessel through a serum cap with a weighed amount of FeS powder (Aldrich), typically 5–10 mg/mL, under nitrogen. The solution was purged with carbon dioxide or nitrogen and the pH was then readjusted. With purging, a suitable amount nitrite/nitrate stock solution was added. The purge was stopped and, after a time, the reaction was sampled, filtered, and analyzed. The pH was maintained by the bicarbonate or phosphate buffer (typically $\pm$ <0.05 units except with bicarbonate buffers down at pH 4 where the variation was $\sim$ $\pm$0.2 units due to the lower concentrations of bicarbonate). In the
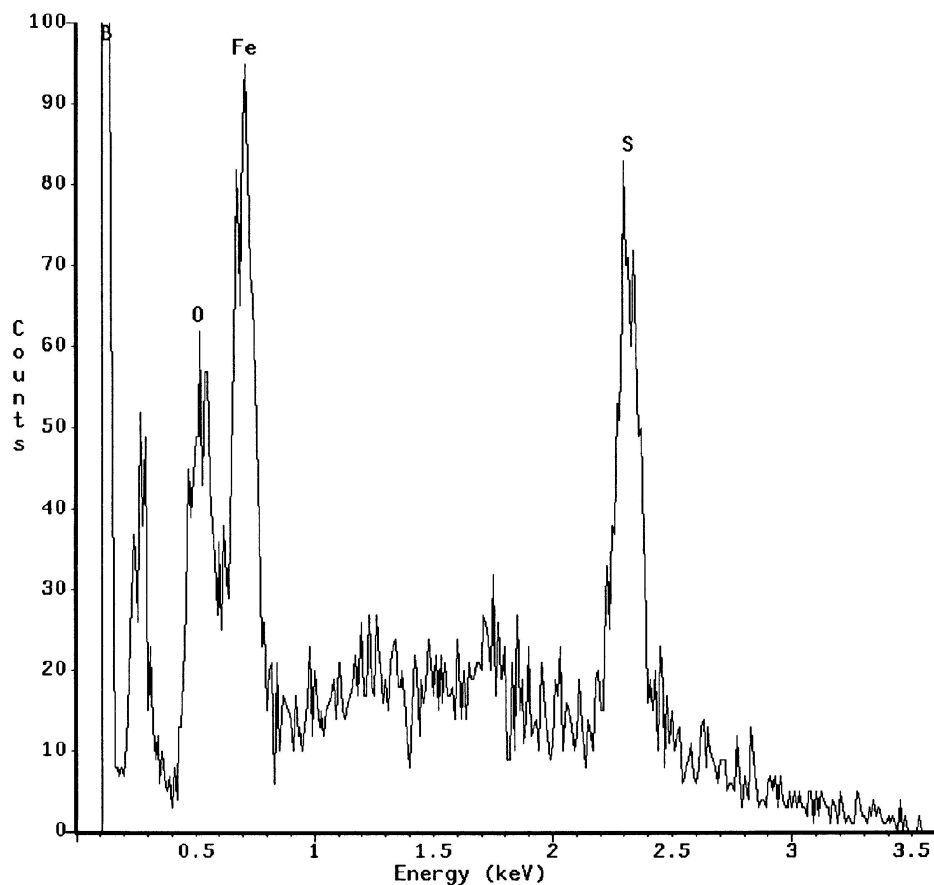
Figure 8. EDX analysis, at 3.5 kV, of the surface of a FeS particle after exposure to buffered water.

experiment under nitrogen shown in Figure 1, the pH was maintained by manual addition of potassium hydroxide. A fresh bottle of FeS was used for this study. Old bottles sometimes showed no activity, presumably due the presence of passivating iron oxide layers on the surface due to air leakage.

Ammonia and nitrite/nitrate analysis was either by ion chromatography. (There was an interference, presumably by sulfide, in the colorimetric method previously used and it was abandoned in favor of ion chromatography). In all cases the potassium salt was used to avoid a conflict between ammonium and sodium in the ion chromatography. Ion chromatography was done on Dionex ion chromatographs: DX-100 for ammonium and 4500i for nitrite. Both instruments were run in suppressed conductivity mode for increased sensitivity.

In experiments on the surface oxidation of FeS, the experiments were run as outlined above. Then stirring was stopped and the larger particles were allowed to settle. A couple drops of this slurry from the bottom of the vial were placed on a

strip of carbon tape and immediately dried, and stored, under vacuo. Spectra were run in a Hitachi S4000 field emission scanning electron microscope with a Noran Voyager light element detector. The layer of particles was thick enough that no carbon signal was seen from the underlying carbon tape though, in any case, all spectra presented were obtained only from the surface of particles. The solution was filtered and the amount of iron oxide precipitate was determined by weight. The filtered solution was then subjected to ion chromatography.

Acknowledgements

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