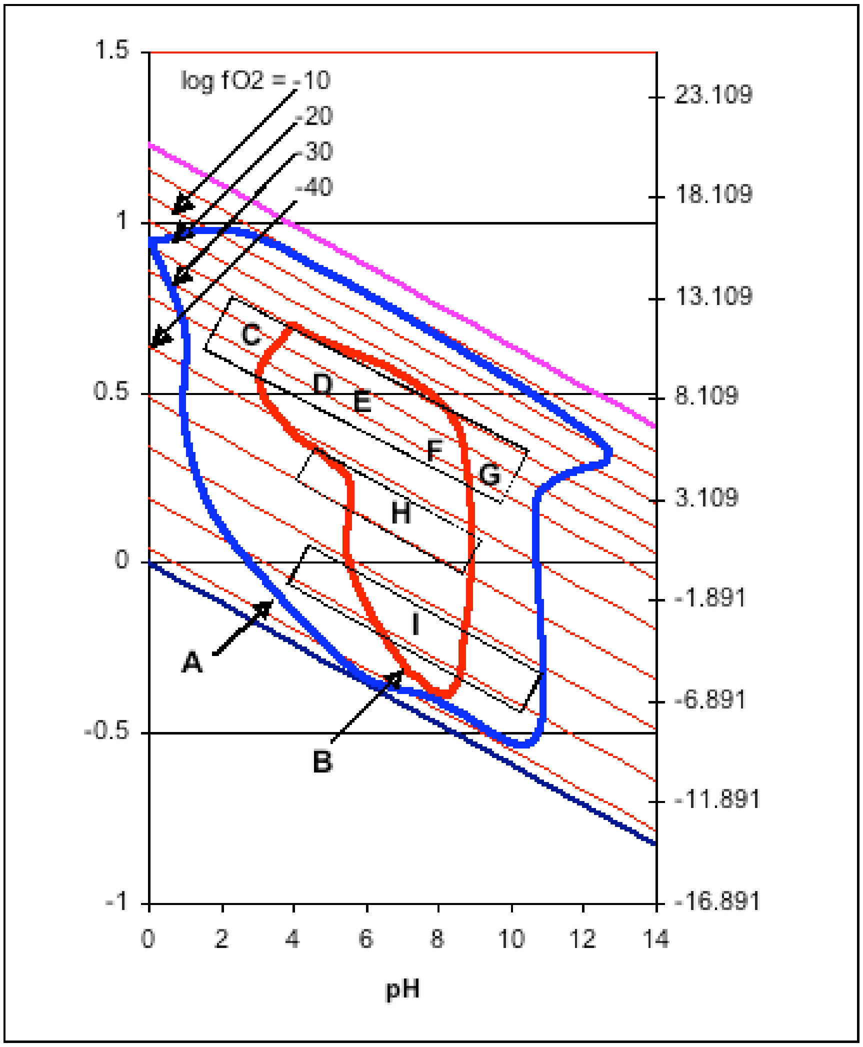

Economic & Environmental Geochemistry, Inc.

Oxygen Fugacity in Eh-pH Space

Equilibrium calculations performed by software routines such as Geochemist's Workbench, MINTEQ PHREEQC, and others are based on equations involving the master variables Eh (or pe) and pH. Resultant solid and aqueous stability fields and reaction paths can then be visualized in the familiar Eh-pH space popularized by Garrels and Christ (1965). Unfortunately, one of these two master variables, Eh, is difficult to very difficult to measure in a meaningful way and commonly is not measured at all. In the absence of dependable Eh data it is necessary to estimate Eh in order to represent reactions involving polyvalent species (e.g., Fe, Mn, As, Se, U, etc.).

One conceptual, but misleading, way to estimate Eh is to substitute the partial pressure (fugacity) of oxygen as an indicator of Eh and to assume that reactions in the presence of air take place in response to 0.21 atmospheres of oxygen. With modeling conditions fixed in this way, all calculations in Eh-pH space will be confined to a line just below the upper stability limit for water. Bass Becking et al. (1960) and Garrels and Christ (op. cit.) showed the fallacy of this approach for all but a few rare surface geologic situations.

This figure shows typical Eh-pH space with the stability limits for water defined by the fugacity of oxygen and hydrogen equaling one atmosphere for the upper and lower limits, respectively. Also shown are oxygen isobars in increments of 1E-5 and 1E-10 atmospheres. The Eh-pH conditions for given Oxygen fugacities are expressed simply as :

$$\boldsymbol{Eh}\ (volts) = 1.23 + \frac{0.0592}{4} \log f_{O_2} - 0.0592\ pH$$

In addition to the theoretical calculations, the observed "limits" (A) and typical range (B) of Eh-pH characteristics of natural waters are shown (after Bass-Backing et al. (op. cit)). Garrels and Christ (op. cit) identified specific environments in Eh-pH space including waters in contact with the atmosphere (C through G). Letters identify general environments: C = mine waters (ARD), D = rain, E = streams, F = normal ocean water and G = aerated saline environments. The combined environments tend to populate a region of Eh-pH space that is parallel to the oxygen isobars, but at significantly lower O_2 partial pressures (typically log P_{O2} = -25 to -35) than would be indicated by 0.21 atm. Transitional environments (H) and those isolated from the atmosphere (I, bog water, euxenic marine, organic-rich saline waters, etc.) also occupy areas of Eh-pH space parallel to P_{O2} isobars

Garrels, R.M and Christ, C.L. (1965) Solutions, Minerals and Equilibria. Harper & Row

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