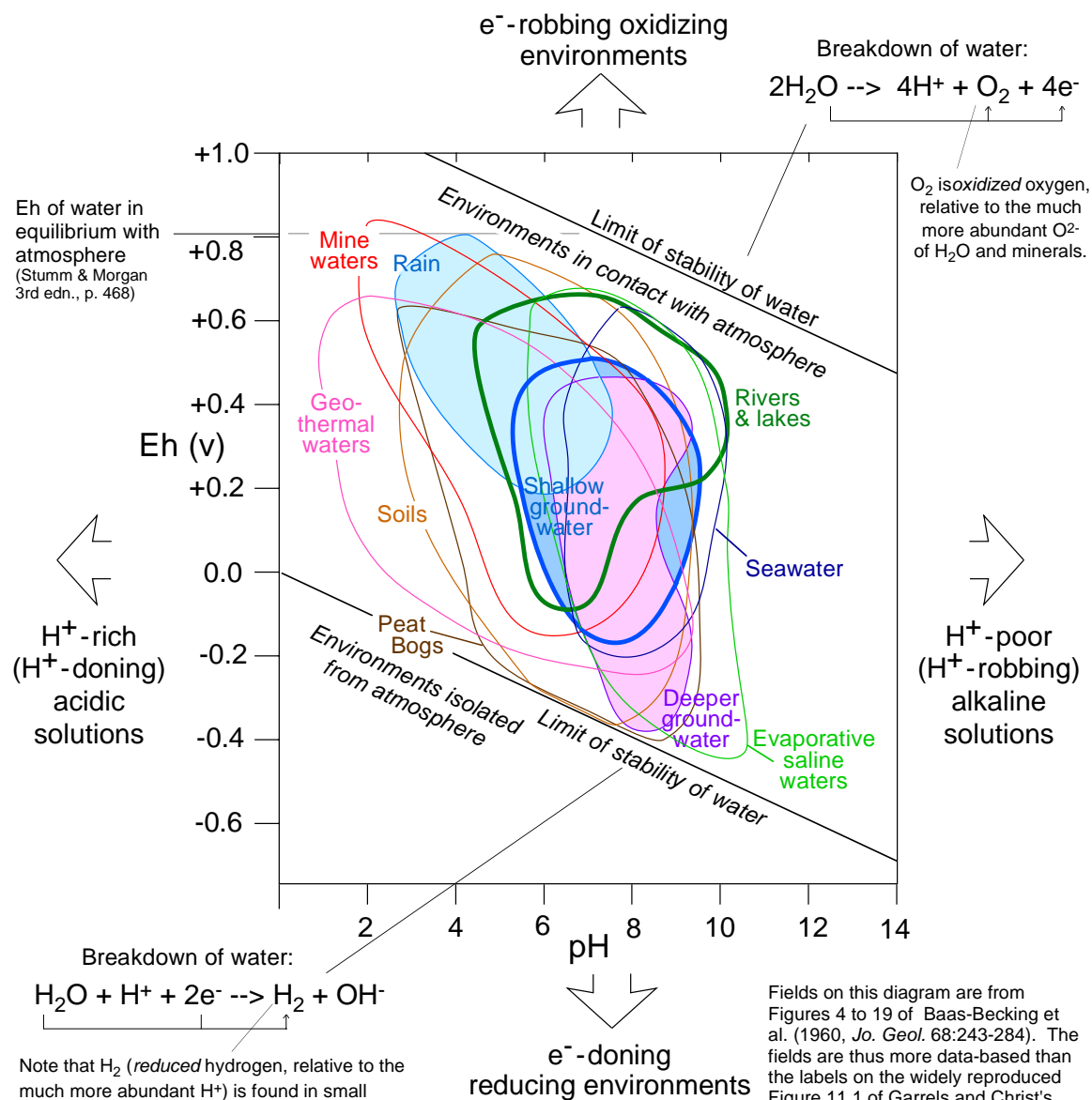


Characterization of solutions by pH and Eh



pH is a measure of the acidity or alkalinity of a solution, where $\text{pH} = -\log a_{\text{H}^+}$. pH is thus less in more acidic (less basic) solutions and greater in less acidic (more basic) solutions. A change of 1 (i.e., from pH=3 to pH=4) represents a ten-fold change in the activity of H^+ . A 1N solution of highly dissociated acid (e.g., 1M HCl) has a pH of 0 (because $a_{\text{H}^+} = 1 = 10^0$). pH is commonly said to have a possible range from 1 to 14, but highly acidic solutions can have pH = -1 (10N) and even -2. At 25°C, $\text{pH} + \text{pOH} = 14$.

Eh is a measure of the redox (oxidation-reduction) state of a solution or, more exactly, its solutes. Eh is a measurement of electrical potential and thus commonly expressed in volts. Values of Eh in nature range from -0.6 to +0.9V, with 0.0 characterizing a solution with no drive to either oxidize or reduce. Accurate measurement of Eh is much more difficult than that of pH, because measurement of Eh requires equilibration with many solutes and even solids.

Unlike pH, Eh is not a measure of concentration of something, and use of the related parameter $\text{pE} = (-\log a_{\text{e}^-})$ requires recognition that pE is a completely theoretical expression, ignoring the reality that the concentration of electrons in a solution is always zero. $\text{pE} = \text{Eh} \div 0.05916$.

The diagram at left shows data from a range of environments. The fields for rainwater, waters of rivers and lakes, shallow ground water, and deeper ground water are highlighted and/or shaded to draw attention to the evolution of water through the water cycle as it becomes less oxidic and more buffered with respect to pH.

Note that H_2 (reduced hydrogen, relative to the much more abundant H^+) is found in small concentrations in some deeper groundwaters (Lovley & Chapelle 1995, *Reviews in Geophysics*).

Fields on this diagram are from Figures 4 to 19 of Baas-Becking et al. (1960, *Jo. Geol.* 68:243-284). The fields are thus more data-based than the labels on the widely reproduced Figure 11.1 of Garrels and Christ's *Solutions, Minerals, and Equilibria*.