

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 O^{2-} . Cations of high ionic potential, like S^{6+} , bond so well to O^{2-} that they make oxocomplexes like SO_4^{2-} (sulfate) that are soluble. In between, cations of intermediate ionic potential like Al^{3+} have sufficient density of charge to bond strongly to 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.

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 Ca^{2+} -like or

Mg^{2+} -like Fe^{2+} cation but in oxidizing conditions is the insoluble Al^{3+} -like 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 U^{4+} to oxidized U^{6+} , accounting for the presence of U as a solid in organic-rich (reducing) sediments but dissolved UO_2 in (oxidizing) seawater. Cr likewise changes from reduced Cr^{3+} in solids to oxidized and dissolved Cr^{6+} , which is why introduction of O_2 to groundwaters can lead to Cr-poisoning problems. The same holds for As^{3+} and 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.

