

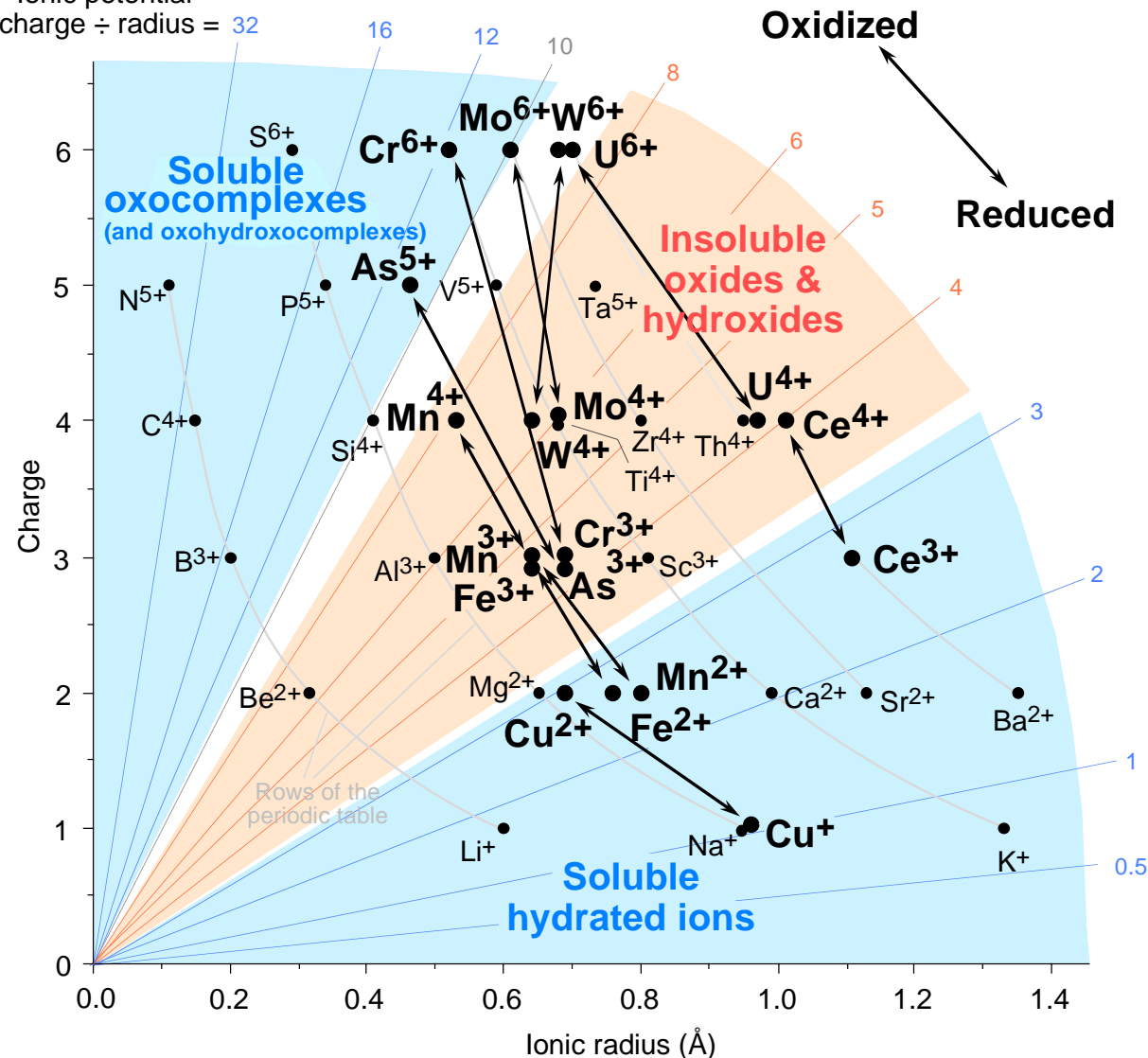
## Redox, ionic potential, and the behavior of cations

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  $\text{Na}^+$  are typically soluble, because they make weak bonds to

$\text{O}^{2-}$ . Cations of high ionic potential, like  $\text{S}^{6+}$ , bond so well to  $\text{O}^{2-}$  that they make oxocomplexes like  $\text{SO}_4^{2-}$  (sulfate) that are soluble. In between, cations of intermediate ionic potential like  $\text{Al}^{3+}$  have sufficient density of charge to bond strongly to  $\text{O}^{2-}$  but not such dense charge as to repel each other, and so they make stable oxides and/or hydroxides and thus are insoluble.

Ionic potential =  
charge  $\div$  radius =



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  $\text{Ca}^{2+}$ -like or  $\text{Mg}^{2+}$ -like  $\text{Fe}^{2+}$  cation but in oxidizing conditions is the insoluble  $\text{Al}^{3+}$ -like  $\text{Fe}^{3+}$  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  $\text{U}^{4+}$  to oxidized  $\text{U}^{6+}$ , accounting for the presence of U as a solid in organic-rich (reducing) sediments but dissolved  $\text{UO}_2$  in (oxidizing) seawater. Cr likewise changes from reduced  $\text{Cr}^{3+}$  in solids to oxidized and dissolved  $\text{Cr}^{6+}$ , which is why introduction of  $\text{O}_2$  to groundwaters can lead to Cr-poisoning problems. The same holds for  $\text{As}^{3+}$  and  $\text{As}^{5+}$ .

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 oxidized form of each element.