Kinetics of Fe(III) reduction in a marine sediment

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Introduction

The importance of reduction of Fe-oxides in marine sediments, as electron accepting process coupled to organic matter oxidation, has received increasing recognition in recent years. The findings of Canfield *et al.* (1993) indicate that up to 50 % of organic carbon oxidation in a marine sediment may proceed by reduction of Fe(III). Thamdrup *et al.* (1994) found in addition reduction of Fe(III) to be an important pathway for reoxidation of dissolved sulphides in sediments.

The source of Fe(III) in sediments is generally heterogeneous: Fe(III) may be present as different Fe-oxides of variable reactivity, as well as in clays in different coordination. Frequently only part of the Fe-oxides in sediments become reduced (Canfield *et al.*, 1992), indicating a kinetic control on the reduction of Fe-oxides. Recently, Postma (1993) presented a kinetic approach to describe the reactivity of synthetic Fe-oxides and of heterogeneous mixtures of Fe-oxides in sediments. The reactivity of polydisperse synthetic Fe-oxides was described by using the rate equation for crystal dissolution (Christoffersen, 1980).

$$J = -dn_{cr}/dt = km_0 F(m/m_0) S(C) \qquad (1)$$

Here J is the overall rate of dissolution (mol/sec), n_{cr} the amount of undissolved crystals, k the rate constant (sec^{-1}), m_0 the initial mass of crystals (mol) and m the mass of crystals at time t. $F(m/m_0)$ is a function of changing crystal sizes, morphology, reactive site density etc. during dissolution and is usually expressed as a exponential function $(m/m_0)^\gamma$. $S(C)$ is a function of the solution composition such as type and concentration of reductant used. For high concentrations of reductant, like ascorbic acid, $S(C)$ may be a constant (Postma, 1993; Banwart *et al.*, 1989) so that the reactivity of a monomineralic polydisperse crystal population can be obtained by determining $F(m/m_0)$. For example for synthetic ferrihydrite it was determined to be $(m/m_0)^{1.1}$.

The reactivity of assemblages of Fe-oxides with variable mineralogy and reactivity, such as present in natural sediments, can be thought to represent a reactive continuum described by a Gamma distribution function (Boudreau and Ruddick, 1991) which leads to an equation for the mass of solid remaining at any time t of the form

$$\frac{m}{m_0} = \left(\frac{a}{a+t}\right)^\nu \qquad (2)$$

Here a and ν are free fit parameters. The corresponding rate equation is

$$\frac{J}{m_0} = \frac{\nu}{a}\left(\frac{m}{m_0}\right)^{1+\frac{1}{\nu}} \qquad (3)$$

Eqn. 3 describes the rate of a reactive continuum as a function of a constant term times the fraction of unreacted mineral to an exponent. This formulation is almost identical to the rate equation for a polydisperse sample of crystals of a single mineral (Eqn. 1). However, where γ in Eqn. 1 can, in principle, be interpretated in physical terms, the corresponding exponent $(1 + 1/\nu)$ has only statistical significance. Likewise, the term ν/a must be considered as an apparent rate constant for a mixture. The interesting aspect is however, that both a polydisperse sample of well defined crystals and a reactive continuum of Fe-oxides can be described by a constant and exponent on m/m_0 which together characterize the intrinsic reactivity of the Fe-oxides present. The reactive continuum model is here used to describe the reactivity of iron in marine sediments of Aarhus Bay.

Materials and methods

Coastal marine sediments from Aarhus Bay, Denmark, at a water depth of 16 m were studied. The sediments consist of silty muds and the upper two cm of the sediment was fully oxidized at the time of sampling. Below this oxidized zone, intensive sulfate reduction and iron sulfide formation takes place and 5 cm depth downward, the porewater is rich in H$_2$S.

Reduction experiments were carried out by suspending sediment into 10 mM ascorbic acid at pH 3. At this level, the rate was demonstrated to be independent of the ascorbic acid concentration (Postma, 1993). The release of dissolved Fe^{2+} was followed by filtering, anoxically, aliquots through

0.2 μm membrane filters and immediate determination of Fe^{2+} with using ferrozine.

Results

Reductive dissolution experiments, with ascorbic acid at pH 3, were performed on sediments from different depths of Aarhus Bay sediments. The results displayed a very fast initial Fe^{2+} release and gradual decrease over time. About 60 % of the pool of Fe(III) in the surface sediment is demonstrated to be highly reactive, while the remaining 40 % is seen to react much more sluggishly. With depth an decrease is observed in the total amount of iron which is extracted by ascorbic acid. This removal seems to take place by shortening the steep initial part of the Fe^{2+}-release curves which can be interpreted as progressive consumption of the most reactive part of the Fe-oxides present in the sediments.

The Fe^{2+} release by ascorbic acid in the 0-2 cm depth interval was modelled with the Gamma distribution function using the total amount of Fe^{2+} extractable by ascorbic acid as m_0 and the best fit of Eqn. 2 is:

$$\frac{m}{m_0} = \left(\frac{554}{554 + t}\right)^{2.1} \qquad (5)$$

The corresponding rate equation is:

$$\frac{J}{m_0} = 1.7 \times 10^{-3} \left(\frac{m}{m_0}\right) \qquad (5)$$

Fits of the rate equation at depths > 2 cm resulted in exponents over m/m_0 ranging from 1.8–2.0 and for the apparent rate constant of 1.5–2.2×10^{-3} sec^{-1}. These results quantify the much wider range in reactivity for the pool of Fe(III) in a sediment as compared to synthetic ferrihydrite.

In a ideal steady state situation, a pool of reactive iron is present in the oxidized surface layer and is then gradually reduced over depth. The total amount of iron extractable by ascorbate in the 0–2 depth interval should then be used as m_0 for modeling Fe-oxide reactivity at all greater depths.

Since the pool of Fe(III) remaining at greater depth is the more refractory part of that initiallly present at 0–2 cm depth, then their reduction curves on m/m_0–time plots must be subsets of the 0–2 cm interval reduction curve, starting at greater time. These can be obtained by substitution of the initial m/m_0 value as starting point for each depth in Eqn. 4. It was found that the data distribution for depths greater than 2 cm is close to the 0–2 cm data which seems to confirm the gradual reduction of the initial pool of Fe(III) over depth as predicted by Eqn. 5 under steady state conditions.

Conclusion

The results of this study indicate that the reactivity of the Fe(III) pool in a marine sediment can be described quantitatively by using a Gamma distribution rate law, and demonstrates the gradual comsumption of the most reactive part of the Fe(III) pool during diagenesis that can be described by the Gamma distribution rate law.

References

Banwart S., Davies S. and Stumm W. (1989) *Colloids and Surfaces* **39**, 303–9.

Boudreau B.P. and Ruddick B.R. (1991) *Amer. J. Sci.* **291**, 507-538.

Canfield D.E., Raiswell R. and Bottrell S. (1992) The reactivity of sedimentary iron minerals towards sulfide. *Amer. J. Sci.* **292**, 659–83.

Canfield D.E., Jørgensen B.B., Fossing H., Glud R., Gundersen J., Ramsing N.B. Thamdrup B., Hansen J.W., Nielsen L.P. and Hall P.O.J. (1993) *Mar. Geol.* **113**, 27–40.

Christoffersen J., (1980) *J. Crystal Growth* **49**, 29–44.

Postma D. (1993) T*Geochim. Cosmochim. Acta* **57**, 5027–34.

Thamdrup B., Fossing H. and Jørgensen B.B. (1994) Manganese, iron and sulfur cycling in a coastal marine sediment (Aarhus Bay, Denmark) *Geochim. Cosmochim. Acta* submitted.