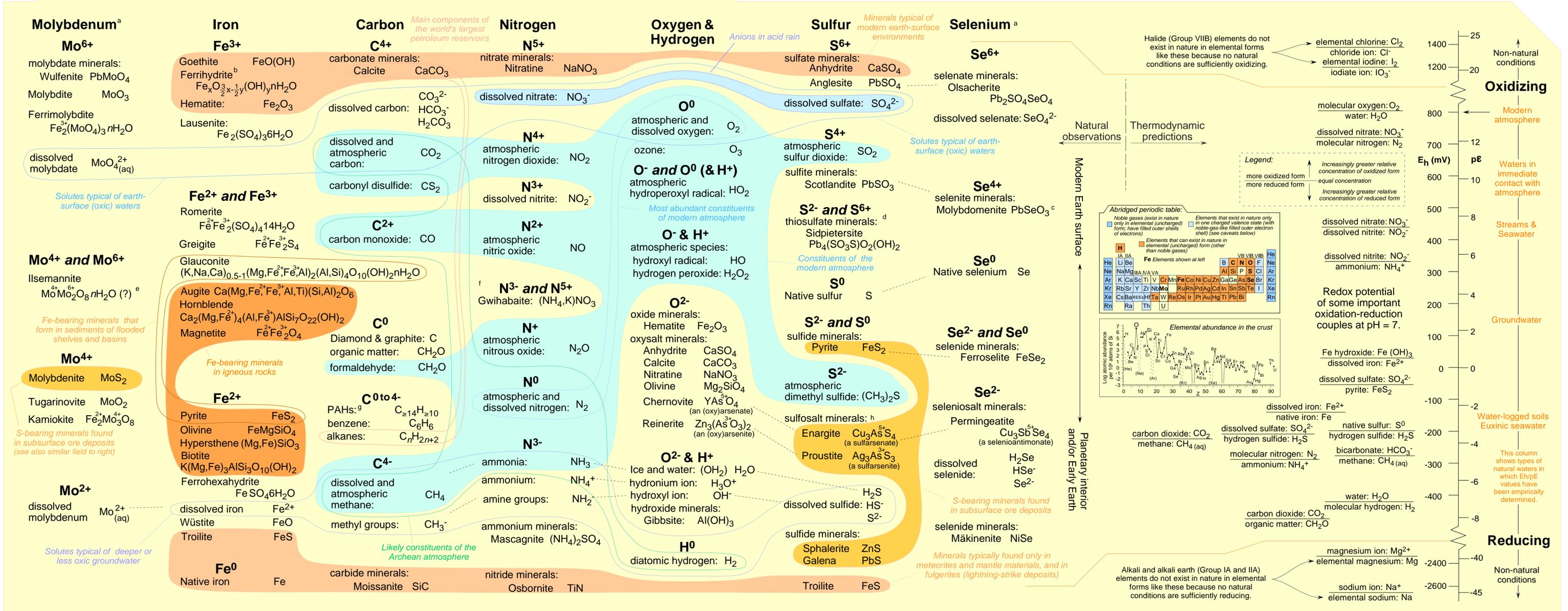


The geochemical redox conditions of some important elements



Principal points illustrated by this chart:

1. The most oxidized minerals and solutes are typical of earth-surface environments, and the most reduced minerals and solutes are representative of mantle materials and meteorites. The chart thus mimics natural geometry, from Earth's surface at the top down to the planetary interior below. Igneous rocks, as well as sediments from flooded shelves and basins, fall in roughly the middle of this range.
2. With regard to time, minerals typical of modern near-surface environments are largely oxidized forms, whereas minerals known mostly from meteorites (and thus identified with conditions during planetary formation) contain the most reduced forms. The constituents of the modern atmosphere are likewise largely more oxidized forms, whereas the interpreted constituents of the Archean atmosphere are largely more reduced forms. The chart thus mimics chronostratigraphy, from redox states of earlier materials and conditions toward the bottom to redox states of younger materials at the top.
3. Points 1 and 2 together illustrate that present variation in redox conditions through space parallels past variation through time.
4. The range of stability of water from Eh = -400 mV to +800 mV dictates the range of possible natural redox conditions, and those elements whose elemental (uncharged) forms reach equilibrium far from those conditions (e.g. Na and Cl) do not exist in elemental form in nature.

5. Many substances contain one element in more than one valence state (e.g., S in pyrite, Fe in magnetite and greigite, and O in hydroperoxyl).
6. Acid rain is also oxidized rain, in that N and S are oxidized to their highest valence states in the formation of acid rain (e.g., SO₂ + 2OH → H₂SO₄ → 2H⁺ + SO₄²⁻).
7. Some substances contain two elements at opposite ends of their respective ranges of valence states (e.g., N³⁻ and S⁶⁺ in mascagnite, Fe²⁺ and S⁶⁺ in ferroxahydrate, and Fe³⁺ and S²⁻ in greigite).
8. Some substances contain one element in two very different valence states (e.g., S⁶⁺ and S²⁻ in sidpietersite and N³⁻ and N⁵⁺ in gwihabaite).
9. The atmosphere contains C, N, O, and S in a range of oxidation states and thus is not an equilibrium system, which would require oxidation of N₂ to NO₃⁻ and oxidation of the other not-completely-oxidized C, N, and S species.
10. Materials with one element in very different valence states, such as C⁴⁺ in carbonate minerals and C⁰ in petroleum, can nonetheless reside together for tens to hundreds of millions of years, as in the world's largest oil fields (e.g. the carbonate-hosted Ghawar Field in Saudi Arabia).
11. Points 8 to 10, and arguably 7 as well, illustrate that natural systems need not reach redox equilibrium, even across very small spatial scales (e.g. within individual minerals) or very long time scales (as in carbonate-hosted accumulations of petroleum).

Ridiculous over-generalization:
 On the left side of the periodic table, nature steals all outer-shell electrons of Group IA, IIA, and IIIA elements, and even most Group IVA elements, leaving them as cations with noble-gas like configurations. On the right side of the periodic table, nature has sufficiently few surplus electrons that Group VB and VIB elements can exist in elemental form, rather than gaining the extra electrons needed to reach noble-gas-like configurations. These two observations suggest electrons are going into some major sink.
 From a different perspective, but showing the same thing, note that positive oxidation states as great as 6+ are common (and even 7+ exists in nature, but rare, perchlorate). On the other hand, negative oxidation states range only as low as 4-, and rarely so, except for C⁴⁻. Again, the implication is that a lot of electrons have gone somewhere.
 So where have so many electrons gone? Mostly to oxygen, the most abundant element in Earth's crust (see chart of abundances) and thus (as O²⁻ in oxides, oxysalts, and water) the dominant player in the give and take of electrons. From this perspective, the peak in the chart of elemental abundances helps explain the top-sided distribution of brown squares in the periodic table and the preponderance of positive, rather than negative, oxidation states in the chart above.

Notes:
^a Selenium may not be an "important element", but it is a proxy here for several elements such as As, Sb, and Te. Mo likewise is a proxy for Cr, W, and U.
^b Published chemical formulae for ferrihydrate vary; the formulation here is an LBR invention encompassing the variation shown in Clark (1993), Gaines et al. (1997), and Mandarino and Black (2004).
^c "Molybdomenite" is an Mo-free mineral; the Greek word "molybdos" actually means "lead".
^d Thiosulfates are sulfates in which one O²⁻ of the SO₄²⁻ group is replaced by an S²⁻ to give a (S²⁻O₃)²⁻ group, which is sometimes written as S₂O₃²⁻.
^e Isemanite is not a thoroughly-studied mineral, and so its chemical formula could be incorrect.
^f In parallel with gwihabaite's range of oxidation states would be dimethyl carbonate ((CH₃)₂CO₃), a proposed additive to gasoline and thus a potential minor component of the atmosphere (Bilde, Møgelberg, Sehested, et al., 1997, *J. Phys. Chem. A.*, v. 101, p. 3514-3525).
^g PAHs are polycyclic aromatic hydrocarbons such as anthracene (C₁₄H₁₀) and benzo(a)pyrene (C₂₀H₁₂) and ultimately graphite, where the number of C atoms approaches infinity and so charge on C approaches zero.
^h Sulfosalts are analogs of oxysalts in which S²⁻ ions replace all of the O²⁻ ions of a tetrahedral radical.

Comments and Caveats:
 For the most part, the minerals listed are only single examples of larger groups. Dashed lines connect chemically analogous substances across otherwise distinct columns. "Shallow" and "deep" are relative terms that may represent centimeters to kilometers of vertical distance. Cl⁺ and I⁵⁺ (as in perchlorate and iodate) are minor exceptions to the claim in the legend of the periodic table that Cl and I have only one valence state, and likewise Ce⁴⁺ and Eu²⁺ are exceptions to the generalization that REEs all have 3+ charge.

Principal sources:
 Minerals and their occurrences are from *Hey's Mineral Index*, (Clark, 1993), *Dana's New Mineralogy* (Gaines et al., 1997), and *Fleischer's Glossary of Mineral Species 2004* (Mandarino and Black, 2004). Atmospheric constituents are from Table 1 of Prinn (2003) in *Treatise on Geochemistry* Volume 4. For the chart of Eh/pE at right, the values used are from, or are compromises between, Figure 1.2 of Sigg (2000), Figure 11.10 of Langmuir (1997), and Tables 8.3 and 8.6a of Stumm and Morgan (1996). Generalizations at far right relating Eh or pE to natural waters with pH = 7 are from Baas-Becking et al. (1960) and Garrels and Christ (1965); the value for the modern atmosphere is from Stumm and Morgan (1996, p. 468).