



Magnetite dissolution in siliceous sediments

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[1] Magnetite dissolution, and consequent loss of magnetization, is widely observed in reducing sedimentary environments, where the decrease in Eh-pH values with depth is driven by bacterially mediated degradation of organic carbon. We have observed low magnetizations in sediments with elevated pore water silica concentrations that arise from diagenesis of biogenic silica and/or silicic volcanic ash. These depletions in magnetization are greater than can be accounted for by dilution with magnetite-poor sediments and suggest that postdepositional destruction of magnetite has occurred. Biosiliceous sediments usually also contain elevated concentrations of organic carbon, which makes it difficult to separate organic-carbon-related magnetite dissolution from other possible mechanisms for magnetite dissolution. However, the extent of magnetite dissolution in the sedimentary sequences that we have studied is not obviously related to the redox-state of the environment. This suggests that other mechanisms might have given rise to magnetite dissolution in these siliceous sediments. Thermodynamic calculations indicate that magnetite is unstable under conditions of elevated dissolved silica concentrations (and appropriate Eh-pH conditions) and predict that magnetite will break down to produce iron-bearing smectite. A survey of magnetic susceptibility and pore water geochemical data from widely distributed Ocean Drilling Program sites supports this observed link between high dissolved silica concentrations and low magnetic susceptibilities. This observed link also holds for environments with low biogenic silica productivity (and low organic carbon content) but with high interstitial silica concentrations due to dissolution of silicic volcanic ashes. Dissolution of magnetite is therefore predicted to be a common feature of siliceous sedimentary environments.

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1. Introduction

[2] There is considerable interest in the magnetic properties of marine sediments because of their potential to provide near-continuous records of variations in the polarity and intensity of the Earth's magnetic field. Such records can, in turn, be utilized to develop a high-resolution stratigraphic tool for precise dating of sediments that lack suitable material for applying stable and radiogenic isotope techniques. However, diagenesis can compromise paleomagnetic analyses because it can significantly modify the magnetic properties of sediments due to oxidation [Henshaw and Merrill, 1980] or dissolution [Karlin and Levi, 1983] of detrital magnetite (Fe_3O_4) grains (the principal carrier of magnetization in marine sediments).

[3] Significant down-core changes in magnetization of marine sediments are generally seen in reducing environments, where bacterially mediated oxidation of organic carbon produces a decrease in pore water Eh-pH values with depth. Seawater sulfate ions provide a source of electrons for bacterial metabolism of organic carbon during bacterial sulfate reduction. Dissolved sulfide, which is highly reactive with Fe-bearing detrital minerals, including magnetite, is produced as a by-product of bacterial sulfate reduction. Sulfidization reactions are so widespread in reducing sedimentary environments that magnetite dissolution is routinely reported in studies of suboxic and anoxic marine sediments [Karlin and Levi, 1983; Channell and Hawthorne, 1990; Karlin, 1990; Leslie *et al.*, 1990; Tarduno, 1994]. Although diagenetic changes in magnetic properties are also observed in oxic sediments [Henshaw and Merrill, 1980; Smirnov and Tarduno, 2000], they do not generally result in a large decrease in magnetization because the most common alteration product in such settings, maghemite ($\gamma\text{-Fe}_2\text{O}_3$), has similar magnetic properties to magnetite [Dunlop and Özdemir, 1997].

[4] We have commonly encountered low magnetizations in sediments with high concentrations of interstitial dissolved silica. These depletions of magnetic minerals are higher than can be attributed solely to dilution by magnetite-poor sediments (such as biogenic silica) and thus imply that

magnetite dissolution has occurred. In cases where these high silica environments also have high organic carbon contents and are reducing in nature, it is likely that low magnetizations were caused by the reduction of Fe^{3+} -bearing magnetite to Fe^{2+} -bearing minerals, such as pyrite [e.g., Canfield and Berner, 1987]. In other cases, silica-rich sediments have anomalously low magnetizations despite being characterized by relatively oxic conditions today. It is possible that reductive dissolution of magnetite occurred at these sites in the past, and that diffusion of pore waters has subsequently obscured the redox state of the sedimentary environments at the time of deposition [e.g., Dickens, 2001]. However, the observation that low magnetizations are also observed in oxic sediments containing high concentrations of dissolved silica derived from volcanic ash (and relatively low initial organic carbon concentrations) has led us to consider an additional mechanism for magnetite dissolution in siliceous sediments, which we describe in this paper.

2. Evidence for Magnetite Dissolution in Siliceous Sediments

[5] The uniform manner in which high-quality lithological, geochemical, paleomagnetic and physical property data are acquired during Ocean Drilling Program (ODP) legs allows testing of the hypothesis that magnetite dissolution is linked to sediments with high pore water silica concentrations. We have therefore compared magnetic susceptibilities, pore water silica levels and other relevant data from diverse ODP sites in order to test this hypothesis.

2.1. North Pacific Ocean

[6] Sediments recovered from the North Pacific Ocean during ODP Leg 145 contain thick intervals rich in biogenic silica [Rea *et al.*, 1993]. Clay-rich sediments yielded high-quality paleomagnetic data for all the Leg 145 sites, but biogenic silica-rich sediments consistently yielded weak and unstable magnetizations [Weeks *et al.*, 1995]. The general trends are evident in Figure 1, where we show magnetic susceptibility, pore water silica, sulfate

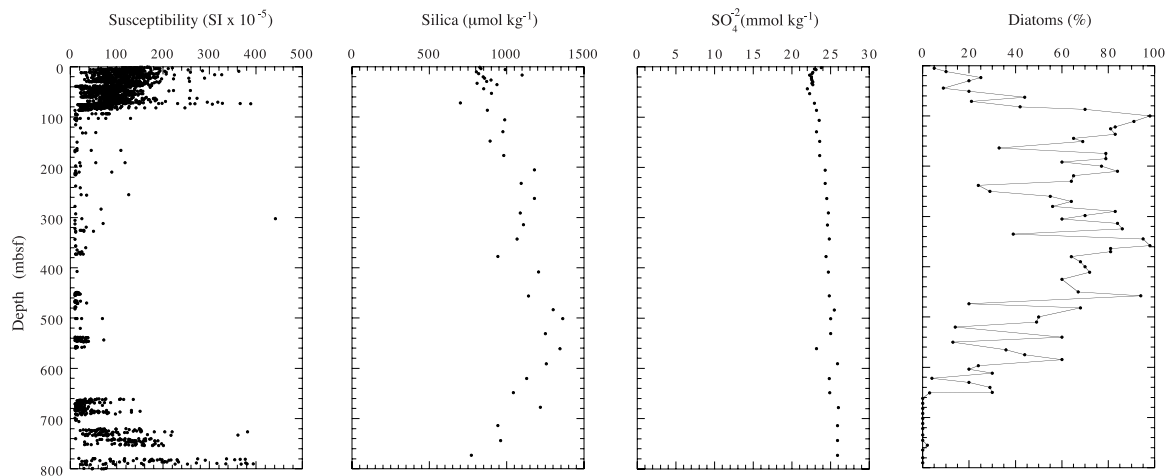


Figure 1. Magnetic susceptibility, pore water silica and sulfate concentrations (all from direct measurements on recovered core) and percentage diatom data (from smear slide analyses) for ODP Hole 883B [Rea *et al.*, 1993].

concentrations, and diatom abundances for Site 883. Magnetite is the dominant magnetic mineral at this site and magnetic susceptibility is a good indicator of magnetite concentration [Roberts *et al.*, 1995]. In addition, Roberts *et al.* [1995] observed that magnetite grains are coarser in diatom-rich intervals of Leg 145 sediments and inferred that fine-grained magnetite was preferentially dissolved via diagenetic reactions.

[7] Average susceptibility above 80 meters below seafloor (mbsf) is $100 \text{ SI} \times 10^{-5}$ ($\pm 1\sigma$) and falls to $24 \pm 2 \text{ SI} \times 10^{-5}$ in the interval between 80 and 570 mbsf. This decrease in magnetic susceptibility coincides with an increase in diatom abundance (Figure 1; Table 1) [Rea *et al.*, 1993]. Below 660 mbsf (there are no magnetic susceptibility data between 570 and 660 mbsf), the average susceptibility rises to $87 \pm 4 \text{ SI} \times 10^{-5}$ and diatom abundance falls to almost zero. Simple dilution of the magnetite-bearing sediment by diatoms would only reduce the average magnetic susceptibility from 100 to $46 \text{ SI} \times 10^{-5}$ between the upper 80 mbsf and the underlying diatom-rich interval, as diatoms only constitute $\sim 50\%$ of the sediments in this interval. Hence some other explanation must be sought to explain the 74% decrease in susceptibility for the interval between 80 and 570 mbsf. Dissolved silica concentrations are also markedly higher ($1110 \pm 35 \mu\text{mol kg}^{-1}$) in the low-susceptibility interval compared to the overlying ($870 \pm 24 \mu\text{mol kg}^{-1}$) and underlying ($852 \pm 141 \mu\text{mol kg}^{-1}$) intervals

with higher susceptibilities. Although there is a comparatively large spread in dissolved silica concentrations in the lowest interval, these values are statistically significantly lower than those in the overlying interval. Pore water sulfate values do not fall much below seawater values, which indicates that sulfate reduction is not currently occurring in these sediments.

2.2. Antarctic Margin

[8] ODP Site 1165, offshore of Prydz Bay, Antarctica, also contains intervals marked by anomalously low magnetic susceptibilities [Florindo *et al.*, 2003]. At this site, susceptibility decreases down-core from average values of $25 \pm 1 \text{ SI} \times 10^{-5}$ in the upper 120 mbsf to $4.0 \pm 0.1 \text{ SI} \times 10^{-5}$ for the interval between ~ 120 and 360 mbsf, and then increases to average values of $29 \pm 1 \text{ SI} \times 10^{-5}$ below 360 mbsf (Figure 2). The relationship with biogenic silica abundances is less clear than for Site 883. For example, smear slide analyses suggest that biogenic silica abundances remain essentially unchanged between the intervals 0 to 120 mbsf ($19.2 \pm 3.1\%$) and 120 to 360 mbsf ($19.4 \pm 2.2\%$), but fall to only $6.3 \pm 1.0\%$ in the interval between 360 and 1000 mbsf (Figure 2) [Florindo *et al.*, 2003]. Hence it is apparent that the change in susceptibilities cannot be solely attributed to dilution by biogenic silica. Again, however, the low susceptibility interval coincides with elevated dissolved silica concentrations (Figure 2; Table 1). It

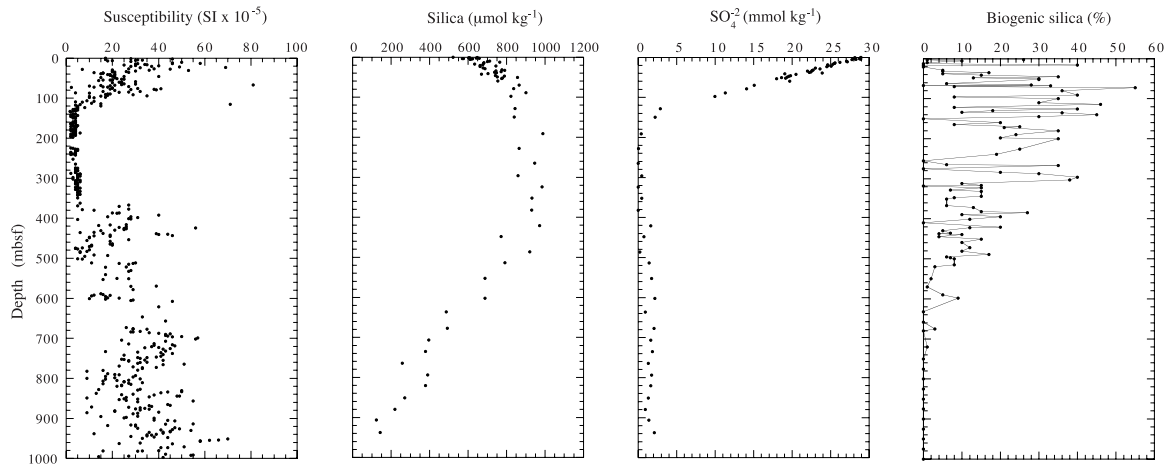


Figure 2. Magnetic susceptibility, pore water silica and sulfate concentrations (all from direct measurements on recovered core) and percentage biogenic silica (diatoms and radiolaria) data from smear slide analyses for ODP Hole 1165C [O'Brien *et al.*, 2001].

is noteworthy that the magnetic properties of the sediment at this site are not obviously related to SO₄²⁻ reduction, because relatively high susceptibilities are observed in the deepest sediments where SO₄²⁻ concentrations are greatly depleted.

2.3. Southwest Pacific Ocean

[9] ODP Site 1124 was drilled offshore of the northeast coast of New Zealand into sediments that consist largely of nannofossil chalk [Carter *et al.*, 1999]. Portions of the sedimentary record are characterized by greenish-gray beds that have a conspicuous biosiliceous component. These beds approximately coincide with an interval between

~290 and 419 mbsf that is characterized by low magnetic susceptibilities (Figure 3). The pore water data set is less extensive at this site compared to sites 883 and 1165. Nevertheless, the low susceptibility zone is again noteworthy for its high dissolved silica concentrations relative to the surrounding layers with higher susceptibilities (Figure 3; Table 1). No smear slide data are available for Site 1124, but gamma ray logs indicate that %K falls from ~1.4 over the interval where magnetic susceptibility is high ($41 \pm 1 \text{ SI} \times 10^{-5}$) to ~0.6 in the zone of low magnetic susceptibility ($8.0 \pm 0.1 \text{ SI} \times 10^{-5}$) (Figure 3) [Carter *et al.*, 1999]. If %K is taken as a crude measure of the relative fraction of detrital matter, this implies that

Table 1. Age, Magnetic Susceptibility, and Pore Water Data for Selected ODP Sites^a

| ODP Site (Location) | Interval, mbsf | Approximate Age, Ma | Mean Susceptibility (SI × 10 ⁻⁵) | Mean Dissolved Silica, μmol kg ⁻¹ | Mean Dissolved Sulfate, mmol kg ⁻¹ |
|--------------------------------|----------------|---------------------|--|--|---|
| 883 (North Pacific Ocean) | 0–80 | 0–2.6 | 100 ± 1 (n = 1437) | 870 ± 24 (n = 15) | 23 ± 0.1 (n = 15) |
| | 80–570 | 2.6–14 | 24 ± 2 (n = 502) | 1110 ± 35 (n = 18) | 24 ± 0.2 (n = 18) |
| | 660–800 | 30–52 | 87 ± 4 (n = 433) | 852 ± 141 (n = 5) | 26 ± 0.3 (n = 5) |
| 1165 (Prydz Bay, Antarctica) | 0–120 | 0–9 | 25 ± 1 (n = 117) | 709 ± 13 (n = 42) | 23 ± 1 (n = 42) |
| | 120–360 | 9–16 | 4 ± 0.1 (n = 124) | 908 ± 22 (n = 8) | 1 ± 0.4 (n = 8) |
| | 360–1000 | 16–22 | 29 ± 1 (n = 270) | 517 ± 66 (n = 18) | 1 ± 0.2 (n = 18) |
| 1124 (Southwest Pacific Ocean) | 0–290 | 0–18 | 41 ± 1 (n = 6064) | 646 ± 35 (n = 17) | 24 ± 0.3 (n = 17) |
| | 290–419 | 18–26 | 8 ± 0.1 (n = 2864) | 1088 ± 46 (n = 5) | 20 ± 1 (n = 5) |
| | 419–500 | 26–65 | 42 ± 4 (n = 1085) | 835 ± 133 (n = 2) | 19 ± 0.3 (n = 2) |
| 998 (Caribbean Sea) | 0–175 | 0–14 | 27 ± 0.4 (n = 3278) | 325 ± 111 (n = 7) | 26 ± 1 (n = 7) |
| | 175–520 | 14–30 | 3 ± 0.1 (n = 3613) | 858 ± 61 (n = 11) | 23 ± 0.3 (n = 11) |

^a Ages for ODP sites 883, 1165, 1124, and 998 are from Weeks *et al.* [1995], Florindo *et al.* [2003], Carter *et al.* [1999], and Siggurdson *et al.* [1997], respectively.

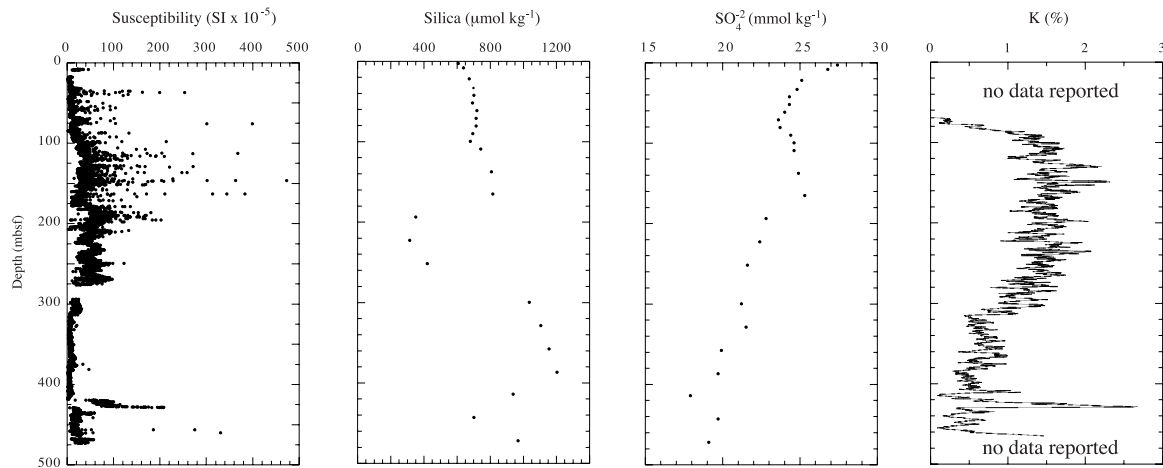


Figure 3. Magnetic susceptibility, pore water silica and sulfate concentrations (all from direct measurements on recovered core) and percentage K data (from down-hole logging) for ODP Hole 1124C [Carter *et al.*, 1999].

the observed susceptibilities are about 2 times lower than would be expected by simple dilution by magnetite-poor sediments.

2.4. Caribbean Sea

[10] High dissolved silica levels are not restricted to sediments enriched in biogenic silica. ODP Site 998 from the Caribbean Sea contains a large number of silica-rich volcanic ash layers that have undergone diagenetic alteration, resulting in elevated concentrations of dissolved silica in the pore waters [Sigurdson *et al.*, 1997]. This raises the possibility that marine sediments in the vicinity of silicic volcanoes, with low biogenic silica productivity, might

provide an alternative source of silica for diagenetic reactions that might affect the stability of magnetite.

[11] At Site 998, magnetic susceptibilities are relatively high in the upper ~175 m of the sediment column (average of $27 \pm 0.4 \text{ SI} \times 10^{-5}$) and then reach low average levels ($3 \pm 0.1 \text{ SI} \times 10^{-5}$) between 175 and 800 mbsf. Below ~800 mbsf, susceptibilities increase down to the base of the hole at ~900 mbsf. The interval of low magnetic susceptibilities is approximately coincident with a higher incidence of volcanic ash layers (Figure 4) [Sigurdson *et al.*, 1997]. Although high magnetic susceptibilities are also found in the region 100–170 m where ash layers are abundant, there is a

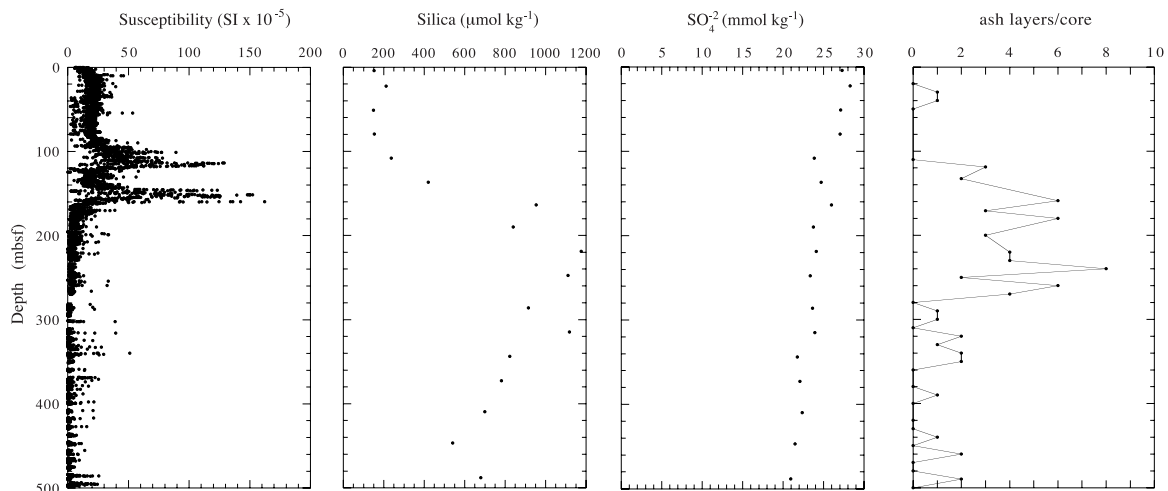


Figure 4. Magnetic susceptibility, pore water silica and sulfate concentrations and number of ash layers per core (all from direct measurements on recovered core) for ODP Hole 998A [Sigurdson *et al.*, 1997].



strong coincidence of elevated dissolved silica levels and low magnetic susceptibilities (Figure 4; Table 1) in the region 200–500 m (data not available below 520 mbsf).

2.5. Summary

[12] Diatoms and radiolaria play an important role in the delivery of organic carbon to the deep-sea [DeMaster *et al.*, 1991, 1996; Tréguer *et al.*, 1995; Nelson *et al.*, 1996]. Zones with low magnetic susceptibilities, of the type identified above, are therefore generally attributed to dissolution of magnetite associated with organic carbon degradation under sulfate-reducing conditions [Karlin and Levi, 1983; Canfield and Berner, 1987]. While there is evidence of past episodes of reductive magnetite dissolution within sediments of the North Pacific red clay province in which depositional conditions are now strongly oxidizing (e.g., as shown by the presence of lower Fe/Sc and higher Ba/Sc ratios [Arnold *et al.*, 1995; Dickens and Owen, 1996]), it is significant that anomalously low magnetic susceptibilities are also observed in sediments with high dissolved silica concentrations from ODP Site 998 in the Caribbean Sea. These sediments are oxic in character, they do not contain high concentrations of biogenic silica and they show no evidence of ever having had high concentrations of organic carbon. Hence, it is appropriate to consider whether mechanisms other than reductive dissolution of magnetite might be responsible for the low magnetic susceptibilities in environments with elevated concentrations of pore water silica.

3. Thermodynamics

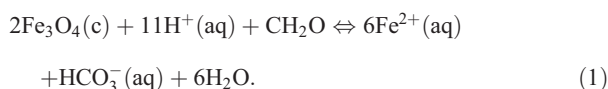
[13] In this section, we consider the thermodynamics of magnetite stability during sedimentary diagenesis with respect to three groups of alteration phases that are commonly observed in marine sediments. These phases are: hematite (α -Fe₂O₃) or goethite (α -FeOOH) or lepidocrocite (γ -FeOOH) (all are characteristic of magnetite alteration under oxic conditions), pyrite (characteristic of magnetite alteration under reducing conditions) and smectite. We do not consider the partial oxidation of magnetite to maghemite, which occurs in oxic marine

sediments, because this reaction does not involve a significant decrease in magnetic susceptibility [Dunlop and Özdemir, 1997]. In contrast, authigenic Fe-oxyhydroxides, hematite, pyrite and clay minerals, which are common components of marine sediments, have much lower magnetic susceptibilities than magnetite. Formation of these phases from magnetite will therefore result in a marked reduction of magnetic susceptibility.

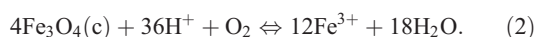
3.1. Oxic Diagenesis

[14] In Figure 5a, the relative stability fields of Fe²⁺ and Fe³⁺ are illustrated for the sediment-water interface (i.e., with the same dissolved concentrations as in typical bottom waters) and in the absence of Fe-bearing solid phases. Under these conditions, the dominant dissolved Fe species is the relatively insoluble Fe³⁺.

[15] If we first consider the simplest case, where magnetite is the only Fe-bearing solid phase present, then dissolution is the only process that influences its stability. Where microbially mediated oxidation of organic carbon results in Fe²⁺ being the dominant species in solution, the reaction can be written as

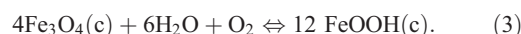


[16] If dissolution of magnetite takes place under oxic conditions (i.e., dissolved oxygen is present in the pore waters) where Fe³⁺ is the dominant species in solution, then the reaction can be written as



Under oxic seafloor conditions, magnetite would be stable but it would be predicted to dissolve as conditions become more reducing (Figure 5b).

[17] The oxidation reaction of magnetite to γ -FeOOH can be written as



Magnetite is predicted to be unstable with respect to phases such as γ -FeOOH under oxic seafloor conditions (Figure 5c). However, the presence of magnetite in oxic deep sea sediments that have been buried for millions of years suggests that the

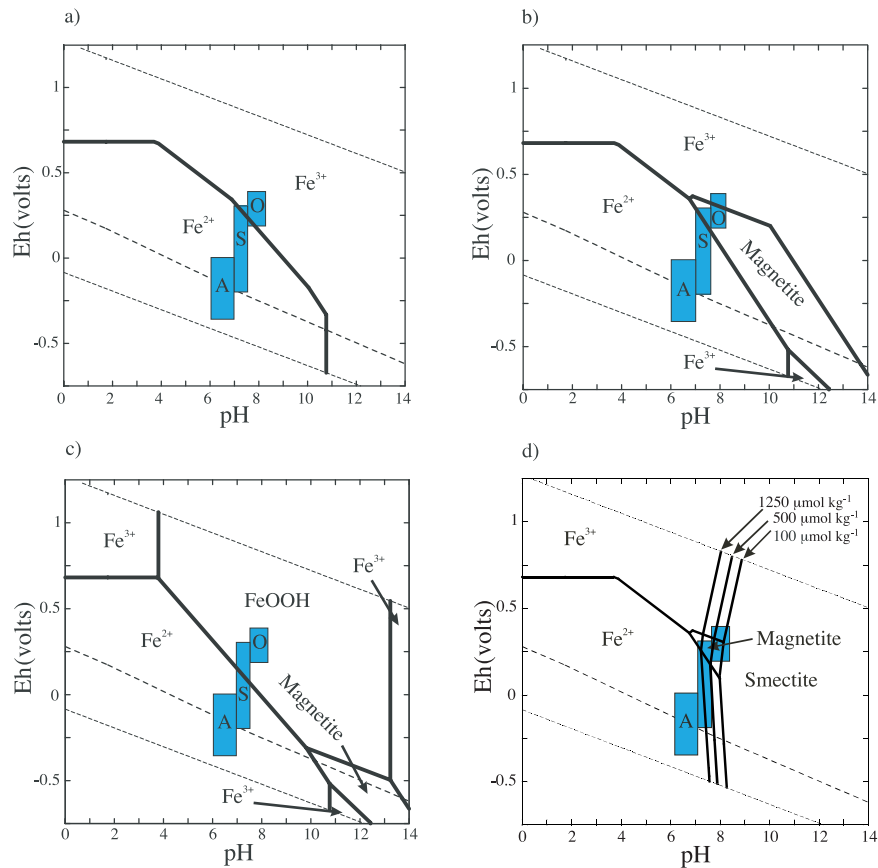
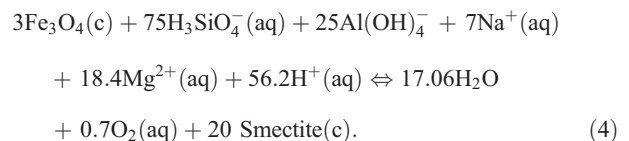


Figure 5. Eh-pH diagrams illustrating the relative stabilities of magnetite, Fe-oxyhydroxide, smectite and dissolved iron in marine waters at 2°C, and dissolved iron and silica concentrations typical of oxic diagenesis. Solid lines indicate boundaries between iron-bearing minerals and dissolved iron species. The heavy dashed line illustrates the boundary between SO_4^{2-} (above the line) and HS^- and S^{2-} (below the line). The fine dashed lines delineate the stability limits of water. The blue boxes indicate the Eh-pH conditions during oxic (O), suboxic (S) and anoxic (A) diagenesis [Boudreau, 1997, and references therein]. All of the thermodynamic diagrams were calculated using data from Helgeson *et al.* [1978], Delaney and Lundeen [1990], and Johnson *et al.* [1992]. (a) Dissolved iron speciation with dissolved iron concentrations of $\sim 1 \text{ nmol kg}^{-1}$; i.e., typical of oxic ocean water. The concentrations of dissolved ions are taken from Bruland [1983]. (b) Magnetite stability field with dissolved iron concentrations of $\sim 1 \text{ nmol kg}^{-1}$. (c) Relative stabilities of magnetite and authigenic Fe-oxyhydroxide with dissolved iron concentrations of $\sim 1 \text{ nmol kg}^{-1}$. (d) Relative stabilities of magnetite and smectite with dissolved iron concentrations of $\sim 1 \text{ nmol kg}^{-1}$, and dissolved silica concentrations of 100, 500 and $1250 \text{ } \mu\text{mol kg}^{-1}$.

kinetics of this reaction are slow at the low temperatures characteristic of the ocean floor. It should be noted that the hematite stability field is indistinguishable from that shown for FeOOH in Figure 5c. Hematite and FeOOH both have low magnetic susceptibilities, therefore the precise mineralogy of the oxidized Fe phase does not influence the arguments presented here.

[18] Clay minerals represent the other major class of Fe-bearing authigenic solid phases in marine sediments, and, because they also have low magnetic susceptibilities it is appropriate to consider

their stability relative to magnetite under oxic conditions. We specifically consider the case of the smectite group because it is one of the most common authigenic clays. Hence the appropriate reaction can be written as



[19] There are two major difficulties in constructing a thermodynamic model of clay mineral stabil-



ity. First, clay minerals, such as smectite, have a wide range of compositions. It is therefore impossible to define stability limits for smectite that would be applicable to all marine sediments. In addition, the uncertainties inherent in all thermodynamic data are magnified in minerals that have high values for the exponents of dissolved species in the equilibrium expression. Despite these uncertainties, trends in the size and position of mineral stability fields in Eh-pH space can yield useful information.

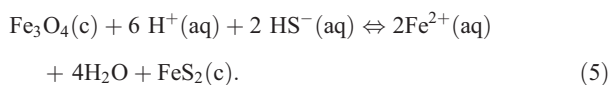
[20] Bottom waters in the deep oceans have dissolved silica concentrations of about $100 \mu\text{mol kg}^{-1}$ [Bruland, 1983]. Within the oxic zone of marine sediments, early diagenesis leads to an increase in dissolved silica concentrations, primarily due to dissolution of biogenic silica tests and other reactive silica-bearing phases such as volcanic ash and (in sites close to mid-ocean ridges) basaltic glass [Gieskes, 1983]. The resultant pore water silica concentrations are variable, but concentrations of $\sim 500 \mu\text{mol kg}^{-1}$ are typical in the upper portion of the sediment column [Gieskes, 1983]. Under such conditions, the smectite stability field expands to lower pH values such that oxic sediment pore waters are poised close to the magnetite-smectite transition zone. In biogenic silica-rich sediments, rapid recrystallization of diatom and radiolaria frustules can result in pore water dissolved silica concentrations up to $1250 \mu\text{mol kg}^{-1}$ [Dixit et al., 2001]. Similarly, the reactive nature of volcanic ash can also result in high pore water silica concentrations [Siggurdson et al., 1997]. As the concentration of dissolved silica increases, the smectite stability field expands to lower pH values, such that magnetite is predicted to be unstable in oxic sediments when silica concentrations reach $1250 \mu\text{mol kg}^{-1}$ (Figure 5d).

3.2. Suboxic-Anoxic Diagenesis

[21] Most marine sediments contain organic carbon, and microbially mediated oxidation of this organic carbon leads to a decrease in the Eh and pH of the sediment pore waters that will in turn affect the stability of magnetite. With progressive oxidation of the organic carbon, concentrations of dissolved oxygen are reduced to close to zero (suboxic con-

ditions). As diagenesis progresses, dissolved Fe^{3+} is reduced to Fe^{2+} and dissolved SO_4^{2-} is reduced to H_2S and HS^- (anoxic conditions) [Froelich et al., 1979]. This results in an increase in dissolved Fe concentrations from $\sim 1 \text{ nmol kg}^{-1}$ in bottom waters to levels as high as $\sim 100 \mu\text{mol kg}^{-1}$. Dissolved SO_4^{2-} concentrations decrease from typical values of 28 mmol kg^{-1} in bottom waters to near zero in totally anoxic waters. Dissolved sulfide concentrations increase from zero in oxic bottom waters to values that are highly variable in reducing pore waters, but concentrations of $\sim 3 \text{ mmol kg}^{-1}$ are not unusual.

[22] The increase in dissolved iron concentrations in reducing environments only results in a small expansion of the dissolved Fe^{3+} field, so that the dissolved Fe speciation at elevated iron concentrations is essentially the same as that illustrated in Figure 5a. As conditions become more reducing, magnetite undergoes dissolution and is replaced by pyrite [Canfield and Berner, 1987]:



If the relative stabilities of magnetite and pyrite are considered, then the increase in dissolved Fe activity results in an expansion of the magnetite stability field (Figure 6a) at higher Eh values. However, under suboxic and anoxic conditions, the presence of dissolved sulfide leads to the replacement of magnetite by pyrite (Figure 6a). This is the main cause for the lowering of magnetization in reducing sediments [Karlin and Levi, 1983; Channell and Hawthorne, 1990; Karlin, 1990; Leslie et al., 1990; Tarduno, 1994]. It should be noted that this reaction is favored even in the presence of low levels of dissolved SO_4^{2-} . The common association of SO_4^{2-} reduction and magnetite dissolution suggests that kinetics are not an inhibiting factor in this reaction.

[23] Dissolved silica concentrations typically reach $500 \mu\text{mol kg}^{-1}$ during suboxic-anoxic diagenesis, with concentrations reaching $1250 \mu\text{mol kg}^{-1}$ in sediments containing abundant biogenic silica and/or volcanic ash [Gieskes, 1983; Dixit et al., 2001]. Again, an increase in dissolved silica concentra-

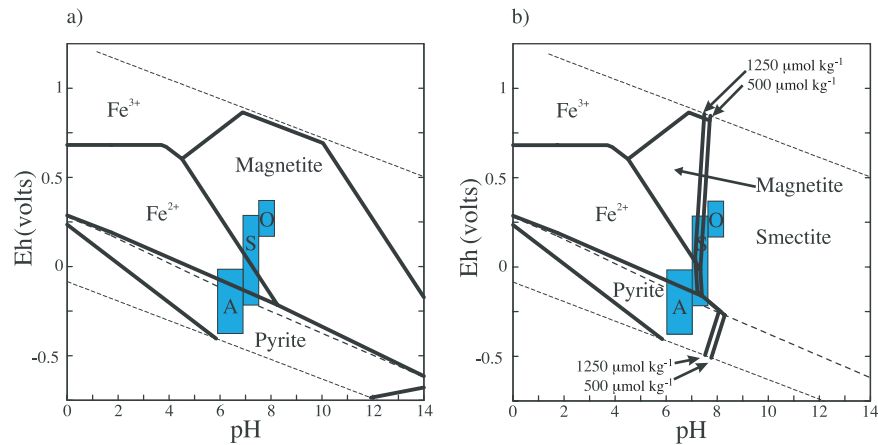


Figure 6. Eh-pH diagrams illustrating the relative stabilities of magnetite, pyrite, smectite and dissolved iron in marine waters at 2°C, and dissolved iron and silica concentrations typical of suboxic-anoxic diagenesis. (a) Relative stabilities of magnetite and pyrite with dissolved iron concentrations of 100 $\mu\text{mol kg}^{-1}$. (b) Relative stabilities of magnetite, pyrite and smectite with dissolved iron concentrations of 100 $\mu\text{mol kg}^{-1}$, and dissolved silica concentrations of 500 and 1250 $\mu\text{mol kg}^{-1}$.

tions results in an expansion of the smectite stability field to lower pH values. As a result, only a small proportion of suboxic sediments lie in the magnetite stability field where dissolved silica concentrations reach 1250 $\mu\text{mol kg}^{-1}$ (Figure 6b).

4. Discussion

[24] Dissolution of magnetite and precipitation of pyrite is primarily dependent on the concentration and reactivity of organic carbon, the concentration of magnetite and on the pore water sulfate concentration [Canfield and Berner, 1987]. The possibility of a wide range of variation in the factors that affect the stability of magnetite (e.g., amounts of organic carbon, magnetite, etc.) means that it is impossible to specify a unique set of Eh-pH conditions that define magnetite stability during diagenesis. Nevertheless, some general observations are possible.

[25] Although magnetite is stable under oxic conditions at the sediment-water interface (Figure 5b), it only requires a relatively small early diagenetic decrease in pH and Eh for magnetite to become unstable and to undergo reductive dissolution. However, early diagenesis also leads to an increase in dissolved iron concentrations that leads to an expansion of the magnetite stability field (Figure 6a). The net result of these two processes is that magne-

tite remains stable until pH drops from ~ 8 to ~ 7 and Eh drops from 0.3 to 0.0 V (Figure 6a).

[26] The Eh-pH diagram shown in Figure 5b predicts that magnetite is unstable where dissolved SO_4^{2-} is replaced by HS^- as the stable dissolved sulfur species. This is consistent with the observation that magnetite grains may be rimmed by pyrite in reducing sediments [Canfield and Berner, 1987]. In terms of the ODP sites discussed above, reductive dissolution of magnetite may have occurred in the low susceptibility zone ($4 \pm 0.1 \text{ SI} \times 10^{-5}$) of Site 1165 from 120–360 mbsf, where dissolved SO_4^{2-} levels are close to zero ($1 \pm 0.4 \text{ mmol kg}^{-1}$) [O'Brien et al., 2001]. However, it does not resolve the question as to why the underlying sediments (360–1000 mbsf) have magnetic susceptibilities ($29 \pm 1 \text{ SI} \times 10^{-5}$) that are higher than those of the uppermost (0–120 mbsf) sediments ($25 \pm 1 \text{ SI} \times 10^{-5}$). This is despite the fact that the SO_4^{2-} concentrations of the lowermost pore waters are only $1 \pm 0.2 \text{ mmol kg}^{-1}$, whereas those of the upper 120 mbsf are only slightly lower than seawater ($23 \pm 0.1 \text{ mmol kg}^{-1}$) (Table 1). It is worth noting that magnetite dissolution and pyrite growth are predicted at Eh-pH conditions where SO_4^{2-} is still the dominant dissolved sulfur species (Figure 5b). In sediments that contain thin zones of sulfate reduction (e.g., in the presence of thin sapropel layers or organic-rich turbidites) magne-



tite can undergo reductive dissolution and the initial depletion in dissolved SO_4^{2-} concentrations can be obscured by subsequent diffusion from overlying and underlying pore waters [cf. *Passier et al.*, 1998]. Hence, even though dissolved SO_4^{2-} concentrations are only slightly below seawater values ($24 \pm 0.2 \text{ mmol kg}^{-1}$) between 80 and 570 mbsf at ODP Site 883, we cannot dismiss the possibility that the low magnetic susceptibilities in this interval are due to pyrite formation at the expense of magnetite dissolution; i.e., it is possible that these sediments were more reducing in the past and that subsequent diffusion of pore waters has raised SO_4^{2-} levels that were once much lower. However, these possibilities are not supported by the observation that the overlying sediments have higher magnetic susceptibilities ($100 \pm 1 \text{ SI} \times 10^{-5}$), but lower SO_4^{2-} concentrations ($23 \pm 0.1 \text{ mmol kg}^{-1}$); i.e., there is no relationship between magnetic susceptibility and the present redox state of the pore waters and dissolved SO_4^{2-} is not diffusing down-core to erase a zone that was originally depleted in SO_4^{2-} . Similarly, the presence of low magnetic susceptibilities ($8 \pm 0.1 \text{ SI} \times 10^{-5}$) in the 290–419 mbsf interval of Site 1124 could be accounted for by reductive dissolution of magnetite and precipitation of pyrite. This hypothesis would be supported by the lowered dissolved SO_4^{2-} concentrations ($20 \pm 1 \text{ mmol kg}^{-1}$), but it would not explain why the underlying sediments have even lower SO_4^{2-} concentrations ($19 \pm 0.3 \text{ mmol kg}^{-1}$) and much higher magnetic susceptibilities ($42 \pm 4 \text{ SI} \times 10^{-5}$).

[27] As noted above, it is not possible to fix the absolute position of the smectite-magnetite transition in Eh-pH space. Nevertheless, it is apparent that increases in dissolved silica concentrations from bottom water values of $\sim 100 \text{ } \mu\text{mol kg}^{-1}$ to values of 500–1250 $\mu\text{mol kg}^{-1}$ result in a significant decrease in the size of the magnetite stability field (Figures 5d and 6b). While pyrite is still predicted to be the stable phase under anoxic conditions, thermodynamic considerations suggest that alteration of magnetite to smectite is favored under oxic-suboxic conditions and high silica concentrations. In this context, it is noteworthy that in the four ODP cores considered above, all zones of low magnetic sus-

ceptibility are coincident with zones of elevated dissolved silica concentrations (Table 1). We cannot preclude the possibility that reductive dissolution of magnetite and precipitation of pyrite occurred at some of these sites. However, the lack of a clear relationship between redox indices (such as dissolved SO_4^{2-} concentrations) and magnetic susceptibilities (both within and between sites) suggests that other explanations, such as magnetite dissolution as a result of elevated interstitial silica concentrations and authigenic formation of smectite, are worthy of consideration. For example, as noted above, the interval of low magnetic susceptibility at Site 883 is not obviously related to the redox state of the sediments, but it is characterized by higher dissolved silica concentrations than the underlying and overlying sediments (Table 1). A similar pattern emerges from the other three sites listed in Table 1. At each site, the zone of anomalously low magnetic susceptibility is characterized by higher dissolved silica concentrations than the adjacent intervals of higher magnetic susceptibility.

[28] Direct observation of alteration of magnetite to smectite is required to fully substantiate the hypothesis that the magnetite-smectite reaction plays a role in magnetite dissolution in sediments containing high concentrations of dissolved silica. Authigenic smectite has been recognized in a wide variety of marine and saline lake settings [*Güven*, 1988], and has been synthesized in the laboratory at low temperatures under conditions that are appropriate to low-temperature diagenesis [*Decarreau and Bonnin*, 1986]. There does not therefore appear to be any kinetic barrier to the magnetite-smectite reaction. The presence of abundant diatoms in the sediments at several of the sites considered here might provide further impetus for the magnetite-smectite reaction because authigenic smectite has been observed growing directly on diatom frustules [*Hoffert*, 1980; *Badaut and Risacher*, 1983].

[29] We know of one example that provides direct evidence for the reactions suggested above. Tuffaceous sediments of the Balder Formation (Lower Tertiary) in the North Sea are composed mainly of altered volcanic ash and siliceous microfossils, which show widespread evidence of authigenic

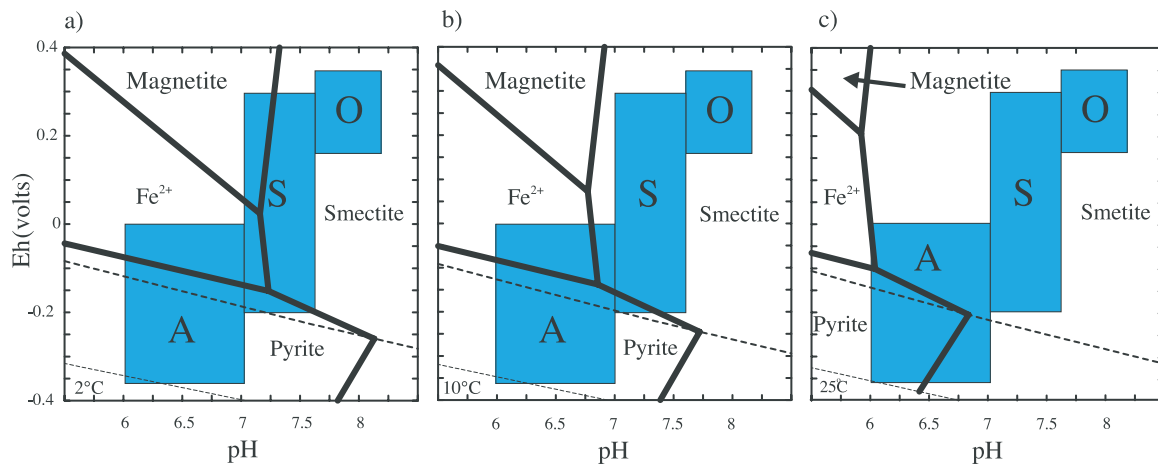


Figure 7. Eh-pH diagrams illustrating the relative stabilities of magnetite, pyrite, and smectite at (a) 2°C, (b) 10°C, and (c) 25°C, with dissolved iron concentrations of 100 $\mu\text{mol kg}^{-1}$ and dissolved silica concentrations of 1000 $\mu\text{mol kg}^{-1}$.

smectite formation [Malm *et al.*, 1984; Bjørlykke and Aagaard, 1992]. Electron micrographs indicate authigenic smectite coatings on volcanic ash particles that have undergone dissolution in the grain interiors [Malm *et al.*, 1984]. The clay mineral assemblage is interpreted to have resulted from the high volcanic debris and diatomaceous ooze contents, which produced high silica concentrations in the pore waters, and which reacted with unstable Fe- and Mg-rich volcanogenic minerals that acted as precursors for smectite formation [Malm *et al.*, 1984; Bjørlykke and Aagaard, 1992]. The ubiquity of clay minerals and the generally low concentrations of magnetite in marine sediments, coupled with the fact that the magnetite-smectite transition has not previously been suggested, mean that direct textural evidence of the alteration of magnetite to smectite may have been overlooked.

[30] Finally, one of the most common occurrences of authigenic smectite arises when heated fluids circulate through sediments. For example, *Buatier et al.* [2001] observed formation of smectite in ODP sites 1029 and 1031 on the flanks of the Juan de Fuca Ridge as a result of off-axis hydrothermal circulation. The temperatures of the fluids responsible for formation of the smectites were estimated at 11–49°C, on the basis of carbonate nodule $\delta^{18}\text{O}$ geothermometry. In terms of magnetite stability, even a small increase in temperature results in a significant expansion of the smectite stability field,

such that alteration of magnetite to smectite would be favored under both oxic and suboxic conditions (Figure 7).

5. Conclusions

[31] Reductive dissolution of magnetite with precipitation of pyrite is the major documented cause of decreased magnetizations during diagenesis of marine sediments. Thermodynamic calculations suggest that this process takes place under lower Eh-pH conditions than open ocean bottom waters, but where dissolved SO_4^{2-} is still present. These calculations also indicate that magnetite should dissolve in sediments where pore water SO_4^{2-} is completely reduced to S^{2-} .

[32] Several ODP sites have been identified where anomalously low magnetic susceptibilities are found in association with high concentrations of dissolved silica. In these cases, the extent of magnetic mineral depletion is greater than can be explained by simple dilution by magnetite-poor biogenic sediments. Although Site 1165 has pore water SO_4^{2-} concentrations that fall close to zero at depths where low magnetic susceptibilities are observed, there is no consistent relationship between the measured redox-state of the pore waters and the magnetic susceptibility of the sediments. While we recognize that previous episodes of anoxic-suboxic diagenesis may have been ob-



scured by subsequent diffusion from oxygenated pore waters, the evidence for this process is not compelling and other explanations are worthy of consideration.

[33] Thermodynamic modeling suggests that magnetite becomes unstable and breaks down to form iron-bearing smectite in the presence of high dissolved silica concentrations. The exact position of the magnetite-smectite boundary is highly dependent on the stoichiometry of the smectite and on the redox state of the sediments. Despite these uncertainties, thermodynamic calculations suggest that increases in dissolved silica concentrations, of the magnitude noted in the ODP pore waters discussed in this study, result in an expansion of the stability field of smectite under Eh-pH conditions typical of oxic-suboxic diagenesis, and would favor dissolution of magnetite to form smectite.

[34] High dissolved silica concentrations are characteristic of deep-sea sediment pore waters found in association with sediments rich in biogenic silica and in those containing abundant silicic volcanic ash. We therefore hypothesize that anomalously low magnetic susceptibilities can arise in these environments as a result of diagenetic dissolution of magnetite to form smectite. Circulation of low-temperature hydrothermal fluids through sediments would also favor (and accelerate) such a reaction.

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