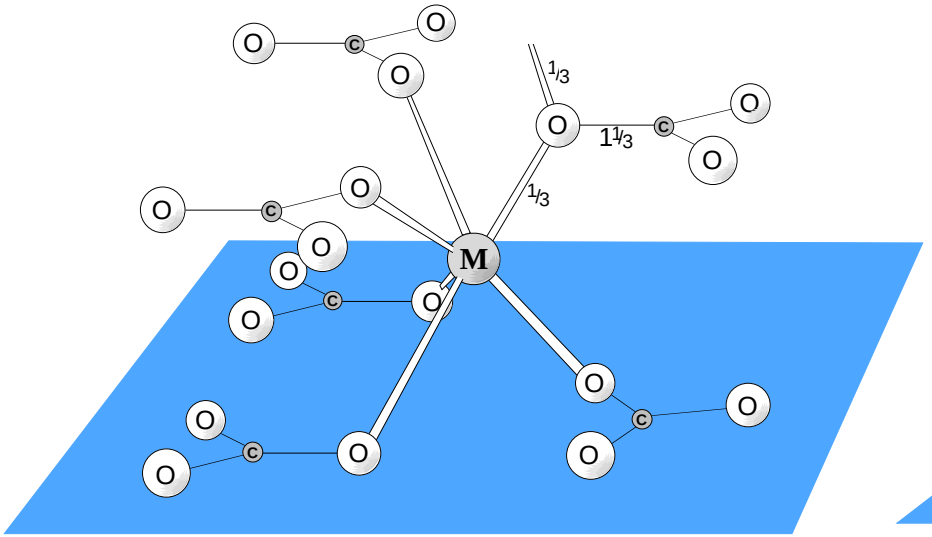
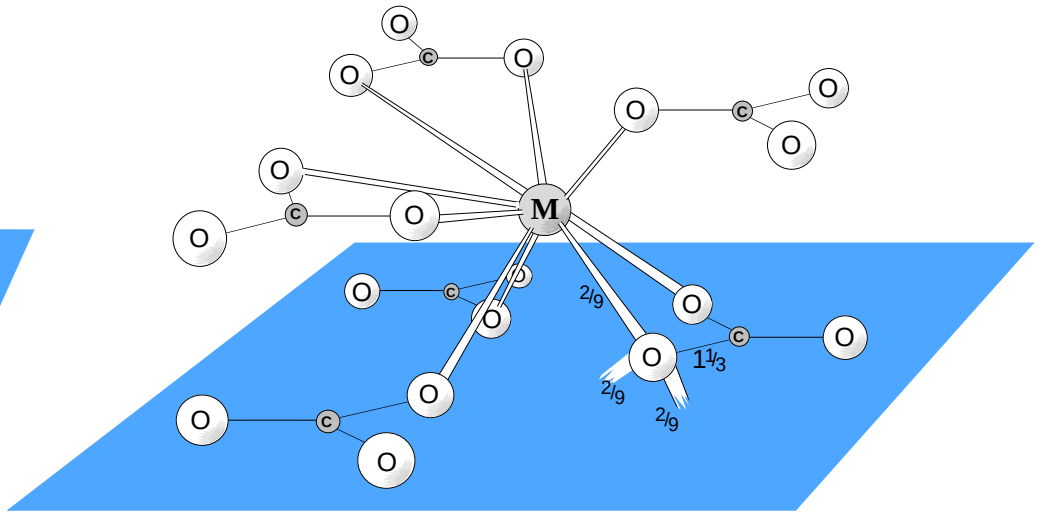
Cation sites in the common carbonate minerals

Rhombohedral (Calcite-Type) Carbonates



Six-fold coordination:
From one 0001 plane of CO_3s,
a bond to one O^{2-} from each of three CO_3 groups;
from other 0001 plane of CO_3s,
a bond to one O^{2-} from each of three CO_3 groups.
Each O^{2-} is bonded to two 2+ cations.

Orthorhombic (Aragonite-Type) Carbonates



Nine-fold coordination:
From one plane of CO_3s (upper one here),
bonds to two O^{2-}s from each of two CO_3 groups
and a bond to one O^{2-} from a third CO_3 group;
from other plane of CO_3s (lower one here),
bonds to two O^{2-}s from one CO_3 group
and bonds to one O^{2-} from each of two other CO_3 groups.
Each O^{2-} is bonded to three 2+ cations.

C Carbon
O Oxygen
M Cation
1/3 Bond Strength

Cation	Radius (Å)	Rhombohedral Mineral	Orthorhombic Mineral
Ni^{2+}	0.69	Gaspeite	
Mg^{2+}	0.72	Magnesite	
Zn^{2+}	0.74	Smithsonite	
Co^{2+}	0.75	Sphaerocobaltite	
Fe^{2+}	0.78	Siderite	
Mn^{2+}	0.83	Rhodochrosite	
Cd^{2+}	0.95	Otavite	
Ca^{2+}	1.00	Calcite	Aragonite
Sr^{2+}	1.13		Strontianite
Eu^{2+}	1.17		(synthetic)
Pb^{2+}	1.19		Cerussite
Ba^{2+}	1.35		Witherite
Ra^{2+}	1.40		(synthetic)

The common carbonate minerals (the anhydrous carbonates of divalent cations) can be divided into two groups on the basis of their cation sites. The six-fold cation site in rhombohedral carbonates (a site in which the cation is nested among six O^{2-}s) can house relatively small cations. The nine-fold cation site in orthorhombic carbonates (a site in which the cation is nested among nine O^{2-}s) can house relatively large cations.

This is significant to $CaCO_3$ because . . .

1) Ca^{2+} is at the threshold of cation sizes for the two groups, so that there are two polymorphs of $CaCO_3$, calcite and aragonite. It's purely a coincidence that the divalent cation that makes the most carbonate material (Ca^{2+}) is at the threshold of cation sizes between the two carbonate mineral groups (see table at left).
2) The relatively small cation site in calcite means that the trace elements common in calcite are the smaller cations (Mg^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, & Sr^{2+}), whereas the relatively large cation site in aragonite means that the trace elements common in aragonite are the larger cations (Sr^{2+}, Pb^{2+}, and Ba^{2+}).