fundamental particles may bear upon a variety of geological problems. For example, the diagenetic conversion of smectite to illite is an important geochemical reaction commonly observed in sediments with increasing depth, or inferred depth, of burial (*18–21*). In the currently accepted transformation mechanism, smectite layers are converted to illite layers by substituting aluminum for silicon and sorbing potassium ions within fixed layer sequences to produce an I-S series of increasing illite content (*22*). The sequence is randomly interstratified until there is more than 50 percent illite layers, at which point, for some unexplained reason, the interstratification sequence becomes regularly arranged.

Using our concept of interstratified clays, randomly interstratified I-S would be composed primarily of populations of elementary illite and smectite particles. During diagenesis, smectite particles become unstable and dissolve, while illite particles are formed. When smectite particles are no longer present the population becomes one of elementary illite particles and, possibly, other thicker illite particles which, when examined by XRD, appear to be regularly interstratified I-S with 50 percent or more illite layers.

As diagenesis continues, the thickness of the fundamental illite particles increases within the population. When the particles become sufficiently thick to produce diffraction maxima with a 10-Å series the clay material is identified by XRD as conventional illite.

We have shown that diagenetic illite with no detectable expanding component is made up of particles 20 to 160 Å thick, with the average being 70 Å (*15*). Thus, the diagenetic conversion of smectite to illite may actually be a recrystallization phenomenon where smectite dissolution and illite precipitation occurs within a population of extremely small phyllosilicate crystals.

Our interpretation also suggests a solution to the currently enigmatic thermodynamic status of interstratified clays (*23, 24*). Although randomly interstratified, I-S would be regarded as two phases, smectite and illite, regularly interstratified I-S could be regarded as a single phase, that is illite 20 to 50 Å thick.

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References and Notes

1. D. M. C. MacEwan and A. Ruiz Amil, in *Soil Components*, J. E. Gieseking, Ed. (Springer-Verlag, New York, 1975), vol. 2, pp. 265–334.
2. C. E. Weaver, *Am. Mineral.* **41**, 202 (1956).
3. S. W. Bailey, *Clay Sci.* **5**, 305 (1981).
4. R. C. Reynolds, in *Crystal Structures of Clay Minerals and Their X-ray Identification*, G. W. Brindley and G. Brown, Eds. (Mineralogical Society, London, 1980), pp. 249–303.
5. Sample collected by J. L. Post, California State University, Sacramento.
6. This sample is analogous to sample MB670 in figure 8 of Nadeau and Reynolds (*20*).
7. Sample collected by V. C. Farmer, from a fracture in a doleritic sill.
8. J. J. Comer, in *The Electron-Optical Investigation of Clays*, J. A. Gard, Ed. (Mineralogical Society, London, 1971), pp. 79–108.
9. W. J. McHardy *et al.*, *Clay Miner.* **17**, 23 (1982).
10. R. W. James, in *The Crystalline State*, L. Bragg, Ed. (Bell, London, 1948), vol. 2, pp. 513–589.
11. G. W. Brindley, in *Crystal Structures of Clay Minerals and Their X-ray Identification*, G. W. Brindley and G. Brown, Eds. (Mineralogical Society, London, 1980), pp. 125–195.
12. J. Méring and A. Oberlin, in *The Electron-Optical Investigation of Clays*, J. A. Gard, Ed. (Mineralogical Society, London, 1971), pp. 193–229.
13. R. Tettenhorst and H. E. Roberson, *Am. Mineral.* **58**, 73 (1973).
14. N. Güven *et al.*, *J. Sediment. Petrol.* **50**, 761 (1980).
15. P. H. Nadeau *et al.*, *Clay Miner.* **19**, 67 (1984).
16. R. C. Reynolds and J. Hower, *Clays Clay Miner.* **18**, 25 (1970).
17. J. W. Gruner, *Am. Mineral.* **19**, 557 (1934).
18. E. A. Perry and J. Hower, *Clays Clay Miner.* **18**, 165 (1970).
19. G. Dunoyer de Segonzac, *Sedimentology* **15**, 281 (1970).
20. P. H. Nadeau and R. C. Reynolds, Jr., *Clays Clay Miner.* **29**, 249 (1981).
21. S. Yariv and H. Cross, *Geochemistry of Colloid Systems* (Springer-Verlag, New York, 1979), pp. 401–430.
22. J. Hower *et al.*, *Geol. Soc. Am. Bull.* **87**, 725 (1976).
23. E. A. Zen, *Geochim. Cosmochim. Acta* **26**, 1055 (1962).
24. P. Aagaard and H. C. Helgeson, *Clays Clay Miner.* **31**, 207 (1983).

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Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling

Abstract. *Computer modeling of 611 high-quality analyses of normal ground waters from diverse geographic areas reveals that aqueous oxidation-reduction reactions are generally not at equilibrium. Multiple redox couples present in individual samples yield computed Nernstian Eh (redox potential) values spanning as much as 1000 millivolts. The computed Eh values do not agree with each other, nor do they agree with the single "master" value measured in the field with a platinum electrode. Because of internal disequilibrium, the use of any measured Eh value as input to equilibrium hydrogeochemical computer models will generally yield misleading results for normal ground waters.*

The concept of oxidation-reduction potential (Eh) is used extensively in many scientific fields. However, some investigators have recognized problems associated with the measurement and interpretation of Eh (*1–4*).

Of the thousands of Eh measurements reported for natural waters, only a few have been successfully interpreted on a quantitative, Nernstian basis. Some Eh measurements have been related to the reversible Fe^{2+}/Fe^{3+} couple in acid mine drainage waters (*5*) and to various dissolved sulfur couples (*6*). In laboratory studies, relatively concentrated solutions of manganous ion saturated with respect to Mn(IV) precipitates yield Eh values in agreement with the Nernst equation (*7*). However, most natural waters have low concentrations of redox elements and are poorly poised, with exchange currents too low to establish a Nernstian Eh during potentiometric measurements.

Most investigators of Eh have emphasized techniques of measurement of Eh, but the most serious problem in applying the concept of Eh to natural low-temperature aqueous systems is the lack of internal equilibrium (*1–4*). The redox potentials observed in natural waters are usually mixed potentials, which are impossible to relate to a single dominant redox couple in solution.

One can test the redox equilibrium in a single sample of water by analyzing for the dissolved species of multivalent elements, correcting the concentrations to activities, and calculating a theoretical Nernstian Eh for each analyzed couple. If all the computed Eh values agree, redox equilibrium probably obtains in the sample. Disagreement among the computed Eh values suggests that the system is at disequilibrium and that there is no single master Eh value.

Few investigators have examined natural water chemistry to determine the extent of redox equilibrium (*5, 8–10*). Papers by Stumm (*1*) and Morris and Stumm (*2*) are noteworthy for presenting arguments for the lack of redox equilibrium in natural waters. However, our results apparently represent the first comprehensive investigation of the degree of reversibility of oxidation-reduction reactions in a large number of ground waters.

A request was made to the National Water Data Exchange (NAWDEX) (*11*) for a search of the entire WATSTORE data base, which contains water data collected by the U.S. Geological Survey.

Table 1. Redox couples and plotting symbols used in the construction of Figs. 1 and 2.

Symbol	Redox couple
◇	Fe^{3+}/Fe^{2+}
▽	$O_{2\,aq}/H_2O$
○	HS^-/SO_4^{2-}
□	$HS^-/S_{rhombic}$
■	NO_2^-/NO_3^-
▼	NH_4^+/NO_3^-
△	NH_4^+/NO_2^-
+	$CH_{4\,aq}/HCO_3^-$
×	$NH_4^+/N_{2\,aq}$
●	$Fe^{2+}/Fe(OH)_{3\,(s)}$
M	Field-measured Eh value

We retrieved analyses for ground waters for which field measurements of Eh and *p*H were available, with data for major ions and at least one redox couple per sample. We used the WATSTORE data base to ensure that procedures of the U.S. Geological Survey had been followed in collecting and analyzing the ground waters. Approximately 150,000 ground water sampling sites were examined, yielding approximately 700 acceptable ground water analyses.

We examined the resulting analyses to eliminate incomplete analyses, time-series data, and analyses out of charge balance by more than 12 percent (milliequivalents of cations minus anions divided by the sum of cations plus anions). We also searched the geochemical literature for additional high-quality analyses. Of the final total of 611 analyses, 507 came from WATSTORE and 104 came from the literature. The mean temperature was 14.0°C; we did not investigate any thermal waters, in which equilibrium might be more closely approached.

The program WATEQFC (*12*) is an equilibrium model for natural waters, derived from WATEQF (*13*). We used WATEQFC to model the equilibrium aqueous chemistry of the waters. A useful feature of WATEQFC is that it computes Nernstian Eh values from analytical data for more than a dozen redox couples. Activity coefficients were computed from the extended Debye-Hückel or Davies expressions (*13*). (The mean ionic strength of the 611 samples was 0.014, with a standard deviation of 0.024.) We corrected the equilibrium constants for temperature, using the Van't Hoff expression (*14*), with a constant enthalpy or a polynomial from WATEQF (*13*).

Figure 1 presents a summary of computed Nernstian Eh data versus field-measured Eh values. (Couples and symbols are summarized in Table 1.) The dashed line in Fig. 1 represents the expected locus of points if all computed redox couples were at internal equilibrium and if each computed Nernstian value of Eh were to match the field measured Eh. The profound lack of agreement between the data points and the dashed line shows that internal equilibrium is not achieved. Further, the computed Nernstian Eh values do not agree with each other.

The data points in Figure 1 fall into several diffuse vertical bands, each corresponding to the Nernstian Eh for a particular redox couple analyzed for the water samples. The horizontal positions of the vertical bands in Fig. 1 chiefly reflect the standard E^0 (electrode potential) values in the Nernst equation for each couple. The breadth of each vertical band reflects the variation in the reported ratios of the oxidized and reduced species in each couple.

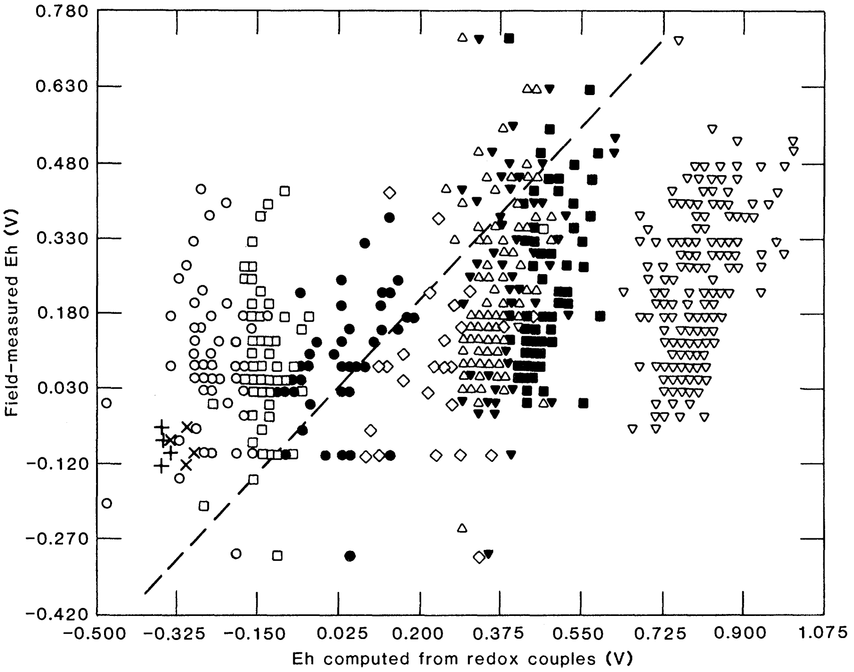

Fig. 1. Diagram showing ten computed Nernstian Eh values versus field-measured Eh values for the same samples measured with a platinum electrode. The dashed line is discussed in the text. Symbols and couples are summarized in Table 1.

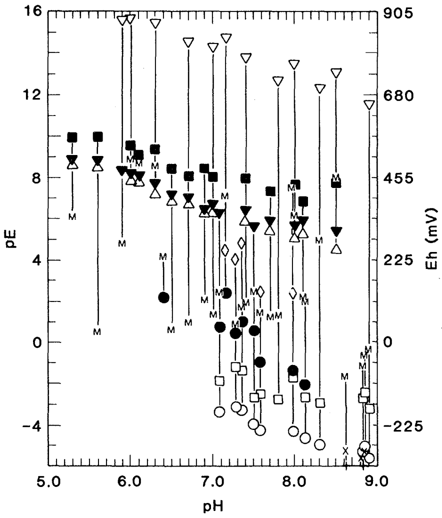

Fig. 2. Comparison of measured and computed Eh values in 30 ground waters as a function of *p*H. Symbols and couples are summarized in Table 1. Points connected by a vertical line are derived from a single water sample.

We next selected a representative subset of 30 ground water analyses, for which multiple redox couples were reported. Following Carpenter and Stoufer (*9*), we connected the Eh data representing individual samples by vertical lines and plotted these values as a function of *p*H in Fig. 2. The symbol "M" marks the field measured Eh, and all other symbols represent computed Nernstian Eh values corresponding to the analyzed couples listed in Table 1.

Figure 2 demonstrates that none of the 30 representative waters exhibits internal redox equilibrium. A wide range of computed Nernstian Eh values coexist, up to as much as 1000 mV. The broad span of computed Eh values reflects the near-complete lack of internal thermodynamic redox equilibrium within individual samples of water.

Delays in chemical analysis and inadequate sample preservation probably led to some postsampling shifts in the redox species in our samples. However, we believe that such factors are unlikely to invalidate our conclusions, because the computed Eh values in Fig. 2 are dependent chiefly upon the E^0 value in the Nernst equation and not upon the ratio of activities of the dissolved species. A change of 1000 in the ratio of SO_4^{2-} to

HS$^-$ results in a change of only about 20 mV in the corresponding computed Eh in Fig. 2, whereas the total vertical range exceeds 1000 mV. The same argument applies to the computed activity coefficients; any realistic change in activity coefficients results in a trivial change in the distribution of computed Eh values.

The *p*H is important in determining the distribution of points in Fig. 2. In fact, the linear correlation among computed *p*E (negative logarithm of the electron activity) (or Eh) values reported in some publications, for example, (*8*), for coexisting aqueous couples appears to reflect an autocorrelation among the dominant *p*H terms in the Nernst equations for each of the couples.

There are published suggestions that Eh measurements might be improved if the values were computed from analyses of "indicator" couples, such as I$^-$/IO$_3^-$ (*15*) or As(III)/As(V) (*16*). Unfortunately, this approach does not circumvent the fundamental difficulty that redox reactions in the waters are not at internal equilibrium among themselves. Therefore, an "indicator" Eh no more represents a master redox value for the water than the usual Eh as measured by a noble-metal electrode. Whitfield (*4*) has suggested that Eh measurements may still be useful as qualitative indicators of the overall redox state of a water sample. However, we believe that it would be better to measure certain sensitive species, such as aqueous oxygen, hydrogen sulfide, or methane as qualitative guides to the redox status of the waters.

The concept of Eh remains a valuable tool for theoretical and pedantic purposes. However, in the apparent absence of internal redox equilibrium, investigators should abandon the use of any measured master Eh for predicting the equilibrium chemistry of redox reactions in normal ground waters. Our conclusions are most severe in the context of predictive computer modeling of the chemistry of natural waters and wastewaters. In order to provide meaningful redox input for such models, it may be necessary to analyze the samples for the dominant ions of every redox element of interest. Wolery (*17*) has suggested this approach for testing the state of redox equilibrium, using his EQ3NR computer model. If any measured Eh is used as input for equilibrium calculations, the burden rests with the investigator to demonstrate the reversibility of the system.

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References and Notes

1. W. Stumm, *Adv. Water Pollut. Res. (Munich)* **1**, 283 (1967).
2. J. C. Morris and W. Stumm, in *Equilibrium Concepts in Natural Waters Systems*, W. Stumm, Ed. (American Chemical Society, Washington, D.C., 1967), p. 270.
3. W. Back and I. L. Barnes, *U.S. Geol. Surv. Prof. Pap. 424C* (1961), p. 366; D. Langmuir, in *Procedures in Sedimentary Petrology*, R. E. Carver, Ed. (Wiley-Interscience, New York, 1971), p. 597; K. A. I. Natarajan, thesis, University of Minnesota (1972); T. Frevert, *Arch. Hydrobiol. Suppl.* **55**, 278 (1979); R. A. Berner, *J. Sediment. Petrol.* **51**, 359 (1981); R. D. Lindberg, thesis, University of Colorado (1983).
4. M. Whitfield, *Limnol. Oceanogr.* **19**, 857 (1974).
5. D. K. Nordstrom, E. A. Jenne, J. W. Ball, in *Chemical Modeling in Aqueous Systems*, E. A. Jenne, Ed. (Symposium Series 93, American Chemical Society, Washington, D.C., 1979), p. 51.
6. R. A. Berner, *Geochim. Cosmochim. Acta* **27**, 563 (1963); J. Boulegue and G. Michard, in *Chemical Modeling in Aqueous Systems*, E. A. Jenne, Ed. (Symposium Series 93, American Chemical Society, Washington, D.C., 1979), p. 25.
7. O. P. Bricker, *Am. Mineral.* **50**, 1296 (1965).
8. D. C. Thorstenson, *Geochim. Cosmochim. Acta* **34**, 745 (1970).
9. A. B. Carpenter and R. N. Stoufer, *Influence of Organic Carbon and Microorganisms on Iron and Sulfide Concentrations in Ground Water* (Document PB-270-640, National Technical Information Service, Springfield, Va., 1977).
10. D. K. Nordstrom, thesis, Stanford University (1977); S. Emerson, R. E. Cranston, P. S. Liss, *Deep-Sea Res.* **26**, 859 (1979); W. E. Galloway, G. E. Smith, C. L. Ho, J. P. Morton, J. K. Gluck, *Report of Investigations, No. 118* (Bureau of Economic Geology, University of Texas, Austin, 1982).
11. M. D. Edwards, *U.S. Geol. Surv. Open-File Rep. 77-259* (1977).
12. D. D. Runnells and R. D. Lindberg, *J. Geochem. Explor.* **15**, 37 (1981).
13. L. N. Plummer *et al.*, *U.S. Geol. Surv. Water-Resources Invest. 76-13* (1976).
14. R. M. Garrels and C. L. Christ, *Solutions, Minerals, and Equilibria* (Freeman, Cooper, San Francisco, 1965).
15. P. S. Liss, J. R. Herring, E. D. Goldberg, *Nature (London) Phys. Sci.* **242**, 108 (1973).
16. J. A. Cherry, A. U. Shaikh, D. E. Tallman, R. V. Nicholson, *J. Hydrol.* **43**, 373 (1979).
17. T. J. Wolery, *Report No. UCRL-53414* (Lawrence Livermore National Laboratory, Livermore, Calif., 1983).

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Homology of Genome of AIDS-Associated Virus with Genomes of Human T-Cell Leukemia Viruses

Abstract. *A T lymphotropic virus found in patients with the acquired immune deficiency syndrome (AIDS) or lymphadenopathy syndrome has been postulated to be the cause of AIDS. Immunological analysis of this retrovirus and its biological properties suggest that it is a member of the family of human T-lymphotropic retroviruses known as HTLV. Accordingly, it has been named HTLV-III. In the present report it is shown by nucleic acid hybridization that sequences of the genome of HTLV-III are homologous to the structural genes* (gag, pol, *and* env) *of both HTLV-I and HTLV-II and to a potential coding region called pX located between the* env *gene and the long terminal repeating sequence that is unique to the HTLV family of retroviruses.*

Human T-cell leukemia virus (HTLV) was first identified as an infectious agent etiologically associated with adult T-cell leukemia (ATL) (*1*). A related but distinct retrovirus was isolated from a T-cell variant of hairy cell leukemia (*2*). These viruses, known, respectively, as HTLV-I and HTLV-II, show a tropism for human T cells, particularly OKT4$^+$ cells, and have the capacity to immortalize and transform normal T cells in culture (*3*), alter certain T-cell immune functions in vitro (*4*), induce the formation of giant multinucleated T cells (*5*), and, in some cases, selectively kill certain T cells (*6*). These properties and data from epidemiologic studies of the acquired immune deficiency syndrome (AIDS), which is uniformly associated with OKT4$^+$ helper cell depletion (*7*), led us and others to speculate (*8*) that a member of the HTLV family might be the etiological agent of this disease. In support of this hypothesis was the finding that up to 80 percent of AIDS patients, but less than 1 percent of non-AIDS patients from similar risk groups, have serum antibodies that react with the envelope protein of HTLV (*9*). However, actual isolations of the known subgroups of HTLV (that is, HTLV-I and HTLV-II) from AIDS patients were infrequent (*10*).

Recently, we reported repeated isolations of a T lymphotropic retrovirus with cytopathic but not immortalizing activity from patients with AIDS (*11*). This virus can be grown in a previously immortalized T-cell line (HT) that is relatively resistant to the cytopathic effects of the virus and can grow in the absence of T-cell growth factor (interleukin-2) (*12*). Using the infected cells as well as purified virus particles in immunological assays, we found that the serum of 80 to 100 percent of AIDS patients and 70 to 80 percent of patients with lymphadenopathy syndrome reacted positively (*13*). On the basis of its T-cell tropism, the size and Mg^{2+} preference of its reverse transcriptase, the size of its major core protein (24,000 daltons) (*14*), some anti-