Distribution: WM-85623
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WMGT rf
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JUL 26 1985

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WM Record File WM-RES
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WM Project 10, 11, 16
Docket No.
PDR ✓
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Distribution:

(Return to WM, 623-SS)

Dr. Malcolm D. Siegel
Division 6431
Sandia National Laboratories
Albuquerque, NM 87185

Dear Dr. Siegel:

SUBJECT: CONTRACT NO. NRC-50-19-03-01/FIN A-1756, "GEOCHEMICAL SENSITIVITY ANALYSIS"

I have reviewed the June, 1985, monthly progress report for the above contract, dated July 12, 1985. Based on my review of this report, progress to date is satisfactory. I do have the following comments:

- We have identified other elements whose thermochemical data we would like Phillips to compile if resources allow: Tc, Co, Ni, and Cr.

- As we discussed, the NRC cannot approve of K. Erickson's planned trip to the MRS symposium in Stockholm.

- I would like to discuss in more detail your ideas regarding the development of site conceptual models and the input you expect from us. I am hoping to visit Sandia in September or October; at that time we will be able to discuss a salt site conceptual model.

- Regarding your concern that the NRC is basically ignorant of your products, my response is that I believe that most of the products to date are not easily usable by the NRC staff. The schedule of this project is such that most of the user-oriented products will not be completed until FY86 and FY87. I encourage you to continue to highlight products from other Sandia contracts that may be of interest to the NRC geochemistry staff.

- I am enclosing some of the notes that Bill Dam got from the USGS course taught by Neil Plummer. If you want more detailed notes on a particular topic, I suggest you contact him directly (427-4543) by August 22. I am also enclosing the latest draft of EPA's HLW standards.

FC	:WMGT	:	:	:	:	:
AME	:WRKelly;mt	:	:	:	:	:
ATE	:85/07/	8508160464 850726 PDR WMRES EXISANL A-1756 PDR	:	:	:	2258

The action taken by this letter is considered to be within the scope of the current contract FIN A-1756. No changes to costs or delivery of contract products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contracted products.

Sincerely,

/S/

Walton R. Kelly
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosures:
As Stated

OFC	:WMGT WRK	:	:	:	:	:	:
NAME	:WRKelly;mt	:	:	:	:	:	:
DATE	:85/07/26	:	:	:	:	:	:

United States Department of the Interior

GEOLOGICAL SURVEY
RESTON, VA. 22092

4100 0600
Manpower Section
November 9, 1984

REPLY REQUESTED BY DECEMBER 5, 1984

WATER RESOURCES DIVISION TRAINING MEMORANDUM NO. 85.09

Subject: PERSONNEL--Training: Geochemistry for Ground-Water Systems (G0212) February 25 - March 8, 1985

ANNOUNCEMENT

The subject training course will be held at the U.S. Geological Survey National Training Center, Denver, Colorado. A schedule of the course is attached.

DESCRIPTION

This 10-day course includes quantitative interpretation of hydrochemical data for ground water that will be discussed in terms of principal reaction mechanisms and their geologic environment. Consideration will be given to basic solution theory, equilibrium thermodynamics, mineral-water interactions, mass balances and the elements of mass transfer. Examples of computational analysis, relevant programs, (such as WATEQF, BALANCE, and PHREEQE), and applications to field problems are included.

ATTENDEES

The course is limited to participants who are currently involved in interpreting field geochemical data. Personnel must have basic familiarity with chemical analyses of natural waters and general background in chemistry equivalent to completion of one year undergraduate university training. Familiarity with aspects of geology, hydrology, and mineralogy is assumed. Attendance will be limited to 24.

DEADLINES

Nominations should be submitted to your respective Regional Hydrologist on the attached application form by December 5, 1984. Nominations from Headquarters, National Research Program (NRP), and the Office of International Hydrology (OIH) personnel should be forwarded to the Chief, Manpower Section. The Regional Hydrologists will will notify the Chief, Manpower Section, and the Chief, National Training Center, of their selections by December 12, 1984.

EQUALIZATION COST	The travel equalization cost for this training course is $1,390. This cost applies only to Water Resources Division attendees.
ADDITIONAL INFORMATION	Information on housing, local transportation, etc., will be mailed directly to the selected attendees by the Training Center. The per diem rate will be actual subsistence not to exceed $75 per day. All students will be expected to remain at the training course until the scheduled closing time.

for Thomas J. Buchanan
Assistant Chief Hydrologist
for Operations

Attachments

WRD Distribution: A, B, S, FO, PO

WATER RESOURCES DIVISION
GEOCHEMISTRY FOR GROUND-WATER SYSTEMS
February 25 - March 8, 1985
Course Coordinator: L. N. Plummer

SCHEDULE

Monday, February 25, 1985

8:00 a.m. - Opening Remarks and Course Overview .....

Review of important constants, terminology

Units of concentration - class problems

Comments on graphical presentation of water quality data

11:00 a.m. - Principles of chemical thermodynamics as they apply to chemical reactions .....

-- calculation of the standard free energy of reaction
-- definition of the equilibrium constant
- activity vs. concentration
- any reaction can be used to test for equilibrium
-- class problems

3:00 p.m. - -- temperature dependence of equilibrium constants.
-- class problems

Tuesday

8:00 a.m. - -- pressure dependence of equilibrium constants ....
-- class problem
-- sources of thermodynamic data

10:30 a.m. - The concept of the predominant species in aqueous solutions .....

-- pH dependence, the carbonate system
-- gas partial pressures; water stability
-- Eh dependence, the iron system
-- class problems

Wednesday

8:00 a.m. - The concept of the predominant species in aqueous solutions (continued from Tuesday) .....

-- Eh - pH dependence, the sulfur system
-- saturation indices
-- class problem

Wednesday (continued)

1:00 p.m. - Overview of main dissolved species in natural waters...

-- non-redox species
-- redox species
-- high salinity

Thursday

8:00 a.m. - Review of the physical-chemical properties of aqueous solutions .....

-- water as a solvent
-- water structure
-- ionic hydration

Review of theoretical models for the thermodynamic properties electrolyte solutions .....

-- Debye-Huckel treatment
-- ion pair formation
-- Bronsted-Guggenheim
-- Pitzer model

Construction of aqueous ion-pairing models for natural waters .....

-- mass balance equations
-- charge balance
-- mass action equations
-- ionic strength
-- activity coefficients
-- thermodynamic data base
-- convergence criteria
-- numerical sequence of calculation

1:00 p.m. - Introduction to the computer program WATEOF .....

-- numerical method
-- aqueous model
-- program listing
-- directions for use
-- class workshop
-- continue workshop into evening

Friday

8:00 a.m. - Interpreting the results from WATEOF .....

-- saturation indices
-- redox relations

Friday (continued)

Thermodynamic interpretation of mineral-water reactions .....

-- writing balanced reactions
-- can we write the right reactions?
-- definition of dissolution reactions
-- saturation indices and the free energy of reaction
-- interpretation of phase relations and slope relationships on mineral-water stability diagrams
-- individual work with those who stay later on Friday

Monday, March 4, 1985

8:00 a.m. - Summary of major controlling reactions in ground water systems

-- summary of major rock-forming minerals .....
-- calcite, dolomite, gypsum system .....
-- ion-exchange .....
-- sulfate reduction, other redox reactions ....
-- silicate reactions .....
-- evaporites, brine evolution .....

Tuesday

8:00 a.m. - The mass balance approach to defining reactions in natural systems .....

-- the plausible phases
-- the mass balance equations as applied to observed analytical data
-- the mass balance approach to redox problems
-- problem session

Wednesday

8:00 a.m. - Introduction to the computer program BALANCE .....

-- mathematics
-- source code
-- directions for use
-- class workshop

Evening workshop on class field problems using WATEQF and BALANCE

Thursday

8:00 a.m. - Summary of important isotopic relationships in hydrogeochemistry .....

-- oxygen, deuterium, tritium
-- carbon
-- sulfur

Introduction to reaction path simulation .....

-- philosophy of reaction modeling
-- introduction to the computer program PHREEQE and PHRQINPT
-- logic of reaction-model indentification
-- evening session on use of PHREEQE and PHRQINPT

Friday

8:00 a.m. - Introduction to reaction path simulation (continued)

-- application of reaction path calculations to isotopic data .....
-- field example of reaction modeling .....

Adjourn at Noon

have copy

Selected References
Geochemistry for Ground Water Systems

Back, W. (1966) Hydrochemical facies and ground water flow patterns in northern part of Atlantic coastal plain. U.S. Geol. Survey Prof. Paper 498A, 42 p.

Baedecker, M. J., and Back, W. (1979) Hydrological processes and chemical reactions at a landfill. Ground Water 17, 429-437.

Ball, J. W., Jenne, E. A., and Nordstrom, D. K. (1979) WATEQ2--A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters. In E. A. Jenne (Ed.) Chemical modeling in aqueous systems. Amer. Chem. Soc. Symposium 93, 817-835.

Ball, J. W., Nordstrom, D. K., and Jenne, E. A. (1980) Additional and revised thermochemical data and computer code for WATEQ2--A computerized chemical model for trace and major element speciation and mineral equilibria of natural waters. U.S. Geol. Survey Water-Resources Invest. 78-116.

Barnes, H. L. (Ed.) (1979) Geochemistry of hydrothermal ore deposits, 2nd Edition. Wiley-Interscience, 798 p.

Barnes, Ivan, and Bentall, Ray (1968) Water-mineral relations of Quaternary deposits in the lower Platte River drainage area in eastern Nebraska. U.S. Geol. Survey Water-Supply Paper 1859-D, 39 p.

Barnes, I., and Hem, J. D. (1973) Chemistry of subsurface waters. Earth and Planetary Sciences Annual Review 1, 157-181.

Bass Becking, L. G. M., Kaplan, I. R., and Moore, D. (1960) Limits of the natural environments in terms of pH and oxidation-reduction potentials. Jour. Geology 68, 243-284.

Berner, R. A. (1981) A new geochemical classification of sedimentary environments. J. Sed. Pet. 51, 359-365.

Benson, L. V. (1982) A tabulation and evaluation of ion exchange data on Smectites. Environ. Geol. 4, 23-29.

Bricker, O. P., and Garrels, R. M. (1966) Mineralogic factors in natural water equilibria. Proc. 4th Rudolphs Conference, Rutgers University, In Faust, S. D., and Hunter, J. V. (Eds.) Principles and Applications of Water Chemistry. John Wiley and Sons, 449-469. ✓

Bricker, O. P. (1982) Redox potential: Its measurement and importance in water systems. In Water Analysis, vol. 1, 55-83. ✓

Busenberg, E. (1978) The products of the interaction of feldspars with aqueous solution at 25°C. Geochim. Cosmochim. Acta 42, 1679-1686.

Champ, D. R., Gulens, J., and Jackson, R. E. (1979) Oxidation reduction sequences in ground water flow systems. Canadian Jour. Earth Sci. 16, 12-23.

Chapelle, F. H., and Knobel, L. L. (1983) Aqueous geochemistry and the exchangeable cation composition of glauconite in the Aquia Aquifer, Maryland. Ground Water 21, 343-352.

Cherry, J. A., Shaikh, A. V., Tallman, D. E., and Nicholson, R. V. (1979) Arsenic species as an indicator of redox conditions in groundwater. Jour. Hydrology 43, 373-392.

Clarke, F. E., and Jones, B. F. (1972) Significance of ground water chemistry in performance of North Sahara tube wells in Algeria and Tunisia. U.S. Geol. Survey Water-Supply Paper 1757-M, 39 p.

Claassen, Hans C. (1982) Guidelines and techniques for obtaining water samples that accurately represent the water chemistry of an aquifer. U.S. Geol. Survey Open-File Report 82-1024, 49 p.

Cleaves, E. T., Godfrey, A. E., and Bricker, O. P. (1970) Geochemical balance of a small water shed and its geomorphic implications. Geol. Soc. Amer. Bull. 81, 3015-3032.

Crerar, D. A., Knox, G. W., and Means, J. L. (1979) Biogeochemistry of bog iron in the New Jersey Pine Barreus. Chem. Geol. 24, 111-135.

Crerar, D. A., Means, J. L., Yuretich, R. F., Borcsik, M. P., Amster, J. L., Hastings, D. W., Knox, G. W., Lyon, K. E., and Quiett, R. F. (1981) Hydrogeochemistry of the New Jersey Coastal Plain, 2. Transport and deposition of iron, aluminum, dissolved organic matter and selected trace elements in stream, ground- and estuary water. Chem. Geol. 33, 23-44.

Curtis, C. D. (1970) Differences between lateritic and podzolic weatherings. Geochim. Cosmochim. Acta 34, 1351-1353.

Drever, J. I. (1982) The geochemistry of natural waters. Prentice-Hall, 388 p.

Edmunds, W. M., Bath, A. H., and Miles, D. L. (1982) Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. Geochim. Cosmochim. Acta 46, 2069-2081.

Edmunds, W. M., and Walton, N. R. G. (1983) The Lincolnshire limestone-hydrogeochemical evolution over a ten-year period. Jour. Hydrology 61, 201-211.

Fenchel, T., and Blackburn, T. H. (1979) Bacteria and mineral cycling, 225 pp.

Florence, T. M. (1983) Trace element speciation and aquatic toxicology. Trends Anal. Chem 2, 162-166.

Foster, M. D. (1950) The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plain. Geochim. Cosmochim. Acta 1, 33-48.

Freeze, R. A., and Cherry, J. A. (1979) Groundwater. See Chap. 7. Prentice-Hall, 604 p.

Fritz, P., and Fontes, J. Ch. (Eds.) (1980) Handbook of environmental isotope geochemistry, Vol. 1, The terrestrial environment. A. Elsevier, New York, 545 p.

Garrels, R. M. (1968) Genesis of some ground waters from igneous rocks. Researches in Geochemistry 2, John Wiley and Sons, N.Y., 405-420.

Garrels, R. M., and Mackenzie, F. T. (1967) Origin of the chemical composition of some springs and lakes. Adv. in Chem. Ser. 67, Amer. Chem. Soc., Washington, D.C., 222-242.

Gat, J. R., and Gonfiantini, R. (Eds.) (1981) Stable isotope hydrology: Deuterium and oxygen-18 in the water cycle. IAEA, Vienna, Tech. Rept. Series No. 210, 337 p.

Gat, J. R., and Galai, A. (1983) Groundwaters of the Arva Valley: An isotopic study of their origin and interrelationships. Israel J. Earth-Sci. 31, 25-38.

Handa, B. K. (1975) Geochemistry and genesis of flouride containing ground waters in India. Ground Water 13, 275-281.

Hanor, J. S. (1979) The sedimentary genesis of hydrothermal fluids. In Barnes, H. L. (Ed.) Geochemistry of hydrothermal ore deposits, 2nd Edition. Wiley-Interscience, 137-172.

Hanor, J. S. (1982) Modification of the quality of water injected into Louisiana Gulf Coast sands: Effects of cation exchange. Environ. Geol. 4, 75-85.

Hanor, J. S. (1982) The origin of high sodium-bicarbonate waters in the Gulf Coastal Plain: A reassessment of the role of carbonate dissolution and ion exchange. GSA Abstract 1982, p. 506.

Heath, R. C. (1984) Ground-water regions of the United States. U.S. Geol. Survey Water-Supply Paper 2242, 78 p.

Helz, G. R., and Sinex, S. A. (1974) Chemical equilibria in the thermal spring waters of Virginia. Geochim. Cosmochim. Acta 38, 1807-1820.

Hitchon, B., Billings, G. K., and Klovan, J. E. (1971) Geochemistry and origin of formation waters in the western Canada sedimentary basin-III. Factors controlling chemical composition. Geochim. Cosmochim. Acta 35, 567-598.

Hoefs, J. (1973) Stable isotope geochemistry. Springer-Verlag, New York, 140 p.

Högfeldt, Erik (1982) Stability constants of metal-ion complexes. Part A: Inorganic ligands. IUPAC Chemical Data Series No. 21., Pergamon Press, New York.

Hollyday, E. F., and McKenzie, S. W. (1973) Hydrogeology of the formation and neutralization of acid waters draining from underground coal mines of western Maryland. Md. Geol. Survey, Rept. Inv. no. 20, 50 p.

Hull, L. C. (1984) Geochemistry of the ground water in the Sacramento Valley, California. U.S. Geol. Survey Prof. Paper 1401-B, 36 p.

Jenne, E. A. (Ed.) (1979) Chemical modeling in aqueous systems. Speciation, sorption, solubility and kinetics. ACS Symposium Series 93, American Chemical Society, Washington, D.C., 914 p.

Johnston, R. H. (1983) The saltwater-freshwater interface in the tertiary limestone aquifer, southeast, Atlantic outer-continental shelf of the U.S.A. J. Hydrol 61, 239-249.

Jones, B. F., Eugster, H. P., and Rettig, S. L. (1977) Hydrochemistry of the Lake Magadi Basin, Kenya. Geochim. Cosmochim. Acta 41, 53-72.

Jones, B. F., Kennedy, V. C., and Zellweger, G. W. (1974) Comparison of observed and calculated concentrations of dissolved Al and Fe in streams. Water Res. Research 10, 791-793.

Kharaka, Y. K., and Barnes, I. (1973) SOLMNEQ: Solution-mineral equilibrium computations. NTIS PB-215 899.

Kharaka, Y. K., Robinson, S. W., Law, L. M., and Carothers, W. M. (1984) Hydogeochemistry of Big Soda Lake, Nevada: An alkaline meromictic desert lake. Geochim. Cosmochim. Acta 48, 823-845.

Kimball, B. A. (1981) Geochemistry of spring water, southeastern Vinta Basin, Utah and Colorado. U.S. Geol. Survey Water-Supply Paper 2074, 30 p.

Kittrick, J. A. (1969) Soil minerals in the Al_2O_3-SiO_2-H_2O system and a theory of their formation. Clays and Clay Minerals 17, 157-167.

Kreitler, C. W. and Browning, L. A. (1983) Nitrogen-isotope analysis of groundwater nitrate in carbonate aquifers: Natural sources versus human pollution. J. Hydrol. 61, 285-301.

Krothe, N. C., and Libra, R. D. (1983) Sulfur isotopes and hydrochemical variations in spring waters of Southern Indiana, USA. Jour. Hydrology 61, 267-283.

Krumbein, W. C., and Garrels, R. M. (1952) Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials. Jour. Geology 60, 1-33.

Langmuir, D. (1971) Eh-pH determination. In Carver, Robert E. (Ed.) Procedures in sedimentary petrology, Wiley, N.Y., 597-634.

Langmuir, Donald, and Whittemore, D. O. (1971) Variations in the stability of precipitated ferric oxyhydroxides. Adv. in Chem. Ser. 106, Amer. Chem. Soc., Washington, D.C., 210-234.

Lasaga, A. C., and Kirkpatrick, R. J. (Eds.) (1981) Kinetics of geochemical processes. Reviews in mineralogy, Vol. 8. Mineralogical Society of America, Washington, D.C., 398 p.

Lerman, A. (Ed.) (1978) Lakes; chemistry, geology, physics. Springer-Verlag, New York, 363 p.

Leve, G. W. (1983) Relation of concealed faults to water quality and the formation of solution features in the Floridan Aquifer, northeastern Florida, U.S.A. J. Hydrol. 61, 251-264.

Miller, W. R., and Drever, J. I. (1977) Chemical weathering and related controls on surface water chemistry in the Absaroka Mountains, Wyo. Geochim. Cosmochim. Acta 41, 1693-1702.

National Research Council, Acid deposition; atmospheric processes in Eastern North America. National Academy Press, Washington, D.C., 375 p.

National Research Council, Groundwater contamination. National Academy Press, Washington, D.C., 179 p.

Nordstrom, D. K. (1977) Thermochemical redox equilibria of Zo Bell's solution. Geochim. Cosmochim. Acta 41, 1835-1841.

Paces, T. (1972) Chemical characteristics and equilibration in natural water-felsic rock-CO_2 system. Geochim. Cosmochim. Acta 36, 217-240.

Paces, T. (1973) Steady-state kinetics and equilibrium between ground water and granitic rock. Geochim. Cosmochim. Acta 37, 2641-2663.

Paces, T. (1978) Reversible control of aqueous aluminum and silica during the irreversible evolution of natural waters. Geochim. Cosmochim. Acta 42, 1487-1493.

Paces, T. (1983) Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments. Geochim. Cosmochim. Acta 47, 1855-1863.

Parkhurst, D. L., Thorstenson, D.C., and Plummer, L. N. (1980) PHREEQE-A computer program for geochemical reactions. U.S. Geol. Survey Water-Resources Invest. 80-96, 210 p.

Parkhurst, D. L., Plummer, L. N., and Thorstenson, D. C. (1982) BALANCE-A computer program for calculating mass transfer for geochemical reactions in ground water. U.S. Geol. Survey Water-Resources Invest. 82-14, 29 p.

Plummer, L. N. (1977) Defining reactions and mass transfer in part of the Floridan aquifer. Water Resources Research 13, 801-812.

Plummer, L. N., Parkhurst, D. L., and Thorstenson, D. C., (1983) Development of reaction models for ground-water systems. Geochim. Cosmochim. Acta 47, 665-686.

Pye, V. I., and Patrick R. (1983) Ground water contamination in the United States. Science 221, 713-718.

Reardon, E. J. (1981) Kd's-can they be used to describe reversible ion sorption reactions in contaminant migration? Ground Water 19, 279-286.

Reardon, E. J., Dance, J. T., and Lolcama, J. L., (1983) Field determination of cation exchange properties of calcareous sand. Ground Water 21, 421-428.

Rubin, J. (1983) Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. Water Resources Research 19, no. 5, 1231-1252.

Schluger, P. R., and Roberson, H. E. (1975) Mineralogy and chemistry of the Patapsco formation, Maryland, related to the ground-water geochemistry and flow system: A contribution to the origin of red beds. Geol. Soc. Amer. Bull. 86, 153-158.

Schoell, M. (1983) Genetic characterization of natural gases. AAPG Bull. 67, no. 12, 2225-2238.

Sposito, G. (1981) The thermodynamics of soil solutions. Oxford University Press, 223 p.

Stumm, W., and Morgan, J. J. (1981) Aquatic chemistry - An introduction emphasizing chemical equilibria in natural waters. John Wiley and Sons, 2nd Edition, 780 p.

Suarez, D. L., and Langmuir, Donald (1976) Heavy metal relationships in a Pennsylvania soil. Geochim. Cosmochim. Acta 40, 589-598.

Thorstenson, D. C. (1970) Equilibrium distribution of small organic molecules in natural waters. Geochim. Cosmochim. Acta 34, 745-770.

Thorstenson, D. C., Fisher, D. W., and Croft, M. G. (1979) The geochemistry of the Fox Hills-Basal Hell Creek Aquifer in southwestern North Dakota and northwestern South Dakota. Water Resources Research 15, 1479-1498.

Turk, John T. (1983) An evaluation of trends in the acidity of precipitation and the related acidification of surface water in North America. U.S. Geol. Survey Water-Supply Paper 2249, 18 p.

Vecchioli, John, Bennett, G. D., Pearson, F. J., Jr., and Cerillo, L. A. (1974) Geohydrology of the artificial recharge site at Bay Park: Long Island, N.Y. U.S. Geol. Survey Prof. Paper 751-C, 23-27.

Westcott, C. C. (1978) pH measurements. Academic Press, 172 p.

White, A. F. (1979) Geochemistry of ground water associated with tuffaceous rocks, Oasis Valley, Nevada. U.S. Geol. Survey Prof. Paper 712-E, 25 p.

White, A. F., Claassen, H. C., and Benson, L. V. (1980) The effect of dissolution of volcanic glass on the water chemistry in a tuffaceous aquifer, Rainier Mesa, Nevada. U.S. Geol. Survey Water-Supply Paper 1535-Q, 34 p.

Whitfield, M. (1974) Thermodynamic limitations on the use of the platinum electrode in Eh measurements. Limnology and Oceanography 19, no. 5, 857-865.

Whittemore, D. O., and Langmuir, D. (1975) The solubility of ferric oxyhydroxides in natural waters. Ground Water 13, no. 4.

Winograd, I. J., and Robertson, F. N. (1982) Deep oxygenated ground water: Anomaly or common occurrence. Science 216, 1227-1230.

Wolery, T. J. (1983) EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations: User's guide and documentation. UCRL-53414, available from NTIS, U.S. Dept. of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

Zack, A. L. (1980) Geochemistry of fluoride in the Black Creek aquifer system of Horry and Georgetown Counties, South Carolina - and its physiological implications. U.S. Geol. Survey Water Supply Paper 2067, 40 p.

Zaporozec, A. (1972) Graphical interpretation of water quality data. Ground Water 10, No. 2.

References on	Are found in
Sources of thermodynamic data Chemical thermodynamics Solution chemistry Geochemistry	"Reference material" for this course
Brines, Evaporites	Lecture Notes
Carbonate ground water	Lecture Notes

Other references are found in articles distributed to the class.

Selected References on the Evolution of Carbonate Ground Water

Atkinson, T. C. (1977) Carbon dioxide in the atmosphere of the unsaturated zone: An important control of groundwater hardness in limestones. J. Hydrol. 35, 111-123.

Back, W., and Hanshaw, B. B. (1970) Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. J. Hydrol. 10, 330-368.

Busenberg, E., and Plummer, L. N. (1982) The kinetics of dissolution of dolomite in CO_2-H_2O systems at 1.5 to 65°C and 0 to 1 atm PCO_2. Amer. Jour. Sci. 282, 45-78.

Deines, P. D., Langmuir, D., and Harmon, R. S. (1974) Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate groundwaters. Geochim. Cosmochim. Acta 38, 1147-1164.

Drake, J. J. (1983) The effects of geomorphology and seasonality on the chemistry of carbonate groundwater. J. Hydrol. 61, 223-236.

Grover, Jr., G., and Read, J. F. (1983) Paleoaquifer and deep burial related cements defined by regional cathodoluminescent patterns, middle Ordovician carbonates, Virginia. AAPG Bull. 67, no. 8, 1275-1303.

Halley, R. B., Harris, P. M., and Hine, A. C. (1983) Bank margin environment. AAPG Memoir 33, 464-506.

Hanshaw, B. B., Back, W., and Rubin, M. (1965) Radiocarbon determinations for estimating groundwater flow velocities in central Florida. Science 148, 494-495.

Hanshaw, B. B., Back, W., and Deike, R. G. (1971) A geochemical hypothesis for dolomitization by ground water. Econ. Geol. 66, 710-724.

Hanshaw, B. B., and Back, W. (1979) Major geochemical processes in the evolution of carbonate aquifer systems. Jour. Hydrol. 43, 287-312.

Harris, W. H., and Matthews, R. K. (1968) Subaerial diagenesis of carbonate sediments: Efficiency of the solution-reprecipitation process. Science 160, 77-79.

Holland, H. D., Kirsipu, T. V., Huebner, J. S., and Oxburgh, V. M. (1964) On some aspects of the chemical evolution of cave waters. Jour. Geol. 72, 36-67.

Langmuir, D. (1971) The geochemistry of some carbonate groundwaters in Central Pennsylvania. Geochim. Cosmochim. Acta 35. 1023-1045.

Lippmann, F. (1973) Sedimentary carbonate minerals. Springer, N.Y., 228 pp.

Morse, J. W. (1978) Dissolution of calcium carbonate in seawater, VI the near equilibrium dissolution kinetics of calcium carbonate-rich deep sea sediments. Amer. Jour. Sci. 278, 344-353.

Pitman, J. I. (1978) Carbonate chemistry of groundwater from chalk, Givendale, East Yorkshire. Geochim. Cosmochim. Acta 42, 1885-1897.

Pearson, F. J., Jr., Fisher, D. W., and Plummer, L. N. (1978) Correction of groundwater chemistry and carbon isotopic composition for effects of CO_2 outgassing. Geochim. Cosmochim. Acta 42, 1799-1807.

Plummer, L. N. (1975) Mixing of seawater with calcium carbonate groundwater. Geol. Soc. Amer. Mem. 142, 219-235.

Plummer, L. N., Vacher, H. L., Mackenzie, F. T., Bricker, O. P., and Land, L. S. (1976) Hydrogeochemistry of Bermuda: A case history of groundwater diagenesis of biocalcarenites. Bull. Geol. Soc. Amer. 87, 1301-1316.

Plummer, L. N., Wigley, T. M. L., and Parkhurst, D. L. (1978) The kinetics of calcite dissolution in CO_2-water systems at 5° to 60°C and 0.0 to 1.0 atm CO_2. Amer. Jour. Sci. 278, 179-216.

Plummer, L. N., Wigley, T. M. L., and Parkhurst, D. L. (1979) Critical review of the kinetics of calcite dissolution and precipitation. In E. A. Jenne (Ed), Chemical Modeling in Aqueous Systems. Amer. Chem. Soc. Symposium Series 93, 537-573.

Plummer, L. N., and Busenberg, E. (1982) The solubilities of calcite, aragonite, and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. Geochim. Cosmochim. Acta 46, 1011-1040.

Rightmire, C. T. (1978) Seasonal variation in PCO_2 and ^{13}C content of soil atmosphere. Water Resources Research 14, 691-692.

Shuster, E. T., and White, W. B. (1972) Source areas and climatic effects in carbonate groundwaters determined by saturation indices and carbon dioxide pressures. Water Resources Research 8, 1067-1073.

Thrailkill, J. (1968) Chemical and hydrologic factors in the excavation of limestone caves. Bull. Geol. Soc. Amer. 79, 19-46.

Thrailkill, J., and Robl, T. L. (1981) Carbonate geochemistry of vadose water recharging limestone aquifers. Jour. Hydrology 54, 195-208.

Wigley, T. M. L., and Plummer, L. N. (1976) Mixing of carbonte waters. Geochim. Cosmochim. Acta 40, 989-995.

Wigley, T. M. L., Plummer, L. N., and Pearson, F. J., Jr. (1978) Mass transfer and carbon isotope evolution in natural water systems. Geochim. Cosmochim. Acta 42, 1117-1139. (See also, Geochim. Cosmochim. Acta 43, 1395.

(pages missing)

VIII. Selected Reference ~~books~~

A. Sources of thermodynamic data

Martell, A. E. and Smith, R. M., 1982, Critical stability constants, v. 5, First supplement: Plenum Press, 604 p.
ion pairs, dissolved species

Naumov, G. B., Ryzhenko, B. N. and Khodakovsky, I. L., 1971, Handbook of thermodynamic data (English translation by G. J. Soleimani, edited by Ivan Barnes and Velma Speltz): NTIS, PB 226 722.
ore deposits, cites Russian lit., some good & bad data

Parker, V. B., Wagman, D. C., and Evans, W. H., 1971, Selected values of chemical thermodynamic properties. Tables for the alkaline earth elements (Elements 92 through 97 in the standard order of arrangement): U.S. Natl. Bur. Standards, Tech. Note 270-6, 106 p.

Parker, V. G., Wagman, D. D., and Garvin, D., 1976, Selected thermochemical data compatible with the CODATA recommendations: U.S. Natl. Bur. Standards, Interim Rept. 75-968, 31 p.

Robie, R. A., Hemingway, B. S., and Fisher, J. R., 1978, Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 Pascals) pressure and at higher temperatures: U.S. Geol. Survey Bull. 1452, 456 p.
very accurate solid data but not internally consistent with ions
updates Robie + Waldbaum 1259

Sadiq, M. and Lindsay, W. L., 1979, Selection of standard free energies of formation for use in soil chemistry: Tech. Bull. 134, Colorado State University, Experiment Station, Fort Collins, CO 80523.

Schumm, R. H., Wagman, D. D., Bailey, S., Evans, W. H., and Parker, V. B., 1973, Selected values of chemical thermodynamic properties. Tables for the Lanthanide (rare earth) elements (Elements 62 through 76 in the standard order of arrangement): U.S. Natl. Bur. Standards, Tech. Note 270-7, 75 p.

Sillen, L. G. and Martell, A. E., 1964, Stability constants of metal-ion complexes: The Chemical Society, Special Publication no. 17. See also Supplement no. 1, Special Publication no. 25, 1971, London.

Smith, R. M. and Martell, A. E., 1976, Critical stability constants, v. 4, Inorganic complexes: Plenum Press, 257 p.

Wagman, D. D., Evans, W. E., Parker, V. B., Schumm, R. H., and Nuttall, R. L., 1981, Selected values of chemical thermodynamic properties: Compounds of uranium, protactinium, thorium, actinium and the alkali metals: U.S. Natl. Bur. Standards, Tech. Note 270-8, 134 p.

Wagman, D. D., Evans, W. H., Parker, V. B., and Schumm, R. H., 1976, Chemical thermodynamic properties of compounds of sodium, potassium and rubidium: An interim tabulation of selected values: U.S. Natl. Bur. Standards, Interim Rep. 76-1034.

best reliable source of thermo data internally consistent

Wagman et al, 1982, The NBS Tables of Chemical Thermodynamic Properties
Jour. Phy. Chem. Ref. Data v. 11 Supplement 2
(Amer. Chem Soc. 1155 16th St. Wash. D.C. 20036 95.00)
reprint of Tech Note 270-3-8

CODATA pub. in Chem. Thermodyn.

Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., and Churney, K. L., 1971, Selected values of chemical thermodynamic properties. Tables for elements 54 through 61 in the standard order of arrangement: U.S. Natl. Bur. Standards, Tech. Note 270-5, 37 p.

Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., 1969, Selected values of chemical thermodynamic properties. Tables for elements 35 through 53 in the standard order of arrangement: U.S. Natl. Bur. Standards, Tech. Note 270-4, 141 p.

Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., 1968, Selected values of chemical thermodynamic properties. Tables for the first thirty-four elements in the standard order of arrangement: U.S. Natl. Bur. Standards, Tech. Note 270-4, 141 p.

Helgeson data base - 300°C & 100Kb - SUPCRIT program

B. Chemical thermodynamics

Darken, L. S. and Gurry, R. W., 1953, Physical chemistry of metals: McGraw-Hill Book Company, New York, 535 p.

* Denbigh, K., 1968, The principles of chemical equilibrium, 2d ed.: Cambridge Univ. Press, Cambridge, England, 494 p.

Gibbs, J. W., 1876, 1878, On the equilibrium of heterogeneous substances: Conn. Acad. Trans., v. III, p. 108-248,, p. 343-524 (in The Scientific Papers of J. Willard Gibbs: Dover Pub., Inc., N.Y., 1968, p. 79-82).

* Klotz, I. M., 1964, Chemical thermodynamics, revised edition: W. A. Banjamin, Inc., New York, 464 p.

Lewis, G. N. and Randall, M., 1961, Thermodynamics, revised by K. S. Pitzer and L. Brewer, 2nd edition: McGraw-Hill Book Company, New York, 723 p.

Prigogine, I. and Defay, R., 1954, Chemical thermodynamics, translated by D. H. Everett: John Wiley and Sons, Inc., New York, 543 p.

Wall, F. T., 1958, Chemical thermodynamics: W. H. Freeman and Co., San Francisco, 422 p.

* excellent books

C. Solution chemistry

Bates, R. G., 1973, Determination of pH: John Wiley and Sons, New York, 479 p.

Baes, C. F. and Mesmer, R. E., 1976, The hydrolysis of cations: John Wiley and Sons, New York, 489 p.

Butler, J. N., 1964, Ionic equilibrium, a mathematic approach: Addison-Wesley Publishing Co., Inc., 547 p.

Latimer, W. M., 1952, The oxidation states of the elements and their potentials in aqueous solutions: Prentice-Hall, Inc., Englewood Cliffs, N.J., 392 p.
Standard ref. new addition is forthcoming

Pourbaix, M. J. N., 1966, Atlas of electrochemical equilibriums in aqueous solutions (trans. J. A. Franklin, Centre Belge d'Etude de la Corrosion): Pergamon Press.

Robinson, R. A. and Stokes, R. H., 1959, Electrolyte solutions, 2nd revised ed.: Butterworths, London, 571 p.

Stumm, W. and Morgan, J. J., 1981, Aquatic chemistry, an introduction emphasizing chemical equilibria in natural waters, 2nd ed.: Wiley-Interscience, New York, 780 p.

D. Geochemistry

Berner, R. A., 1980, Early diagenesis, a theoretical approach: Princeton University Press, Princeton, N.J., 241 p.

Berner, R. A., 1971, Principles of Chemical sedimentology: McGraw-Hill, New York, 240 p.

Broecker, W. S. and Oversby, V. M., 1971, Chemical equilibria in the earth: McGraw-Hill.

Drever, J. I., 1982, The geochemistry of natural waters: Prentice-Hall, 388 p.

Faure, G., 1977, Principles of isotope geology: John Wiley and Sons, 464 p.

Fenchel, T. and Blackburn, T. H., 1979, Bacteria and mineral cycling: Academic Press, 225 p.

Freeze, R. A. and Cherry, J. A., 1979, Groundwater: Prentice-Hall, 604 p.

* Fritz, P. and Fontes, J. Ch., 1980, Handbook of environmental isotope Geochemistry, vol. 1: Elsevier Scientific Pub. Co., 545 p.

Garrels, R. M. and Christ, C. L., 1965, Solutions, minerals and equilibria: Harper and Row, New York, 456 p.

Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water: U.S. Geol. Survey Water-Supply Paper 1473, 363 p.

Hoefs, J., 1973, Stable isotope geochemistry: Springer-Verlag, 140 p.

Horne, R. A., 1969, Marine chemistry: Wiley-Interscience, 568 p.

Lerman, A., 1978, Lakes, chemistry, geology, physics: Springer-Verlag, 363 p.

Krauskopf, K. B., 1967, Introduction to geochemistry: McGraw-Hill Book Company, New York, 721 p.

Whitfield, M. and Jagner, D., 1981, Marine electrochemistry, a practical introduction: John Wiley and Sons, 529 p.

References
on Brines

* Billings, G. K., Hitchon, B., and Shaw, D. R. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin. Chem. Geol 4, 211-223.

* Braitsch, O. (1971) "Salt deposits: Their origin and composition". Springer-Verlag, N.Y., 297 p.

Carpenter, A. B. (1978) Origin and chemical evolution of brines in sedimentary basins. Okalahoma Geol. Survey Circular 79, 60-77.

Clayton, R. N., Friedman, I., Graf, D. L.; Mayeda, T. K., Meents, W. F., and Shimp, N. F. (1966) The origin of saline formation waters, 1. Isotopic composition. J. Geophys. Res. 71, 3869-3882.

* Collins, A.G. (1975) Geochemistry of oilfield brines. Elsevier Scientific Publishing Co., Amsterdam, 496 p.

Coplen, T. B., and Hanshaw, B. B. (1973) Ultrafiltration by a compacted clay membrane - I. Oxygen and hydrogen isotopic fractionation. Geochim. Cosmochim. Acta 37, 2295-2310.

Davis, S. N. (1964) The chemistry of saline waters by R. A. Krieger - Discussion. Ground Water 2, p. 51.

Drever, J. I. (1982) The geochemistry of natural waters. Prentice-Hall, 388 p.

Eugster, H. P., and Hardie, L. A. (1978) Saline lakes. In Lakes, Chemistry, Geology, Physics, A. Lerman (Ed), Springer-Verlag, N.Y., 237-293.

Eugster, H. P., and Jones, B. F. (1979) Behavior of major solutes during closed-basin brine evolution. Amer. Jour. Sci. 279, 609-631.

Eugster, H. P., Harvie, C. E., and Weare, J. H. (1980) Mineral equilibria in a six-component seawater system, $Na-K-Mg-Ca-SO_4-Cl-H_2O$, at 25°C. Geochim. Cosmochim. Acta 44, 1335-1347.

Frape, S. K., Fritz, P., and McNutt, R. H. (1984) Water-rock interaction and chemistry of groundwaters from the Canadian Shield. Geochim. Cosmochim. Acta 48, 1617-1627.

Graf, D. L. (1982) Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. Geochim. Cosmochim. Acta 46, 1431-1448.

Graf, D. L., Friedman, I., and Meents, W. F. (1965) The origin of saline formation water, II. Isotopic fractionation by shale micropore systems. Illinois Geol. Survey Circ. 393, 32 p.

* Graf, D. L., Meents, W. F., Friedman, I., and Shimp, N. F. (1966) The origin of saline formation waters, III. Calcium chloride waters. Illinois Geol. Survey Circ. 397, 60 p.

* Hanshaw, B. B., and Coplen, T. B. (1973) Ultrafiltration by compacted clay membrane, II. Sodium ion exclusion at various ionic strengths. Geochim. Cosmochim. Acta 37, 2311-2327.

Hardie, L. A., and Eugster, H. P. (1970) The evolution of closed basin brines. Mineral. Soc. Amer. Spec. Paper 3, 273-290.

Hardie, L. A. (1983) Origin of $CaCl_2$ brines by basalt-seawater interaction: Insights provided by some simple mass balance calculations. Min. and Petrol. 82, 205-213.

Hardie, L. A. (1984) Evaporites: Marine or non-marine? Amer. Jour. Sci. 284, 193-240.

Harvie, C. E., and Weare, J. H. (1980) The prediction of mineral solubilities in natural waters: The $Na-K-Mg-Ca-Cl-SO_4-H_2O$ system from zero to high concentration at 25°C. Geochim. Cosmochim. Acta 44, 981-997.

Harvie, C. E., Weare, J. H., Hardie, L. A., and Eugster, H. P. (1980) Evaporation of seawater: Calculated mineral sequences. Science 208, 498-500.

Harvie, C. E., Eugster, H. P., and Weare, J. H. (1982) Mineral equilibria in the six-component seawater system, $Na-K-Mg-Ca-SO_4-Cl-H_2O$ at 25°C, II. Compositions of the saturated solutions. Geochim. Cosmochim. Acta 46, 1603-1618.

Harvie, C. E., Møller, N., and Weare, J. H. (1984) The prediction of mineral solubilities in natural waters: The $Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O$. Geochim. Cosmochim. Acta 48, 723-751.

Hitchon, B., and Friedman, I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, I. Stable isotopes of hydrogen and oxygen. Geochim. Cosmochim. Acta 33, 1321-1349.

* Kharaka, Y. K., and Berry, F. A. F. (1973) Simultaneous flow of water and solutes through geological membranes, I. Experimental investigation. Geochim. Cosmochim. Acta 37, 2577-2603.

* Kharaka, Y. K., and Smalley, W. C. (1976) Flow of water and solutes through compacted clays. Amer. Assoc. Petrol. Geol. Bull. 60, 973-980.

Krieger, R. A. (1963) The chemistry of saline waters. Ground Water 1, 7-12.

* Leonard, A. R., and Ward, P. E. (1962) Use of Na/Cl ratios to distinguish oil field from salt-spring brines in western Oklahoma. U.S. Geol. Survey Research 1962, Article 52, B126-B127.

* Lerman, A. (1970) Chemical equilibria and evolution of chloride brines. Mineral. Soc. Amer. Spec. Pap. 3, 291-306.

Manheim, F. T., and Horn, M. K. (1968) Composition of deeper subsurface waters along the Atlantic continental margin. Southeastern Geology 9, 215-236.

Stewart, F. H. (1963) Marine Evaporites. Data of Geochemistry, 6th Ed. U.S. Geol. Survey Prof. Paper 400Y, 52 p.

* White, D. E. (1965) Saline waters of sedimentary rocks. In Fluids in subsurface environments - A symposium, Memoir No. 4. Amer. Assoc. Petrol. Geol. 1965, 342-366.

Usiglio, M. J. (1849) Etudes sur la composition de l'eau de la Méditerranée et sur l'exploitation des sels qûelle contient. Ann. Chim. Phys. 27(3), 172-191.

REFERENCES

Fritz, P., and Fontes, J. Ch., 1980, eds., Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment: Amsterdam, Elsevier, v. 1A, 545 p.

IAEA, 1980, Arid-zone Hydrology: Investigations with isotope techniques: Vienna, Interna. Atomic Energy Agency, 265 p.

IAEA, 1981a, Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle, Gat, J. R. and Gonfiantini, R., scientific eds: Vienna, Interna. Atomic Energy Agency, 339 p.

IAEA, 1981b, Statistical treatment of environmental isotope data in precipitation: Vienna, Interna. Atomic Energy Agency, 255 p.

IAEA, 1983a, Guidebook on nuclear techniques in hydrology: Vienna, Interna. Atomic Energy Agency, 439 p.

Jager, E., and Hunziker, J. C., 1979, eds., Lectures in Isotope Geology: New York, Springer-Verlag, 329 p.