

# Stability and solubility of carbonate minerals of divalent cations

The plot below shows the thermodynamic stability, and thus the solubility, of some carbonate minerals of divalent cations. Blue is used to highlight the **rhombohedral** carbonate minerals like calcite, where the inter-radical cation (e.g.,  $\text{Ca}^{2+}$  in calcite) is nested among six  $\text{O}^{2-}$  anions. Red is used to highlight the **orthorhombic** carbonates like aragonite, where the inter-radical cation (e.g.,  $\text{Ca}^{2+}$  in aragonite) is nested in a larger cation site among nine oxygens.

Things to note include

1) Smaller cations make rhombohedral carbonate minerals, and larger cations form orthorhombic carbonate minerals, as one would expect from the difference in coordination.

2) Within each group, cations with radii near the middle of their respective group form less soluble, and thus more stable, minerals.  $\text{Fe}^{2+}$  in siderite and  $\text{Cd}^{2+}$  in otavite are examples among the rhombohedral carbonate minerals. On the other hand, cations at the end of each range are more soluble.  $\text{Mg}^{2+}$  in magnesite and  $\text{Ca}^{2+}$  in calcite are examples among the rhombohedral carbonate minerals. These observations define the two "windows" of greater stability in the diagram.

3)  $\text{Ca}^{2+}$  falls at the boundary between the rhombohedral and orthorhombic carbonate minerals, accounting for the existence of two common polymorphs of  $\text{CaCO}_3$ , calcite and aragonite.

4) The two most common carbonate minerals, calcite and aragonite, are both more soluble than minerals of other cations because  $\text{Ca}^{2+}$  falls outside the windows of the two

mineral groups. For example, calcite is more soluble than otavite, siderite, rhodochrosite, and smithsonite, and aragonite is more soluble than strontianite and cerussite.

5) The two most abundant  $2+$  cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , fall outside the rhombohedral and orthorhombic windows and therefore form relatively soluble carbonate minerals.

6) A mineral of two cations at the ends of a group is more stable than the minerals of single cations. For example, dolomite is more stable than magnesite and calcite, and alstonite is more stable than aragonite and witherite.

These facts help account for many of the interesting issues of carbonate petrology: #3 for why waters may precipitate one  $\text{CaCO}_3$  mineral under certain conditions but another  $\text{CaCO}_3$  mineral under other conditions; #4 for why both of the  $\text{CaCO}_3$  minerals are so soluble, giving us both caves and speleothems; and #5 and #6 for why dolomitization is so common and the dolomite problem so important. It would be a much less interesting world if our carbonate deposits consisted of carbonates of  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$  and thus did not offer so much mineralogical variability and such susceptibility to dissolution, reprecipitation, and diagenetic alteration.

