

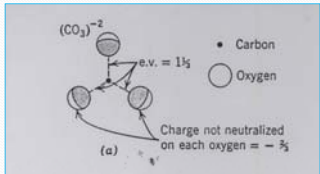
Carbonate Mineralogy

Carbonate Mineralogy

- Carbonate Minerals
 - Crystal Habit
- CaCO₃ System
 - CaCO₃ Polymorphs
 - Mg substitution for Ca
 - Precipitation of CaCO₃
- (Ca·Mg(CO₃)₂) System



Carbonate Minerals



- Composed of:
 - One or more cations + CO₃= complex anion
 - CO₃ complex anion forms equilateral triangular, which gives minerals a rhombic shape.
 - C-O bonds are short, ionic bonds that are relatively stable.

- There are as many as 69 different carbonate minerals.
- Variants formed by loosely bonding other anions such as: (OH)⁻, F⁻, Cl⁻, (PO₄)₃⁻, (SO₄)₂⁻.
- Most hydrous forms are metastable and form as weathering products.

Common Carbonate Cations

Table 1. Atomic weights and ionic radii of common elements contained within carbonates. Data from Mason (1962)

Element	(Common ionic state)	Atomic weight	Ionic radius (Å)
B		10.82	0.23
Fl	(-1)	19.00	1.36
Na	(+1)	22.99	0.95
Mg	(+2)	24.32	0.66
S	(+6)	32.07	0.30
Cl	(-1)	35.46	1.81
K	(+1)	39.10	1.33
Ca	(+2)	40.08	0.99
Mn	(+2)	54.94	0.80
Fe	(+2)	55.85	0.74
Ni	(+2)	58.71	0.69
Cu	(+2)	63.54	0.72
Zn	(+2)	65.38	0.74
Sr	(+2)	87.63	1.12
Ba	(+2)	137.36	1.34
Pb	(+2)	207.21	1.20

Handwritten notes:
 HgCO₃ = Magnesite
 CaCO₃ = calcite or aragonite
 MnCO₃ = rhodochrosite
 FeCO₃ = siderite

Crystal Structure

- 2 common forms:
 1. Hexagonal-Rhombohedral
 2. Orthorhombic
- Monoclinic with (OH) is rare. Malachite and Azurite


Common Cations versus Crystal Form

Hexagonal-Rhombohedral				Orthorhombic			
Mg	Cu	Zn/Fe	Mn	Ca	Sr	Pb	Ba
.66	.72	.74	.80	.99	1.12	1.2	1.34

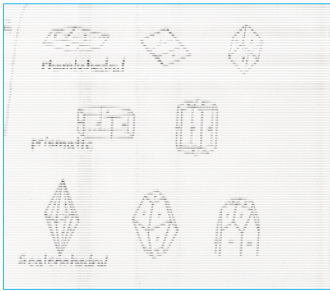
- Smaller cations (Mg, Fe, Mn, Zn, and Cu) are energetically favored in rhombohedral configurations.
- Larger cations (Sr, Pb, and Ba) favored in the larger orthorhombic structure.
- Ca is intermediate size and fits into either configuration.

Hexagonal-rhombohedral - Calcite Group

- Six-fold coordination (2 cations/oxygen w/in CO₃ group and 1 C)
- Each cation layer bonded to 6-O in adjacent layers



Common Hexagonal-Rhombohedral Crystal Forms

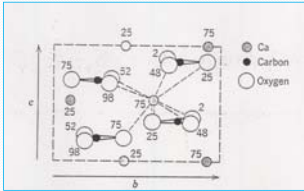


Common Hexagonal-Rhombohedral Minerals

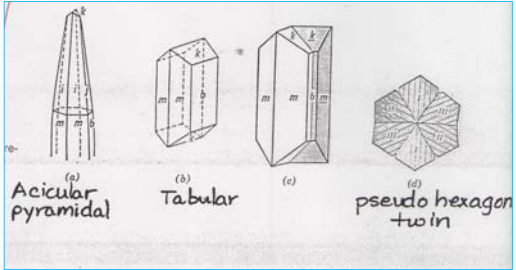
- Calcite CaCO_3
- Magnesite MgCO_3
- Siderite FeCO_3
- Rhodochrosite MnCO_3
- Smithsonite ZnCO_3
- Dolomite $\text{CaMg}(\text{CO}_3)_2$
- Ankerite $\text{Ca}(\text{Mg, Fe})(\text{CO}_3)_2$

Orthorhombic – Aragonite Group

- Nine-fold coordination (3 cations/oxygen).
- Each cation bonded 9-O. CO₃ arranged into two layers per cation layer.



Common Orthorhombic Crystal Forms



Common Orthorhombic Minerals

- Aragonite CaCO_3
- Witherite BaCO_3
- Strontianite SrCO_3
- Cerussite PbCO_3

Miscellaneous other structural forms:

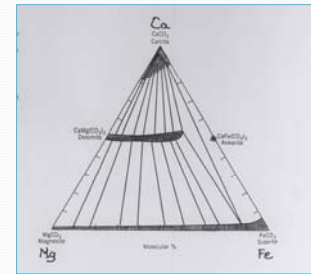
- Monoclinic with hydroxyl (OH)-
 - Azurite $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$
 - Malachite $\text{Cu}_2(\text{OH})_2(\text{CO}_3)$
- Hydrated Carbonates
 - Trona $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$

CaCO_3 System

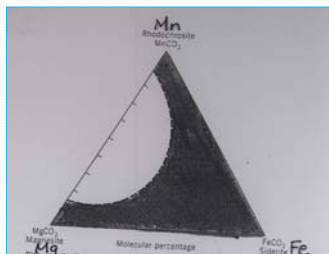
- CaCO_3 minerals are seldom pure, but tend to incorporate other cations within their lattices.
- Rhombohedral shaped calcite tends to incorporate the smaller cations
- Orthorhombic shaped aragonite incorporates large cations.

- Complete solid-solution substitution of other cations for Ca does not occur on the earth's surface.

- Usually only a small % of substitution occurs due to 15% size difference in ionic radius between Ca and the other cations



Complete solid-solution or substitution does occur in other carbonate minerals for instance Mg-Fe and Fe-Mn, where the difference in ionic radius size is less than 15; but not Mn-Mg



Mg substitution for Ca

- Mg commonly substitutes for Ca in calcite because it is such small cation.

2 forms depending on % Mg:

- **Low-magnesian calcite** = contains <1% Mg
- **High-magnesian calcite** = contains >1% Mg (4 -20 mole% MgCO_3).

- Low Mg calcite is the most stable at surface temperatures and pressures.
- However, carbonate sediments in the ocean are typically high Mg calcite and aragonite. Why?

High Mg calcite commonly precipitated from ocean water because Mg is 3 times more abundant than Ca.

- Low Mg Calcite is typically precipitated from fresh water because the concentration of Mg is much lower.

	mg/kg	SEA WATER	mg/kg	Dissolved solids %	Milli-moles	Atomic elements
RIVER WATER						
Na ⁺	6.1	10,760	30.6	368	63.1	
Mg ²⁺	0.1	1,264	3.7	33.2	5.13	
Ca ²⁺	10.0	974	1.9	17.1	2.68	
K ⁺	2.3	38	1.1	7.95	0.96	
SO ₄ ²⁻	13.1	0.015	8			
Cl ⁻	7.8	0.01	0.015			
SO ₂	11.2	0.002				
HCO ₃ ⁻	28.4	0.003				
B ³⁺	—	0.01				
H ₂ BO ₃ ⁻	—	0.01				
Total	118.2					
SEA WATER						
Ca ²⁺	19,353	35.2	345			
SO ₄ ²⁻	2,712	7.1	28.2			
HCO ₃ ⁻	142	0.4	2.3			
B ³⁺	47	0.2	0.84			
BH ₂ BO ₃ ⁻	28	0.07	0.43			
Total	33,182	99.9*	118.3			

(Ca Mg(CO₃)₂) Dolomite System

- Dolomite is formed when Ca=Mg concentration in rhombohedral crystal habit.
- Dolomite is organized into discrete layers of Ca and Mg cations separated by layers of CO₃ anions. Once formed dolomite is a relatively stable mineral.

- Dolomite precipitated from hypersaline brines with elevated Mg content forming *protodolomite*.
- More commonly dolomite forms by recrystallization of calcite and aragonite.

- Mg is smaller than Ca, so the lattice spacing of pure dolomite is considerably smaller than calcite.
- So when calcite is diagenetically altered to dolomite, intercrystalline porosity is created.

Fe and Mn substitution in dolomite

- Both Fe and Mn commonly substitute for Mg
- Form ankerite (Ca(Mg,Fe,Mn)(CO₃)₂). When Fe substitution is up to 70 mole%.
- Fe substitution into dolomite decreases the stability of the mineral

