Notes to accompany
"A table of systematic mineralogy"

Most treatments of systematic mineralogy involve either long lists or long strings of text that are not integrated to provide a larger perspective on the entire suite of known minerals. Table I ("A table of systematic mineralogy I: basic categories") attempts to provide that perspective. From left to right, the table moves from uncharged atoms (the native elements) to cations bonded to single anions (e.g., fluorides, chlorides, oxides, and sulfides) and then to cations bonded to anions that are part of radical groups or complex ions (e.g., sulfates, carbonates, and silicates). From top to bottom, the table progresses from minerals with 1- anions (the halides) to minerals with 2-, 3-, and 4- anions. The red shading of the table shows where the most common mineral groups fall, but it also shows that there are many other less well-known groups of minerals too (e,g, fluosalts, sulfarsenites, and phosphides).

It's also interesting to see the parts of Table I where no minerals exist. For example, there are fluosalts, but there are no chlorosalts, bromosalts, or iodosalts (for example, there's no $NaBCl_4$ mineral). That's partly because the Cl^-, Br^-, and I^- ions are large, and they can't coordinate around a highly charged cation like Si^{4+} (where they would at best yield a silicate-like $SiCl_4^0$ cluster with no net charge) or Se^{6+} (where they would at most yield a selenate-like $SeCl_4^{2+}$ cluster with net positive charge). It's also because they're large and little-charged, so that their density of charge is low, and so they bond only weakly to cations, rather than making the strong bonds typical within radical groups.

The non-existence of another set of minerals becomes apparent in the lower right part of Table I. There are no nitrosalt, phosposalt, arsenosalt, bismuthosalt, carbosalt. or silicisalt minerals with sulfate-like formulas like $CaSP_4$. That's partly an issue of large size again, because large anions like P^{3-} would allow at most three-fold coordination around a small highly charged cation like S^{6+}. However, it's also a matter of redox chemistry. Very reducing conditions are required to generate N^{3-}, P^{3-}, As^{3-}, C^{4-}, and S^{4-} ions. Those reducing conditions would make impossible the existence of a highly-charged central cation like S^{6+}, P^{5+}, N^{5+}, or C^{4+} — those candidates for the central cation of a nitrosalt or phosphosalt would be reduced to S^0 or S^{2-}, P^{3+} or P^{3-}, and so on. Thus there are no minerals at the lower right of Table I because the reducing conditions required to generate 3- and 4- anions like P^{3-} and C^{4-} preclude the existence of a highly positively charged central cation around which the anions could cluster to make a radical group.

With that said, one can move up in Table I to the sulfosalts (and seleniosalts and tellurisalts). The same logic of redox chemistry applies here: reducing conditions sufficient to put S, Se, and Te in their S^{2-}, Se^{2-}, and Te^{2-} states, rather than their S^{6+} or S^{4+}, Se^{6+} or Se^{4+}, and Te^{6+} or Te^{4+} states, would generally be too reducing to oxidize an element to give a highly charged central cation around which to cluster a radical group. There are thus only a few sulfarsenates, where As is oxidized to its 5+ charge to allow AsS_4^{3-} clusters, but there are many more sulfarsenites, where As has only 3+ charge to form AsS_3^{3-} clusters. The weaker attraction of these less-charged central cations to their S^{2-} anions, compared to that in oxy-salts, is one of the reasons that "sulfosalt" is a term used by mineralogists for classifying minerals according to structure, but not a term used much by chemists who classify solids according to the solutes from which they precipitate.

These redox considerations are treated further in Table II ("A table of systematic mineralogy II: redox implications"). If one considers the large-scale range of redox conditions from the oxygenated Earth surface and atmosphere at one extreme to either Earth's deep interior and the low-O_2 environment of outer space at the other extreme, one finds that some minerals (oxides and oxysalts) are characteristic of Earth-surface environments, whereas the minerals lower in Table II are more typical of more reducing deeper environments or of meteorites and cosmic dust. Thus the seemingly purely chemical framework of Table I provides, with Table II, a large-scale environmental perspective on systematic mineralogy.