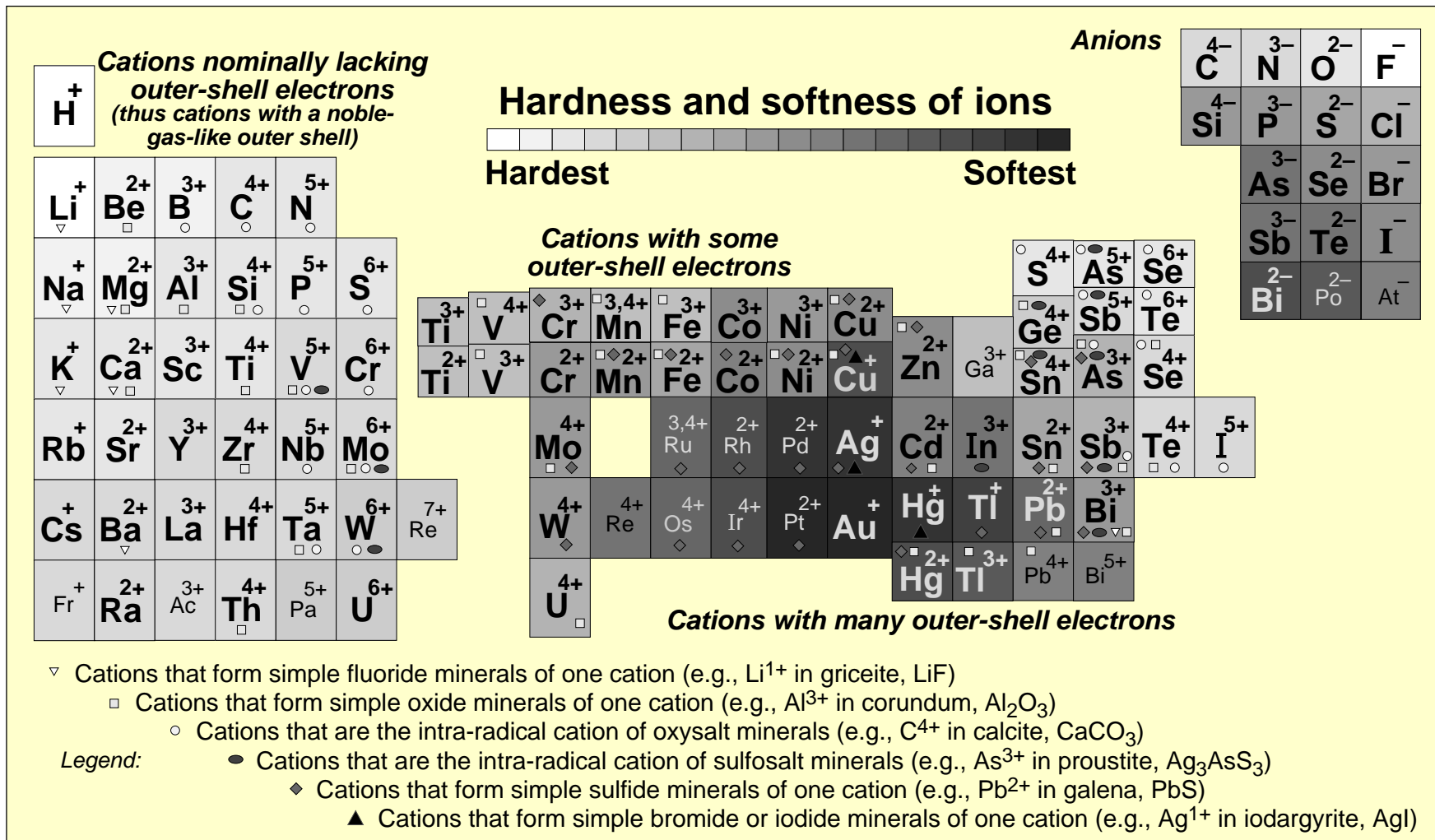


Hardness and softness of ions

Ions can be categorized as hard or "Type A" (behaving as hard spheres and forming more ionic bonds) or soft or "Type B" (deforming from a spherical shape and forming more covalent bonds). Cations with no outer-shell electrons (e.g., Na¹⁺, Mg²⁺, Al³⁺, etc., all of which have a neon-like outer shell) all are conventionally considered hard cations. On the other hand, cations with at least some outer-shell electrons (e.g., Mn²⁺ and Fe²⁺) are considered intermediated in this categorization, and cations with many outer-shell electrons (e.g., Ag¹⁺ and Hg¹⁺) are considered soft.

Hardness and softness of ions is shown on the periodic table below with shading for each of the cells of the table. The table presents hardness and softness of cations and anions as a spectrum, acknowledging that although cations like Mo⁶⁺ and U⁶⁺ have nominally lost their six outer-shell electrons, they in fact retain some of those electrons, and their large size also make them softer than a cation like Li¹⁺ that is small and has definitely lost all of its outer-shell electrons.

One reason that the hardness-softness concept is important in the Earth Sciences is that it allows an understanding of why some substances exist as minerals and some do not. Harder cations bond well to harder anions, and softer cations bond well to softer anions. The small symbols below show the result: the harder cations form fluoride, oxide, and oxysalt minerals, whereas the softer cations tend more to form sulfide and sulfosal minerals, and the softest cations form bromide and iodide minerals.



The hardness-softness concept comes from Pearson, R.G. (1968) Hard and soft acids and bases, HSAB, Part I: Journal of Chemical Education, v. 45, p. 581-587; Schwarzenbach, G. (1961) The general, selective, and specific formation of complexes by metallic ions: Advances in Inorganic Chemistry and Radiochemistry, v. 3, p. 257-285; and Stumm, W. & Morgan, J. J. (1996) Aquatic Chemistry (3rd edition), John Wiley & Sons, New York. The periodic table above is based on that of Railsback, L.B. (2003) An earth scientist's periodic table of the elements and their ions:

Geology, v. 31, p. 737-740. The mineral occurrences shown are from that paper, from Figure 1 of Railsback, L.B. (2005) A synthesis of systematic mineralogy: American Mineralogist, v. 90, p. 1033-1041, and from Figure 2 of Railsback, L.B. (2007) Patterns in the compositions of oxysalt and sulfosal minerals, and the paradoxical nature of quartz: American Mineralogist, v. 92, p. 356-369. The spectrum of hardness and softness is from Figure 8 of Railsback (2007).