Redox, ionic potential, and the behavior of cations

Some elements can have more than one positive oxidation state (i.e., they can form multiple cations), and the behavior of those different cations can be very different. This page explores that idea.

Solubility of cations depends on their ionic potential, or charge divided by radius, which is a measure of density of charge. Cations of low ionic potential like Na⁺ are typically soluble, because they make weak bonds to O²⁻. Cations of high ionic potential, like S⁶⁺, bond so well to O²⁻ that they make oxocomplexes like SO₄²⁻ (sulfate) that are soluble. In between, cations of intermediate ionic potential like Al³⁺ have sufficient density of charge to bond strongly to O²⁻ but not such dense charge as to repel each other, and so they make stable oxides and/or hydroxides and thus are insoluble.

Oxidation and reduction change some elements from a cation in one of these groups to a cation in another group. One important example is Fe, which in reducing conditions is the soluble Ca²⁺-like or Mg²⁺-like Fe²⁺ cation but in oxidizing conditions is the insoluble Al³⁺-like Fe³⁺ cation. Mn behaves likewise. Ce behaves likewise but from 3⁺ to 4⁺, giving Ce anomalies in distributions of rare-earth elements.

Other elements change from a reduced insoluble form to a soluble oxidized form. U changes from reduced U⁴⁺ to oxidized U⁶⁺, accounting for the presence of U as a solid in organic-rich (reducing) sediments but dissolved UO₂ in (oxidizing) seawater. Cr likewise changes from reduced Cr³⁺ in solids to oxidized and dissolved Cr⁶⁺, which is why introduction of O₂ to groundwaters can lead to Cr-poisoning problems. The same holds for As³⁺ and As⁵⁺.

To summarize, different redox conditions can lead to very different behaviors of an element, with important geologic and environmental implications. However, we cannot say that, for all elements, reduced forms are more soluble (which is true for Fe and Mn) or that oxidized forms are more soluble (which is true for U, Cr, Mo, and As). Instead, we have to think in terms of ionic potential, and how that parameter changes from the reduced to the oxidized form of each element.