

Chemical Kinetics in Aquatic Systems is an upper level course for graduate students in chemical oceanography. The course description, outline and bibliography from last time are given below.

CHEMICAL KINETICS IN AQUATIC SYSTEMS

(Ocean 580) 3 credits

INSTRUCTOR: Steven Emerson

This course explores chemical processes that are not at equilibrium in the marine geochemical system. We cover cases in which diffusion and reaction rates conspire to explain observed chemical distributions in the environment. Emphasis is placed on reaction rates for which the rate mechanism has been described in laboratory experiments. The course content of each week is:

1. Reaction Rate mechanisms (Review of the theory and mechanisms)
2. Molecular diffusion rates (Theory and observations)
3. Air-Water Exchange in the environment; diffusion and reaction of CO₂
4. Oxidation by oxygen; reaction rates for Mn²⁺, Fe²⁺, HS⁻
5. Organic matter degradation and preservation
6. CaCO₃ (calcite) dissolution and preservation
7. SiO₂ (opal) dissolution and preservation
8. Kinetic isotope fractionation in partially open systems; the effects on δ¹⁸O and δ¹⁵N
9. Rates of silicate mineral dissolution (weathering); surface reactions and dissolution

The course will meet three times per week. Each week the schedule will consist of a lecture in the first meeting, a co-operative learning discussion of a research paper in the second and a presentation of a related topic and/or problem solution by students in the third. There will be problems and short papers with presentations.

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AQUATIC KINETICS (OCEAN 580)
COURSE SCHEDULE - SPRING 2002

<u>WEEK</u>	<u>SUBJECT</u>	<u>READING</u>
1. April 1	Introduction, Reaction Rate Mechanisms, Reaction Rate Catalysis	Emerson and Hedges Book Chapter
2. April 15	Diffusion; Theory, Gases and Ions in Water	Jahne, Heinz and Dietrich (1987)
3. April 22	CO ₂ Reaction and Diffusive Transport	Wolf-Gladrow, Bijma and Zeebe (1999)
4. April 29	Isotope Fractionation in Open Systems	Brandes and Devol (1997)
5. May 6	Fe, Mn and HS ⁻ Oxidation Kinetics	Davies and Morgan (1989)
6. May 13	Organic Matter Degradation Kinetics	Wang and Van Cappellen (1996)
7. May 20	CaCO ₃ Dissolution Kinetics	Hales and Emerson (1997) Keir (1980)
8. May 27	Opal Dissolution Kinetics	Dixit, Van Cappellen and van Bennekom (2001)
9. June 3	Dissolution Kinetics of Oxides and Silicate (Weathering)	Furrer and Stumm (1986)
10. June 10	Student Presentations	

BIBLIOGRAPHY
AQUATIC KINETICS (OCEAN 580), 2002
Steven Emerson

I. MOLECULAR DIFFUSION

A. Gases in Water

Jahne, B., G. Heinz and W. Dietrich (1987) Measurement of the diffusion coefficients of sparingly soluble gases in water. *J. Geophys. Res.*, 92, 10,767-10,776.

Hayduk, W. and H. Laude (1974) Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions. *AIChE J.*, 20, 611-615.

Wise, D.L. and G. Haughton (1966) The diffusion coefficients of ten slightly soluble gases in water at 10-60 °C. *Chem. Eng. Sci.*, 21, 999-1010.

B. Ions in Water

- Li, Y.-H. and S. Gregory (1974) Diffusion of ions in seawater and in deep-sea sediments. *Geochim. Cosmochim. Acta*, 38, 703-714.
- Ben-Yaakov, S. (1972) Diffusion of sea water ions. I. Diffusion of sea water into dilute solution. *Geochim. Cosmochim. Acta*, 36, 1395-1406.

II. REACTION RATES

A. Chemical Kinetics - General Books

- Moore, J.W. and Pearson, R.C. (1981) Kinetics and Mechanism. John Wiley & Sons, New York, 455 pp.
- Wilkinson, F. (1980) Chemical Kinetics and Reaction Mechanisms. Van Nostrand, New York, 335 pp.
- Gardiner, W.C. (1964) Rates and Mechanisms of Chemical Reactions. W.A. Benjamin, New York, 284 pp.

B. Chemical Kinetics with an Environmental Perspective

- Brezonik, P. (1994) Chemical Kinetics and Process Dynamics in Aquatic Systems. Lewis Publishers, Boca Roton, 754 pp.
- Schwarzenbach, Geschwend and Imboden (1993) Environmental Organic Chemistry. John Wiley & Sons, New York, 681 pp.
- Stumm, W. (1990) Aquatic Chemical Kinetics. Wiley Interscience, New York.
- Lasaga, A.C. and Kirkpatrick, R.J. (1981) Kinetics of geochemical processes. *Reviews in Mineralogy*, 8, Mineralogical Society of America, Washington, D.C.

C. Catalysis

- Lehninger (1982) Biochemistry [Chapter 9, Enzymes].
- Hoffman, M.R. (1981) Thermodynamic, kinetic and extrathermodynamic considerations in the development of equilibrium models for aquatic sciences. *Envir. Sci. Technol.*, 15, 345-353.
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- Laidler, K.J. and P.S. Bunting (1973) The Chemical Kinetics of Enzyme Action. Oxford University Press, Oxford, 468 pp.

D. Photochemical Reactions

- Zafiriou, O. (1985) Atmospheric, oceanic, and interfacial photochemistry as factors influencing air-sea exchange fluxes and processes. In. Role of Air-Sea Exchange in Geochemical Cycling. Riedel, New York.
- Zafiriou, O. (1984) Natural Water Photochemistry, *Envir. Sci. and Tech.*, 18, 358

III. INDIVIDUAL ELEMENT REACTION RATES - Laboratory Studies

A. CO₂ Hydrolysis

- Zeebe, R. E. and D. A. Wolf-Gladrow (2001) CO₂ in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier, N. Y.

- Johnson, K.S. (1982) Carbon dioxide hydration and dehydration kinetics in seawater. *Limnol. Oceanogr.*, 27, 849-855.
- Jones, P.M., L. Haggett and J.L. Longridge (1964) The hydration of carbon dioxide. *J. Chem. Ed.*, 41, 610-612.

(a) Catalysis

- Pocker, Y. and D.W. Bjorkquist (1977) Stopped-flow studies of carbon dioxide hydration and bicarbonate dehydration in H₂O and D₂O acid-base and metal ion catalysis. *J. Am. Chem. Soc.*, 99, 6537-6543.
- Khalifah, R.G. (1971) The carbon dioxide hydration activity of carbonic anhydrase. *J. Biol. Chem.*, 246, 2561-2573.

B. Mn(II) Oxidation

- Von Langen, P., K. Johnson, K.Cole, and V Elrod (1997) Oxidation kinetics of manganese (II) in seawater at nanomolar concentrations, *Geochim. Cosmochim. Acta*, 61, 4945-4954.

(a) Catalysis

- Davies, S. and J.J. Morgan (1989) Manganese (II) oxidation kinetics on metal oxide surfaces. *J. Colloid and Interface Sci.*, 129, 63-77.
- Hastings, D. and S. Emerson (1986) Oxidation of manganese by spores of a marine Bacillus: Kinetic and thermodynamic considerations. *Geochim. Cosmochim. Acta*, 50, 1819-1824.
- Tebo, B. and S. Emerson (1986) Microbial manganese (II) oxidation in the marine environment: A quantitative study. *Biogeochem.*, 2, 149-161.
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- Sung, W. and Morgan, J.J. (1981) Oxidative removal of Mn(II) from solution catalyzed by the g-FeOOH (lepidocrocite) surface. *Geochim. Cosmochim. Acta*, 45, 2377-2384.

C. Mn(III and IV) Reduction

- Stone, Allan (1987) Microbial metabolites and the reductive dissolution of manganese oxides: Oxalate and pyruvate. *Geochim. Cosmochim. Acta*, 51, 919-925.
- Stone, A.T. (1987) Reductive dissolution of manganese (III/IV) oxides by substituted phenols. *Envir. Sci. Technol.*, 21, 979-987.
- Stone, A. T. and J.J. Morgan (1987) Reductive dissolution of metal oxides. In Aquatic Surface Chemistry (W. Stumm, ed.). Wiley Interscience, New York, pp. 221-254.

D. H₂S Oxidation by O₂

- Chen, K. and J.C. Morris (1972) Kinetics of oxidation of aqueous sulfide by O₂. *Envir. Sci. Technol.*, 6, 529-537.
- O'Brien and Birkner (1977) Kinetics of oxygenation of reduced sulfur species in

aqueous solution. *Envir. Sci. Technol.*, 11, 1114-1120.

Almgren and Hagstrum (1979) The oxidation rate of sulfide in sea water. *Water Res.*, 8, 395-400.

Millero, F.J. (1986) The thermodynamics and kinetics of the hydrogen sulfide system in natural waters. *Mar. Chem.*, 18, 121-147.

Millero, F., S. Hubinger, M. Fernandez and S. Garnett (1987) Oxidation of H₂S in seawater as a function of temperature, pH and ionic strength. *Envir. Sci. Technol.*, 21, 439-443.

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Chen, K. and J.C. Morris (1972) Oxidation of sulfide by O₂: Catalysis and inhibition. *Proc. Am. Soc. Civ. Eng., JAI*, 215-227.

Hoffman, M.R. and Lim (1979) Kinetics and mechanism of the oxidation of sulfide by oxygen. *Envir. Sci. Technol.*, 13, 1406-1412.

E. Oxidation of Fe(II)

Millero, F. (1989) Effect of ionic interactions on the oxidation of Fe(II) and Cu(I) in natural waters. *Mar. Chem.*, 28, 1-28.

Millero, F.J., S. Sotolongo and M. Izaguirre (1987) The oxidation kinetics of Fe(II) in sea water. *Geochim. Cosmochim. Acta*, 51, 793-801.

Roekens, E.J. and R.E. Van Greiken (1983) Kinetics of iron (II) oxidation in seawater of various pH. *Mar. Chem.*, 13, 195-202.

Davison and Seed (1983) The kinetics of oxidation of ferrous iron in synthetic and natural waters. *Geochim. Cosmochim. Acta*, 47, 67-79.

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Sung, W. and J.J. Morgan (1980) Kinetics and products of ferrous ion oxygenation in aqueous systems. *Envir. Sci. Technol.*, 14, 561-568.

Tamura, J.K., et al. (1976) The effect of ferric hydroxide on the oxygenation of ferrous ions in neutral solutions. *Corrosion Sci.*, 16, 197-207.

F. Oxidation of V(IV)

Wehrli, B. and W. Stumm (1988) Oxygenation of vanadyl (IV). Effect of coordinated surface hydroxyl groups and OH. *Langmuir*, 4, 753-758.

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IV. APPLICATIONS TO THE ENVIRONMENT

A. CO₂ Diffusive Transport and Reaction

(a) Laboratory Studies

Goldman, J. and M. Dennett (1983) Carbon dioxide exchange between air and seawater: No evidence for rate catalysis. *Science*, 220, 199-201.

Hoover, T. and D. Berkshire (1969) Effects of hydration on carbon dioxide exchange across an air-water interface. *J. Geophys. Res.*, 74, 456-464.

(b) Models

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B. Organic Matter Degradation

(a) Laboratory Studies

- Westrich, J.T. and R.A. Berner (1984) The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested. *Limnol. Oceanogr.*, 28, 236-249.

(b) Field Studies

- Archer, D., J. Morford and S. Emerson (2002) A model for suboxic sedimentary diagenesis suitable for automatic tiling and gridded global domains, *Glob. Biogeochem. Cycles*, (in press).
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C. Calcium Carbonate Dissolution Kinetics

(a) Laboratory Studies

- Hales, B. and S. Emerson (1997) Evidence in support of first-order dissolution kinetics of calcite in seawater, *Earth Planet Sci. Letters*, 148, 317-327.
- Arakaki, T. and A. Mucci (1995) A continuous and mechanistic representation of calcite reaction controlled kinetics in dilute solutions at 25°C and 1 atm total pressure. *Aquatic Geochem. I*, 105-130.
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- Keir, R.S. (1980) The dissolution kinetics of biogenic calcium carbonates in seawater. *Geochim. Cosmochim. Acta*, 44, 241-252.
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(b) Field Studies

- Hales, B., S. Emerson, and D. Archer (1994) Respiration and dissolution in the sediments of the western North Atlantic: Estimates from models of in situ microelectrode measurements of purewater oxygen and pH. *Deep-Sea Res.*, 41, 695-719.
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D. Opal (SiO₂) Dissolution Kinetics

(a) Laboratory Studies

- Dixit, S., P. Van Cappellen, A. J. van Bennekom (2001) Processes controlling solubility of biogenic silica and pore water build-up of silicic acid in marine sediments, *Marine Chem.*, 73, 333-352.
- Rimstidt, J.D. and H.L. Barnes (1980) The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta*, 44, 1683-1699.
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(b) Field Studies

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E. Oxide and Silicate Mineral Dissolution Kinetics

(a) Laboratory Studies

Stumm, W. and E. Wieland (1990) Dissolution of oxide and silicate minerals: rates depend on surface speciation in Aquatic Chemical Kinetics (W. Stumm, ed.) Wiley Interscience, New York, 367-400.

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Berner, R.A. (1978) Rate control of mineral dissolution under earth surface conditions. *Am. J. Sci.*, 278, 1235-1252.

F. Isotope Fractionation in Diffusive Systems

Stover, A. K. and P. D. Quay (2000) Hydrogen and carbon kinetic isotope effects during soil uptake of atmospheric methane, *Glob. Biogeochem. Cycles*, 14, 25-39.

Brandes, J. A. and A. H. Devol (1997) Isotope fractionation of oxygen and nitrogen in coastal marine sediments, *Geochim. Cosmochim. Acta*, 61, 1793-1801

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