

# The late diagenetic conversion of pyrite to magnetite by organically complexed ferric iron

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Received 27 April 1995; accepted 5 December 1995

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## Abstract

The geochemistry of late stage diagenetic replacement of pyrite by magnetite was investigated by laboratory experiments of pyrite dissolution and magnetite precipitation involving organically complexed ferric iron. The design of the experiments is based on the hypothesized geochemical conditions for in situ diagenesis in the Pennsylvanian age Belden Formation, an organic-rich carbonate in northwestern Colorado with pyrite grains rimmed with magnetite that contains a Cretaceous paleopole position. The geochemistry is applicable to both deep and near surface reactions involving pyrite, magnetite and organic matter and bears upon the geologic interpretation of secondary chemical remanent magnetizations (CRM).

Aqueous solutions of ferric-ligand complexes and pyrite were heated (60°C) for 60 days in the absence of light and at low partial pressures of oxygen. Additional experiments with each ligand were performed both in the presence of bentonite and without ferric iron (ligand only). Raising the pH to  $\geq 8.5$  produced a ferrous hydroxide precipitate, and subsequent heating (90°C) resulted in the formation of magnetite.

Ferric complexes of oxalate, salicylate and acetylacetonate resulted in pyrite dissolution and magnetite formation. The activity of strongly reducing ligands (e.g., catechol) or unsaturated Fe(III)-exchange capacity (particularly in experiments with bentonite or with solutions of uncomplexed ligands) can result in an effective reduction of ferric iron concentration and prevent pyrite dissolution and/or interfere with the crystallization of magnetite. The bentonite acted to adsorb dissolved species and also underwent direct dissolution, especially by the oxalate ligands. Although these reactions could occur at any depth, a continuing supply of molecular oxygen (more available in near surface settings) would result in the formation of hematite or the production of acidic sulfate conditions, whereas at greater depths (or restricted porosity), the redox gradation is halted at magnetite. The results of this study thus provide a likely geochemical mechanism for the replacement of pyrite by magnetite during the latter stages of diagenesis.

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## 1. Introduction

Of the minerals that comprise sedimentary rocks, magnetic phases, such as magnetite, are somewhat unique in that they can be analyzed with geophysical techniques to provide a broad spectrum of geological

information. For example, the natural remanent magnetization (NRM) residing in magnetite or other minerals which contain a depositional magnetization can be used to constrain the geologic age of a rock. Similarly, the age of secondary magnetizations acquired long after deposition can be assessed. Many secondary magnetizations reside in authigenic magnetite (e.g., McCabe and Elmore, 1989; Suk et al.,

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1993) and, in some cases, in magnetic iron sulfide minerals, such as greigite or pyrrhotite (Reynolds et al., 1990; Krs et al., 1992). In sediments, the nondestructive measurement of magnetic susceptibility and other magnetic properties have been used to detect the presence of magnetite-forming microbes (Stolz et al., 1990) and to augment geochemical profiles of early diagenetic processes (Karlin, 1990).

Whereas dissolution of magnetite associated with the pyritization of organic-rich sediments has been documented by several workers (e.g., Canfield and Berner, 1987), instances of the reverse process (magnetite replacement of pyrite) during the latter stages of diagenesis have also been reported (Reynolds, 1990; Suk et al., 1990). It has been recently hypothesized that one likely chemical pathway for the late stage diagenetic conversion of pyrite to magnetite involves the oxidation of pyrite by Fe(III) complexed to organic ligands (Brothers et al., 1994). This process may have produced magnetite rims on pyrite grains encased in fecal pellets in the Cretaceous age Belden Limestone (Colorado) and imparted a secondary chemical remanent magnetization (CRM) to

the rock (Fruit et al., 1995). In the present study, simulation experiments were performed to constrain the chemical and physical parameters that produced magnetite-rimmed pyrite grains in the Belden Limestone. The petrographic characteristics of this limestone were used as a guide in the design of the experiments.

### 1.1. Geologic setting

The Belden Formation is a marine Pennsylvanian age limestone. At Sweetwater Creek, Colorado, the limestone contains magnetite-rimmed pyrite grains encased in fecal pellets (Fig. 1). The magnetite rims carry a CRM with a paleopole position that falls on the Cretaceous part of the apparent polar wander path for North America (Fruit et al., 1995). The maximum burial temperature at Sweetwater Creek has, based on Rock-Eval  $T_{\text{max}}$  values, been estimated to be 150°C (Nuccio et al., 1989). Because this temperature is too low to cause acquisition of a thermoviscous magnetization, the Cretaceous remanence is interpreted to be a CRM.



Fig. 1. A reflected light photomicrograph of a thin section of the Belden Formation, showing the outline of a fecal pellet (*F*) containing pyrite grains (*P*) with replacement rims of magnetite (*M*). The fecal pellet is 250  $\mu\text{m}$  in diameter.

The formation of magnetite appears to have resulted from a series of in situ diagenetic processes resulting from thermal alteration of the limestone and associated organic matter. Petrographic examination indicates that permeability is very low, thus precluding the likelihood of mixing with fluids from outside the system. A microbial pathway is excluded at this time because of the depth of burial at the time of formation (~ 3657 m).

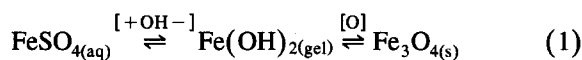
## 1.2. Background

The formation of authigenic magnetite in sedimentary systems has been attributed on the basis of field studies to several processes, including: (1) fluid mixing and associated rock/fluid interactions, (2) in situ alteration during diagenesis, and (3) microbial activity. Rock/fluid interaction is the process most commonly proposed, often in concert with orogenic events (e.g., Oliver, 1992; Suk et al., 1993). Elmore et al. (1987) and Elmore et al. (1993a) have related the formation of authigenic magnetite to the migration of hydrocarbons. Similarly, the mixing of fluids with different temperatures, ionic strengths or redox levels can result in the precipitation of iron minerals. For example, the upward diffusion of Fe(II) which was produced in underlying zones of organic decay into near surface zones containing dissolved oxygen results in the growth of iron hydroxides (Karlin, 1990; Leslie et al., 1990). Also, the migration of petroleum into shallow reservoir rocks has been suggested to cause the reduction of ferric iron (Machel and Burton, 1991). The role of organic complexation in secondary magnetite formation remains largely unexplored although organic ligand complexes are thought to play a significant role in the transport and accumulation of metals (Filby and Van Berkel, 1987; Gize and Manning, 1993).

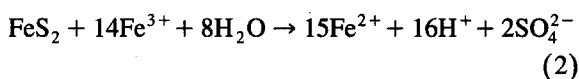
The second process involves in situ changes in redox chemistry (such as kerogen maturation or thermal alteration of a petroleum reservoir) as a consequence of increasing temperature with depth of burial (Plaster-Kirk et al., 1995). The third process requires bacterial activity for which the thermal and chemical boundaries have not yet been clearly determined (Stolz et al., 1990; Blakemore and Blakemore, 1991), but one may anticipate that this is mainly important in near surface environments.

The specific chemical reactions which produce magnetite in sedimentary environments are not well established. Laboratory synthesis of magnetite has been accomplished (1) by pH-sensitive oxidation of ferrous hydroxide gels with a nitrate oxidant (Sugimoto and Matijevic, 1980; Schwertmann and Cornell, 1991), (2) by alkaline anodic oxidation (Öjefors, 1976), (3) by equilibration of ferric oxyhydroxides with a concentrated solution of ammoniacal ferrous iron (Jolivet et al., 1992), and (4) by biologically mediated reactions (Stolz et al., 1990; Skinner, 1993). The formation of associated maghemite, either directly or by rapid oxidation of ultra-fine grains of magnetite, commonly occurs with each method.

The replacement of pyrite by magnetite may be considered to occur, like many other diagenetically and metamorphically formed minerals, by a surface dissolution/reprecipitation mechanism (Fig. 2). In the laboratory, the active process of dissolution/reprecipitation has been observed and documented in the course of magnetite synthesis from ferrous sulfate solutions via a ferrous hydroxide gel intermediate (Sugimoto and Matijevic, 1980):



Since the anaerobic oxidative dissolution of pyrite results in a ferrous sulfate solution, according to the following reaction,

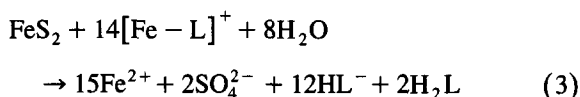


(Garrels and Thompson, 1960), the pyrite-to-magnetite transformation can plausibly occur via reaction (2) in the dissolution stage and reaction (1) in the reprecipitation stage. The basic fluids in equilibrium with the surrounding carbonate matrix of the Belden Limestone provide a source for the hydroxide ions required to neutralize the hydrogen ions produced from (2) and to form the ferrous hydroxide gel intermediate in (1).

Examination of the shapes of the pyrite grains and the magnetite rims in the photomicrograph of the Belden Formation (Fig. 1) indicates that the magnetite formed as a replacement of an existing cubic pyrite grain and not as an overgrowth. The shape of each grain retains a cubic habit characteristic of pyrite while the inner demarcation of magnetite re-

placement is irregular and suggestive of a dissolution process (R. Reynolds, U.S.G.S., pers. commun., 1994). This is congruent with the concept of a dissolution/precipitation mechanism discussed earlier, and thus the likely role of ferric iron as a reactant is underscored since magnetite requires 1.6 times more iron per unit volume than pyrite.

Although (2) generally occurs under acidic conditions due to the extremely low solubility of ferric hydroxide complexes, Moses et al. (1987) have shown that the reaction can occur near pH 7. However, if the ferric iron in (2) occurs as a ferric-ligand complex, then the reaction can proceed under less acidic conditions as well as at lower redox potentials than are encountered during aerobic pyrite oxidation, as follows:



where L is any organic ligand. The involvement of ferric-ligand complexes in redox reactions such as (3) is supported by studies of near surface systems. Humic acid (naturally concentrated in fecal pellets) contains several forms of ferric-ligand complexes, which have been identified and studied spectroscopically (Schnitzer and Khan, 1978; Senesi and Calderoni, 1988). Additionally, ferric iron has been extracted from soils along with humic acid in the form of microcrystalline goethite (Fontes et al., 1992). Working in a modern system with many similarities to the Belden paleoenvironment, Luther et al. (1992) experimentally demonstrated the oxidation of pyrite by ferric salicylate and postulated that similar naturally occurring ferric complexes acted to dissolve pyrite in tidal marshes in response to fluctuating oxygenation of surface waters. Lastly, although the oxidation of pyrite under ‘reducing’ conditions is generally disregarded, Stumm and Sulzberger (1992) have noted that “[complex] formation reactions of Fe(III) and Fe(II) with organic and inorganic ligands to form solute and solid complexes makes it possible that electron cycling of Fe(III)–Fe(II) transformations can occur over the entire range within the stability of water...”. It is well understood that the redox potential of a reaction is reduced by the formation of complexes to the reacting metal according to the magnitude of the formation constant. However,

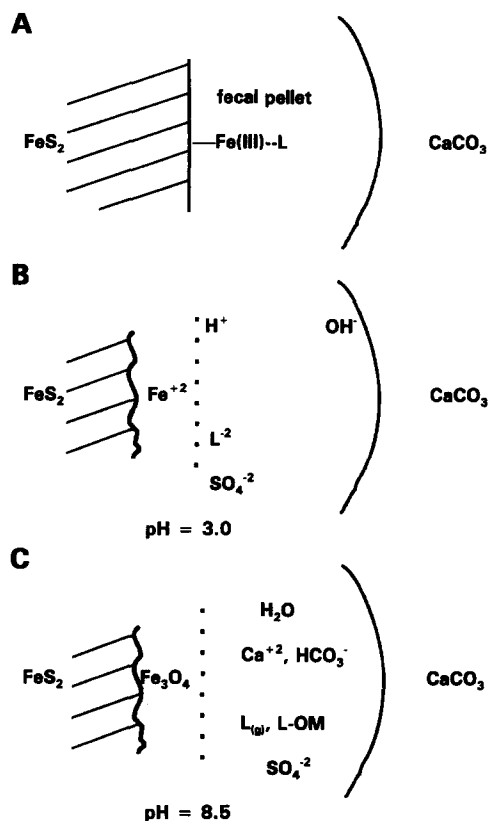


Fig. 2. A diagrammatic representation of the dissolution of a pyrite grain within a fecal pellet and the subsequent formation of a magnetite rim during diagenesis. (A) Pennsylvanian deposition, geochemically heterogeneous ( $\sim 25^\circ\text{C}$ ). (B) Pyrite dissolution after burial ( $\sim 60^\circ\text{C}$ ). (C) pH equilibration and formation of Cretaceous magnetite ( $\sim 90^\circ\text{C}$ ). The rate of magnetite formation is probably rapid on a geologic timescale.

this fact is often neglected in the unavoidable choices of simplifying assumptions required to categorize geochemical processes.

### 1.3. Hypothetical model

The simulation experiments described below are based on the fecal pellets acting as microenvironments of humic substances which were substantially pH- and redox-isolated from a matrix of nonhomogeneous calcareous sediment. During early diagenesis, low Eh conditions from the decay of the organic-rich sediment resulted in the formation of pyrite. The only ferric iron which remained was complexed with

the humic substances by carboxylic, salicylic or other organic moieties. As temperature and pressure increased with burial, the maturation of humic substances caused the release of complexing functions. The more soluble ferric iron-complexes came in contact with the pyrite grains, causing oxidative dissolution, which in turn resulted in localized decreases in pH. Subsequent equilibration with the basic pore waters from the surrounding limestone lead to the precipitation of magnetite via a ferrous hydroxide gel intermediate (Fig. 2).

The integrity of the fecal pellet microenvironment, especially during the early stages of the pyrite dissolution process, is assumed in the design of these experiments. In natural systems, the influence of microenvironments upon the distribution of chemical species within a given sedimentary horizon is an area of active research. Microenvironments were suggested by Canfield (1989) to account for key divergences from modelled data in his study of the pyritization of sediments. Fluctuating levels of hydrologic oxygenation, which frequently occur in nearshore marine environments (van Breeman, 1988; Luther et al., 1992), can produce ferric iron in accessible pores while inaccessible, organically encrusted pores remain reduced. The preservation of fecal pellets, the occurrence of both botryoidal pyrite and hematite concretions and the absence of bioturbation within the rock matrix of the Belden Formation indicates a poorly mixed, heterogeneous sedimentary system, congruent with the concept of a microenvironment.

The ligands used in this study (Table 1) represent appropriate model compounds for the chemical be-

havior of humic substances and include compounds containing carboxylic, salicylic, amino acid and carbonyl moieties, which have been identified by several workers as the most active chemical functions involved in the complexation of metals by humic substances (Jackson et al., 1978; Schnitzer and Khan, 1978; Thurman, 1985; Goodman, 1988). The similarities of chemical behavior and spectroscopic properties shared by humic substances and melanoidins have been studied by several workers (e.g., Hoering, 1973; Larter and Douglas, 1980; Ertel and Hedges, 1983). Oxalate compounds occur naturally and have been studied in soils and sediments as well as supergene environments (Sato, 1992), oilfield brines (Crossey, 1991) and artificially matured humic acids (Surdam et al., 1984). Thus, the variety of ligands employed in the experiments described below include a wide range of structural complexity (from single, well-defined compounds to substances of unknown structure) as well as a representative selection of complexing functions.

No laboratory experiment is a complete simulation of naturally occurring events, and some mention of the pertinent differences is appropriate. First, natural pore waters contain a much larger variety of cationic species than were included in the experimental solutions (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ). In the present study, these additional cations were not included in order to simplify the system by minimizing the number of chemical components. Also, the organic constituents and their concentrations are highly variable in fecal pellets and other sedimentary organic materials. Additionally, ferrous

Table 1  
Initial compositions of the organic ligands for each set of experiments <sup>a</sup>

Humic acid	Oxalic acid	Melanoidin	Salicylic acid	Catechol	Gorgonians	Acetylacetone
<b>Hu</b> <sup>b</sup>	<b>Ox</b>	<b>M1</b>	<b>Sal</b>	<b>Cat</b>	<b>Gor</b>	
Sewanee R. 29.7 mg/ml pH 7	0.3 M pH 1	'immature' (partly condensed) 11.5 mg/ml	saturated soln pH 7	saturated soln pH 7	fermented corals, 327 mg solid pH 6.5	
<b>HuFe</b> <sup>b</sup>	<b>FeOx</b>	<b>M2</b>	<b>FeSal</b>	<b>FeCat</b>	<b>FeGor</b>	<b>FeAcac</b>
Above w/ 0.43 mg/ml $\text{Fe}^{3+}$ pH 7	0.05 M $\text{Fe}_2(\text{Ox})_3$ pH 4.8	'mature' (well condensed) 8 mg solid	above w/ 0.1 M $\text{Fe}^{3+}$ pH ~ 9.0	above w/ 0.1 M $\text{Fe}^{3+}$ pH ~ 8.5	above w/ 0.43 mg/ml $\text{Fe}^{3+}$ pH 6.5	saturated soln $\text{Fe}_2(\text{C}_5\text{H}_8\text{O}_2)_3$ pH 4.8

<sup>a</sup> All systems contained acetic acid (0.05 mM) and separate experiments were conducted for most ligands in the presence of bentonite. See text for details.

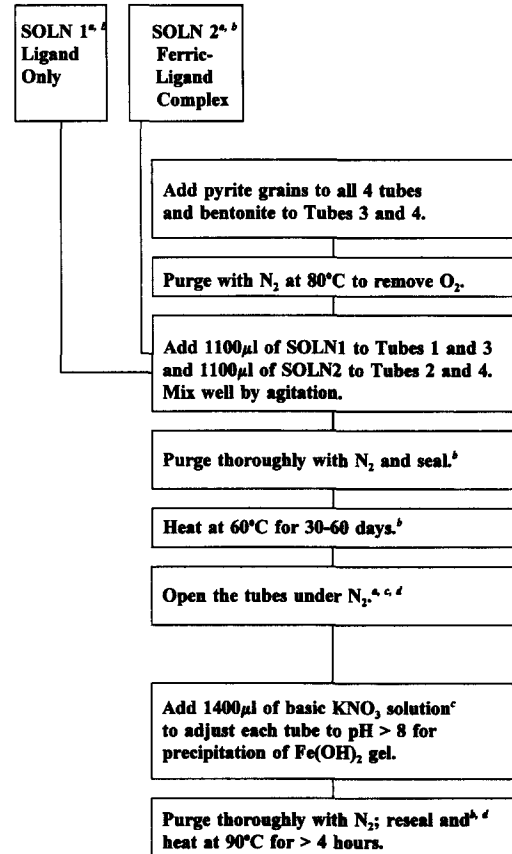
<sup>b</sup> Abbreviations for ligands with (e.g., HuFe) and without (e.g., Hu) ferric iron.

hydroxide gel exists in a metastable thermodynamic state and is kinetically labile so that the conceptual separation of the pyrite oxidation stage from the magnetite formation stage is somewhat artificial. Lastly, solid phases in the simulations described below were poorly compacted and overburden pressure was thus not considered.

## 2. Experimental

Pyrite samples of 25 mg (Ward's Scientific, ground and sieved manually through a 1 $\phi$  screen) were loaded into 25 cm  $\times$  4 mm i.d. Pyrex<sup>®</sup> tubes. The surface of the pyrite was not treated to remove the oxidized monolayer and therefore represents the minimal ('blank') experimental concentrations of ferric iron. Bentonite (ca. 70 mg) was added to half of the tubes. After the addition of the solid phases, the tubes were purged with N<sub>2</sub> at 80°C to minimize the adsorbed O<sub>2</sub>. A set of four experiments was performed in duplicate for each ligand shown in Table 1, although all experiments involving melanoidin (M) also contained oxalate (such as FeOxM2). A flowchart depicting the experimental steps for each ligand is shown in Fig. 3. The set includes duplicate experiments with the ligand only (1), with the ligand–ferric complex (2), with bentonite and the ligand only (3), and with bentonite and the ferric-ligand complex (4). Exceptions to this pattern are M1 ('immature' melanoidin), which included no trials with bentonite, and acac (acetylacetonate), for which a set of five experiments were performed with the ferric salt, but none with the ligand only or with bentonite.

The components of each solution are listed in Table 1. All solutions were prepared by dissolving the ligand in 0.02 *mM* acetic acid. The melanoidin was prepared by refluxing under N<sub>2</sub> (without rigorous exclusion of O<sub>2</sub>) 1.71 g L-lysine, 0.89 g L-histidine, 1.00 g L-arginine and 9.04 g D-glucose in 100 ml of water at 70°C for 6 days. A 25 ml aliquot of 'immature' melanoidin was removed at this time and was not separated from the uncondensed sugar and amino acids. The 'mature' melanoidin was heated an additional 8 days at 100°C, precipitated from solution with 0.1 *M* HCl, washed and gently dried under N<sub>2</sub>. Saturated solutions of salicylate and cate-



and continued to be purged with N<sub>2</sub> at 60°C during the removal of aliquots for analysis of Fe<sup>2+</sup>, pH and SO<sub>4</sub><sup>2-</sup>. Next, the simulation of magnetite formation was initiated by adding sufficient deoxygenated basic nitrate solution to raise the pH above 8.5 in the individual tubes. This amounted to a crude titration since the pH of each experiment varied according to the extent of pyrite dissolution and system buffering capacity. Final pH values ranged from 8.5 to 11. After continued purging with N<sub>2</sub> for more than 45 min, the tubes were resealed and heated overnight at 90°–95°C. The tubes which contained the catechol and acetylacetonate ligands were heated under a flow of N<sub>2</sub> in a 90°C water bath. All samples were shielded from light, except for brief, unavoidable periods of exposure during mixing and sampling operations.

### 2.1. Analytical

A summary of the types of analyses performed and the stages at which the tubes were sampled is

provided in Fig. 3. The pH values were measured using pH paper, accurate to ±0.25 pH units. Ferrous iron concentrations (from 50 μl aliquots) were measured on a Bausch and Lomb Spectronic 20 with 1,10-phenanthroline using a standard addition technique (Skoog and West, 1982). Five standards were used to minimize the effect of spectral interference from the ligands themselves. Analyses were not performed for ferric or total iron concentrations. Sulfate concentrations (from 100 μl aliquots taken from one experiment of each duplicate set) were measured by gravimetric titration with BaCl<sub>2</sub>. The formation of magnetite was determined by measuring the increase in low field (0.1 mT) magnetic susceptibility (MS), a technique which has been used to assess the amount of magnetite in soils (Maher, 1988), sediments (Karlin, 1990) and rocks (Richter and van der Pluijm, 1994). The MS was measured at least 4 times during the course of the experiments by placing the Pyrex® tube containing the entire sample into the coil of a Sapphire Instruments Model SI-2 coil-inductance-ratio susceptibility instrument.

Table 2  
Mass magnetic susceptibility for minerals pertinent to these experiments

Minerals	MS (in 10 <sup>-6</sup> emu/g) <sup>a</sup>	Reference
<i>Diamagnetic minerals:</i>		
Average	-0.34	Richter and van der Pluijm (1994)
Quartz	-0.54	O'Reilly (1984)
Water	-72.0	O'Reilly (1984)
This study—average initial value	-1.0	
<i>Paramagnetic minerals:</i>		
Most Fe salts	80	O'Reilly (1984)
Siderite	100	Carmichael (1982)
Pyrite	130	Carmichael (1982)
Montmorillonite	11	Carmichael (1982)
<i>Anti-ferromagnetic:</i>		
Hematite	48–480	Collinson (1983)
Goethite	22–56	Dekkers and Rochette (1992)
<i>Ferrimagnetic:</i>		
Magnetite or maghemite (isolated spherical grain)	45,360	Collinson (1983)
Magnetite (dispersed submicron grains, < 2% of matrix)	40,283–88,808	Maher (1988)
Magnetite—this study (< 0.00026% of matrix)	2.4–100	
Pyrrhotite	8–800	Collinson (1983)

<sup>a</sup> Conversion to SI mass units: 1 m<sup>3</sup> kg<sup>-1</sup> = 1000/4π emu g<sup>-1</sup>.

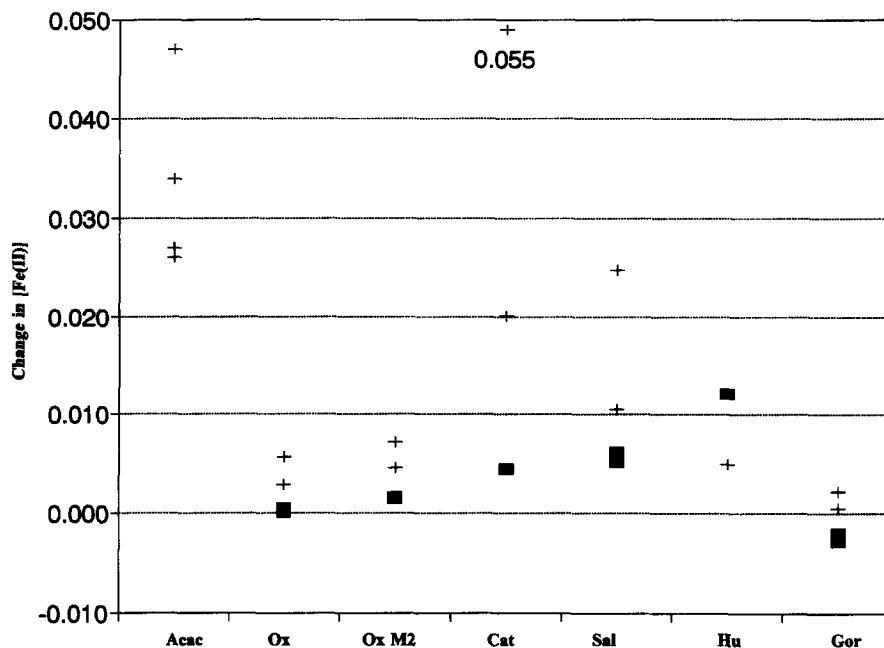


Fig. 4. A plot of the change (final minus initial) in molarity of Fe(II) for each ligand, both with (+) and without (■) complexed ferric iron. The increase in Fe(II) is proportional to the amount of pyrite dissolved. The precision is  $\pm 2\%$  (except 5% for Fe Cat). See Table 1 for abbreviations.

Table 3

Concentrations of reaction products measured at the end of the pyrite dissolution stage from experiments with and without added ferric iron

Ligand	Without Fe <sup>3+</sup> (ligand only)			With Fe <sup>3+</sup> -ligand complex		
	[Fe <sup>2+</sup> ] <sup>a</sup>	[SO <sub>4</sub> <sup>2-</sup> ] <sup>b</sup>	increase in pH <sup>c</sup>	[Fe <sup>2+</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	increase in pH
Ox	0.0001	0.0746 <sup>d</sup>	0.05	0.0029	0.0024	4.2
Ox M2	0.0015	0.0245	NC (0)	0.0071	— <sup>e</sup>	NC (1)
Ox C <sup>f</sup>	0.019	0.0013	NC (1)	0.0058	0.0034	0.5
Ox M2 C	0.0081	0.0013	NC (0)	0.0057	0.0064	1.7
Cat	0.009	0.016	6.5	0.157	0.042	2.0
Cat C	0.020	0.043	7.0	0.146	0.0710	3.3
Sal	0.0058	0.0133	3.5	0.0128	0.0201	0.5
Sal C	0.0024	0.0090	3.5	0.017	0.0163	2.0
Hu	0.021	0.298	NC (7)	0.024 <sup>g</sup>	0.249	NC (7)
Hu C	0.020	0.289	NC (7)	0.017	0.273	NC (7)
Gor	0.0018	0.020	NC (7)	0.0057	0.011	NC (7)
Gor C	0.0013	0.011	NC (7)	0.0029	0.014	NC (7)

<sup>a</sup> Ferrous concentrations shown are in molarity ( $\leq \pm 5\%$ ).

<sup>b</sup> Sulfate concentrations shown are in molarity ( $\pm 7\%$ ).

<sup>c</sup> NC = no change; constant pH value shown in parentheses.

<sup>d</sup> Unrealistically large value reflects interference from oxalate ions.

<sup>e</sup> Sulfate aliquot for this sample was lost.

<sup>f</sup> C = contains clay (bentonite).

<sup>g</sup> Actual value shown was taken from the duplicate experiment; other values represent that experiment in the duplicate set which was analyzed for sulfate.



The total MS of a sample is the sum of the diamagnetic, paramagnetic, anti-ferromagnetic and ferrimagnetic contributions from each mineral according to its weight fraction in the sample. The MS of magnetite is substantially larger than other minerals which may coexist in these experiments (Table 2). Therefore, when magnetite with a MS of  $45,360 \times 10^{-6}$  emu/g (SI mass units:  $57,000 \times 10^{-8}$  m<sup>3</sup>/kg) is present in one of the experimental tubes, even in milligram quantities, it accounts for almost 100% of the MS. When magnetite is not present, the MS is dominated by the 3.8 g of diamagnetic Pyrex (MS  $\sim -1.0 \times 10^{-6}$ ). No distinction, however, is made by this technique between magnetite and maghemite since the magnetic properties of these minerals are similar. Because both minerals form under similar conditions at these temperatures (as mentioned above), it is likely that some amount of maghemite was produced. For convenience, we will refer to both phases as magnetite. The formation of magnetite was verified by powder X-ray diffraction on crystals precipitated from larger volumes of corresponding chemical composition. Aside from magnetite, pyrrhotite is the only mineral with a substantial MS which might occur in these samples. However, MS measurements made during the pyrite dissolution stage rule out pyrrhotite (or magnetite) growth, and the conditions are too oxidizing for pyrrhotite formation during the experimental magnetite formation stage due to the presence of nitrate.

### 3. Results and discussion

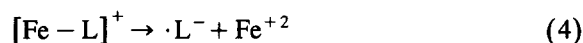
#### 3.1. Pyrite dissolution stage

The pyrite dissolution reaction (1) produces an aqueous solution of Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> ions. The extent of pyrite dissolution in each experiment, as measured by Fe(II) production, is shown in Fig. 4. In each case, reaction of the pyrite with the ferric-ligand complex resulted in a higher concentration of Fe(II) than the ligand alone, indicating that the presence of Fe(III) facilitates pyrite dissolution. Corresponding increases in SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> ions were also observed (Table 3). Of the various ligands tested, ferric-acetylacetonate, ferric-salicylate and ferric-oxalate appeared to be the most effective complexes for

pyrite dissolution. The reactions with ferric-humate and ferric-gorgonians did not appear to proceed appreciably.

Even though the ferric-ligand experiments resulted in increases of the reaction products, the relative sulfate values appear to be too high. This may be due to analytical interferences with the gravimetric measurement of sulfate, especially by coprecipitation of barium oxalate or entrainment of excess barium ions or bentonite grains in the precipitate. Similarly, adsorption of ferrous iron and pH buffering activity can reduce the measured values of these products. In general, however, the difficulty in evaluating species distributions in these systems (especially those involving poorly characterized components, like humic acid) precludes a definitive assessment of reaction stoichiometry.

Direct reduction of the Fe(III) by the complexing ligand could conceivably compete with pyrite oxidation, by reactions such as:



where L is any organic ligand. However, as detailed below, under the conditions of these experiments (moderate temperatures, absence of light, anaerobic), such reactions proceed to a negligible extent with most of the ligands employed. Oxidation of oxalate by Fe(III) requires photoexcitation (Stumm and Sulzberger, 1992). Thermal degradation of solid ferric oxalate proceeds by a redox mechanism, but does not occur below 250°C (Glasner et al., 1963). Similarly, thermal decomposition of uncomplexed oxalic acid in aqueous solution is negligible at 150°C or below (Crossey, 1991). Also, thermal decomposition of ferric-acetylacetonate does not occur below 150°C (Wendlandt, 1967). Catechol, however, readily undergoes oxidation by Fe(III) at low pH (Pelizzetti et al., 1974), and the high (0.1 M) concentration of Fe(II) present in the ferric-catecholate solution prior to the pyrite reaction likely resulted when the acidic solution of Fe(III) was added to the catecholate during preparation of the ferric-ligand complex. Salicylic acid, also a phenol, has been shown to reduce the Fe(III) in ferric hydroxides, although the reaction proceeds minimally compared to catechol (Lakind and Stone, 1989). Melanoidin has been shown to reduce ferric iron (Hoering, 1973) and humic acid is

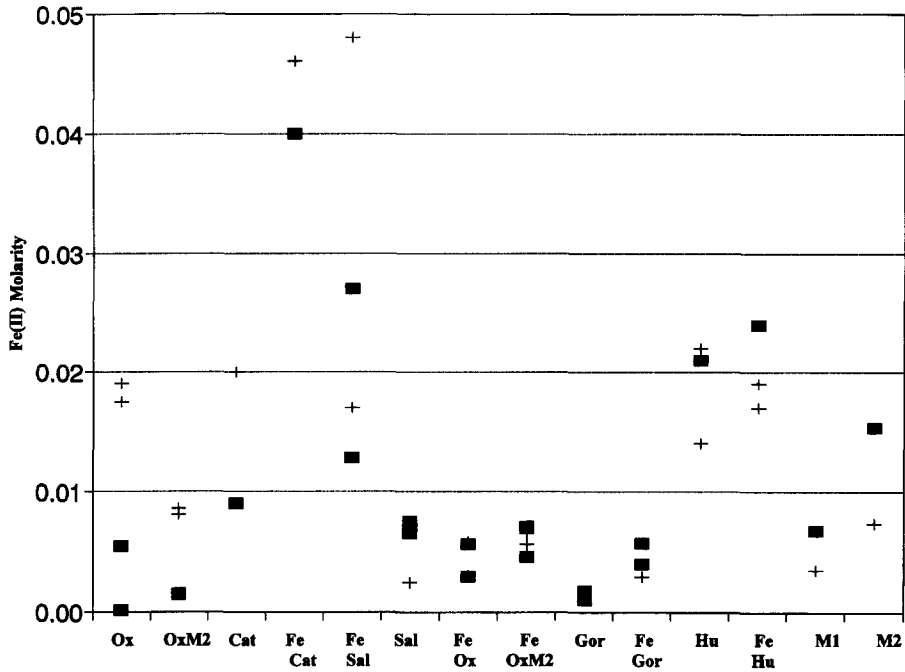


Fig. 5. A plot of the molarity of Fe(II) for each ligand and complex with (+) and without (■) bentonite (analyzed after the pyrite dissolution stage). When bentonite was included in the experiment, ligands which are plotted on the left showed increases in [Fe(II)], while ligands plotted on the right contained lower [Fe(II)] than the same systems without bentonite. The precision is  $\pm 2\%$  (except 5% for Fe Cat). The Fe Cat values are reduced by 0.1 for scale (actual values: 0.146 with bentonite and 0.140 without). See Table 1 for abbreviations.

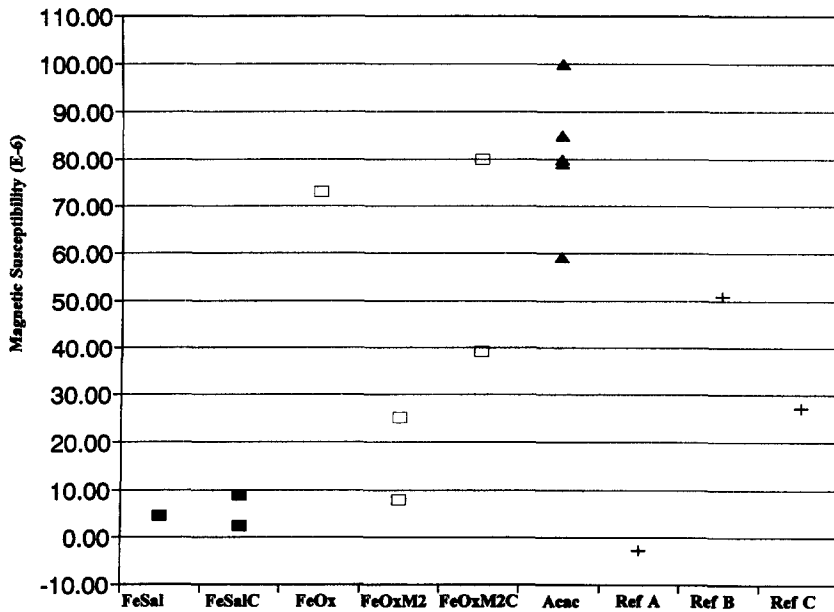


Fig. 6. A plot of MS ( $\pm 1E-6$ ) for those experiments which produced magnetite from the solutions of dissolved pyrite and ligand. The MS is proportional to the mass of magnetite (ca. 4.5 mg for  $100E-6$ ). Ref A is an average value for all non-magnetite samples and blanks, including hematite, siderite and pyrite. Ref B is a synthetic magnetite, made without organic ligands. Ref C is a very finely ground igneous magnetite.

known to act as both a reducing and a complexing agent (Szilagy, 1972; Schnitzer and Khan, 1978).

The final concentrations of Fe(II) for most of the systems in the presence and absence of bentonite are shown in Fig. 5. The nature of its effect on pyrite dissolution is unclear because bentonite interacts with most of the systems' components. First, the clay mineral surface is known to adsorb organic compounds, cations (including ferrous and ferric iron) and  $H^+$  ions. Such adsorption would affect the equilibrium by altering reactant and product concentrations and possibly reducing the final concentration of Fe(II) measured. Second, ferric-montmorillonite, in particular, has been shown to have strong catalytic activity in redox reactions (Wang and Huang, 1991). Those ligands which show an increased Fe(II) concentration in the presence of the bentonite (those on the left side of Fig. 5) have aromatic structures, which more readily align with the flat surface of a clay during catalysis. Finally, some of the ligands, oxalate in particular, are known to dissolve montmorillonite by surface complexation of aluminum sites in the mineral structure (Surdam et al., 1984). Dissolution of montmorillonite may be a direct source of some of the Fe(II) measured, since iron commonly occurs in montmorillonite both as a structural replacement and adsorbed in the interlayers.

### 3.2. Magnetite formation stage

Upon increasing pH and continued heating, magnetite was produced in some of the ferrous solutions of dissolved pyrite, as indicated by a substantial increase in magnetic susceptibility (Fig. 6). Magnetic susceptibility is proportional to the mass of magnetite produced and also is affected by grain size. Unlike the pyrite grains in the Belden Formation (0.03 mm wide), the experimentally reprecipitated magnetite is not constrained to the original grain boundaries of the dissolved pyrite cubes. This is because of the low pH values during pyrite dissolution and the lack of volume constraints in the experimental tubes (4 mm i.d.).

Most of the systems which formed magnetite contained at least 0.015 M ferrous iron in solution, although there was no correlation between the mass of the magnetite produced and ferrous iron concentrations. Of the ligands employed, acetylacetonate

and oxalate produced the most magnetite. Differences in the mass of magnetite formed from solutions containing different ligands are in agreement with previous studies on the growth of synthetic magnetite (Sugimoto and Matijevic, 1980 and references therein).

Consideration of those experiments which produced no detectable magnetite delineate the geochemical constraints for its precipitation. The first variable, ferrous iron concentration, has been discussed above. However, of those solutions which did contain  $\geq 0.015$  M ferrous iron concentrations, magnetite was not produced from any 'ligand only' experiment. In addition, two experiments (ferric catecholate and ferric humate), despite containing sufficient ferrous iron and ferric ligand complexes, did not form magnetite. Two factors may be involved here, both involving ligand-metal sorption. First, physical and chemical adsorption of metal species to organic compounds interferes with crystallization processes, most notably by altering the concentrations of the metal species which participate in crystallization (conventional masking of precipitates) and by preventing association of bonding species. Steric factors were also considered by Dekkers and Schoonen (1994) to play a role in the prevention of iron sulfide crystallization by traces of humic acids, which, the authors demonstrated, have a strong affinity for fresh sulfide surfaces. Thus, even though the formation of the green gel was visually observed in most of the experiments immediately upon mixing with the basic solution, subsequent equilibration of the precipitate may have caused it to redissolve due to adsorption or complexation of iron species by free organic ligands. Similarly, rapid complexation of ferric ions by excess free organic ligands produced during magnetite formation may reduce the redox potential of the solution and lead to the formation of undetectable, superparamagnetic grains.

Bentonite also appeared to prevent magnetite formation in some experiments, probably by surface adsorption. The experiments with bentonite and ferric oxalate with 'mature' melanoidin (Fe-Ox M2) did not form magnetite, but the same experiment without bentonite did. However, the ferric salicylate experiments, both with and without bentonite, produced magnetite. Therefore, it appears that the cation-exchange capacity of the system, with respect to both

organic and mineral surface components, directly affects the growth of magnetite grains. Experiments which contain a larger variety of cations in solution will be required to study this effect.

### 3.3. Implications for geologic interpretations

The association of pyrite with organic-rich environments, such as oil source rocks and salt marsh sediments, is well known. The pyritization of organic-rich sediments with depth by the reactions of dissolved sulfur species with iron oxides and hydroxides is an area of active research (Canfield, 1989; Leslie et al., 1990). However, studies of the reverse process of pyrite oxidation have generally focussed on well-oxygenated, carbon-poor settings. The results of this study underscore the concept that pyrite oxidation can occur along a continuum of redox conditions and that ferric iron can play a significant role at any point. At one end of the redox spectrum is the development of acid sulfate soils from well-aerated and drained pyritic rocks or sediments, as discussed by van Breeman (1988). Under slightly more reducing conditions in poorly drained tidal salt marshes, studied in detail by Luther et al. (1992), oxidative dissolution of pyrite by organically complexed Fe(III) forms part of a redox cycle active during fluctuating levels of groundwater oxidation. Although waterlogged, the porous uncompact sediments remain accessible to atmospheric oxygen (and light) to provide Fe(III) recharge as a function of the cycle. Under still more reducing conditions within the organic-rich Viola Limestone of southern Oklahoma during Permian time, authigenic magnetite formed pervasively throughout the impermeable zones, apparently occurring as replacement rims around pyrite and with other grain morphologies (Elmore et al., 1993b). However, hematite occurs in alteration zones adjacent to vein-filled fractures. The hematite formed from the action of basinal fluids upon the host limestone via the fracture porosity and may occur as pseudomorphs after pyrite. The conditions in the Belden Formation and in the unfractured Viola represent the most reducing in the spectrum: inaccessible to light or dissolved oxygen and a lack of oxidative recharge from basinal fluids or other sources.

## 4. Conclusions

Magnetite was formed experimentally from pyrite in the presence of organic ligands complexed to ferric ions. By analogy, this general chemical reaction sequence provides a possible geochemical explanation for the diagenetic replacement of pyrite by magnetite associated with organic-rich carbonates, such as the Belden Formation, and for the associated secondary CRM's.

Differences in the behavior of the ligands with respect to both pyrite dissolution and magnetite formation were observed. Organic ligands interacted with the other components in several ways, especially by affecting the redox level of the system, complexing ferric ions, and possibly dissolving bentonite and pyrite directly. The effect of clays was observed to be complex, affecting ligand behavior, going into solution, acting as a pH buffer and apparently adsorbing one or more iron species.

## Acknowledgements

We thank the Dept. of Energy (Grant No. DE-FG02-93ER 14397) for support of this research and Martin Schoonen for his very helpful comments and suggestions. (SB)

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