

Earth and Planetary Materials

Spring 2013

Lecture 6
2013.01.28

More on (oxyhydr)oxides

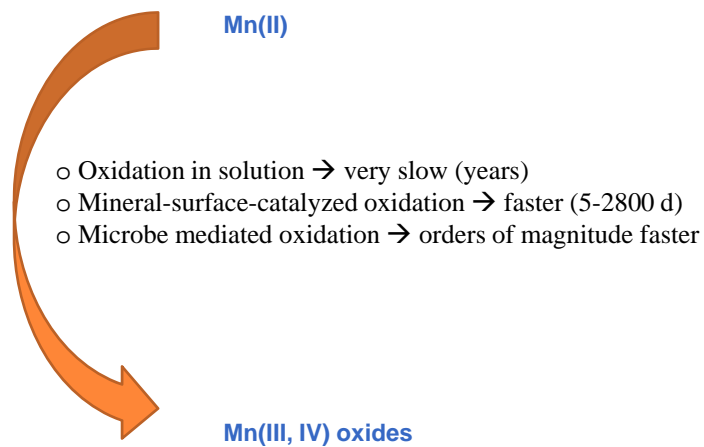
Fe oxides
Mn oxides

Mn (oxyhydr)oxides

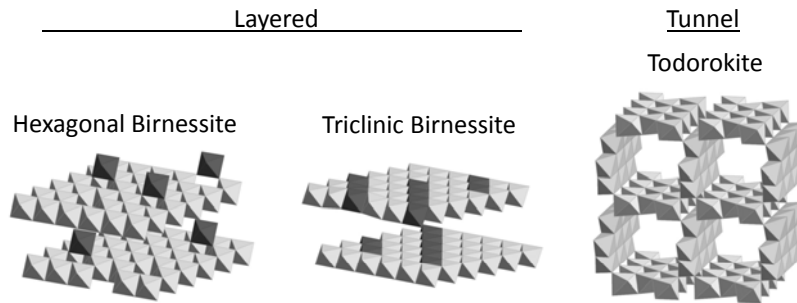
- The most extensive deposition of Mn oxides today occurs in the oceans as nodules, microconcretions, coatings, and crusts (estimated coverage 10 – 30% of the deep Pacific floor)
- Mn exists as 2+, 3+, and 4+; oxide minerals are varied, complex, and hard to identify



Mn (oxyhydr)oxides



Structure of biogenic Mn oxides – limited

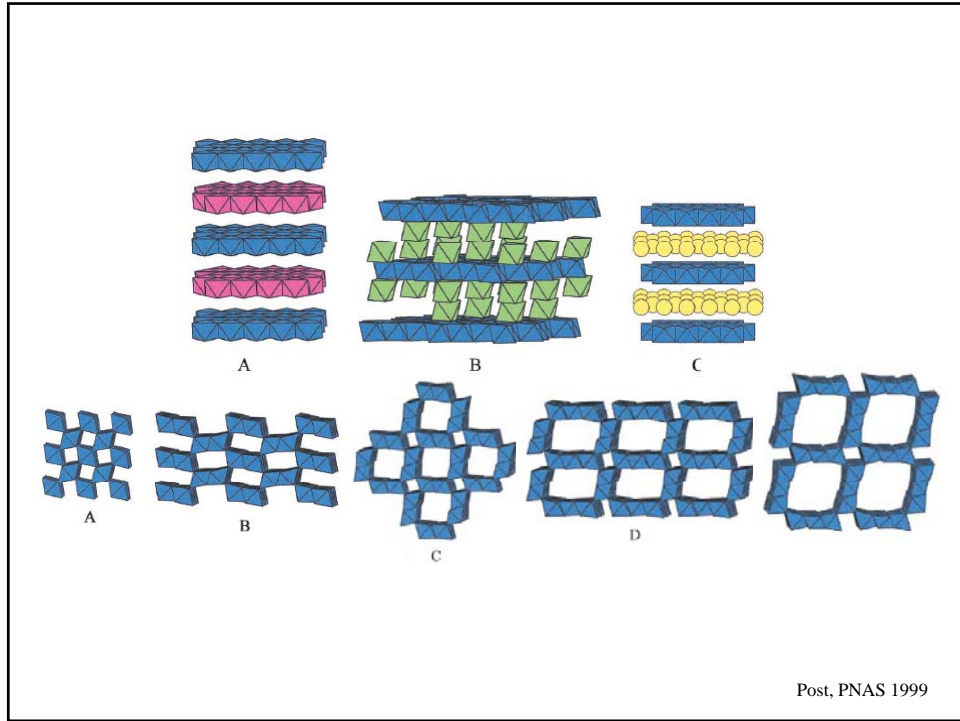


More than 30 known Mn oxide minerals

Table 1. Important Mn oxide minerals

Mineral	Chemical formula
Pyrolusite	MnO ₂
Ramsdellite	MnO ₂
Nsutite	Mn(O,OH) ₂
Hollandite	Ba _x (Mn ⁴⁺ , Mn ³⁺) ₈ O ₁₆
Cryptomelane	K _x (Mn ⁴⁺ , Mn ³⁺) ₈ O ₁₆
Manjiroite	Na _x (Mn ⁴⁺ , Mn ³⁺) ₈ O ₁₆
Coronadite	Pb _x (Mn ⁴⁺ , Mn ³⁺) ₈ O ₁₆
Romanechite	Ba ₆₆ (Mn ⁴⁺ , Mn ³⁺) ₅ O ₁₀ ·1.34H ₂ O
Todorokite	(Ca, Na, K) _x (Mn ⁴⁺ , Mn ³⁺) ₆ O ₁₂ ·3.5H ₂ O
Lithiophorite	LiAl ₂ (Mn ⁴⁺ , Mn ³⁺) ₂ O ₆ (OH) ₆
Chalcophanite	ZnMn ₃ O ₇ ·3H ₂ O
Birnessite	(Na, Ca)Mn ₇ O ₁₄ ·2.8H ₂ O
Vernadite	MnO ₂ ·nH ₂ O
Manganite	MnOOH
Groutite	MnOOH
Feitknechtite	MnOOH
Hausmannite	Mn ²⁺ Mn ₂ ³⁺ O ₄
Bixbyite	Mn ₂ O ₃
Pyrochroite	Mn(OH) ₂
Manganosite	MnO

Post, PNAS 1999

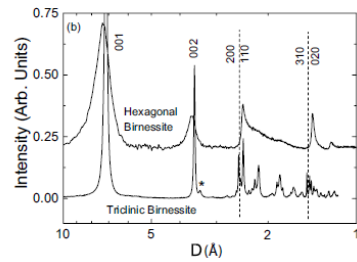


Dendrites of Mn oxides

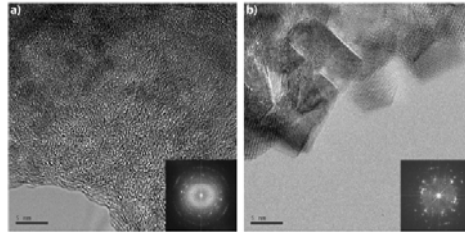


Structure identification difficult

- XRD analyses do not easily distinguish different minerals, must combine with TEM, SEM, IR spectroscopy, and microprobe work



Webb et al. Am Min 2005



Learman et al. Geochim Cosmochim Acta 2011

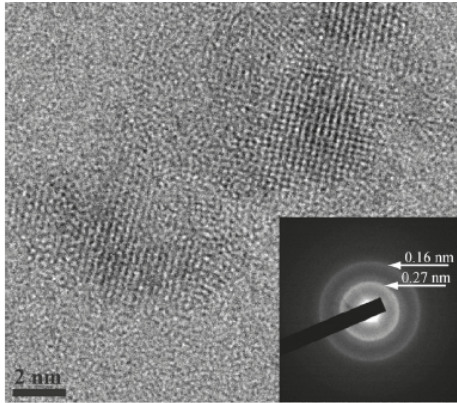
Iron (oxyhydr)oxides

- Interaction of dissolved iron with oxygen yields iron oxide and iron oxyhydroxide minerals
- Initial precipitation → ferrihydrite

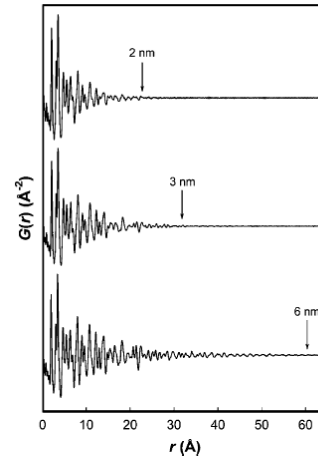


Ferrihydrite

- Extremely fine grained – a few nanometers in size
- Nanocrystalline vs amorphous?



Tang et al. Chem Mater 2010

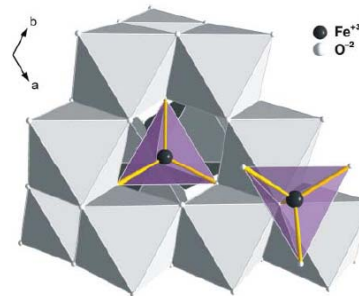


Michel et al. Chem Mater 2007

Ferrihydrite

Debates about the structure

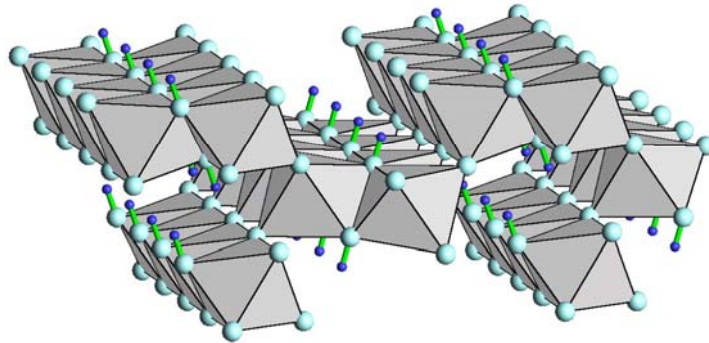
- Existence of tetrahedral Fe
- Structural organization



Michel et al. Science 2007

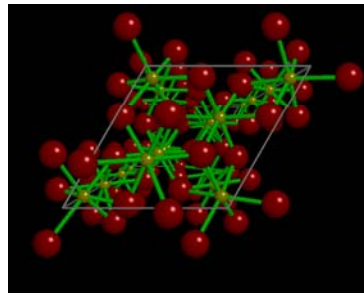
Goethite α -FeOOH

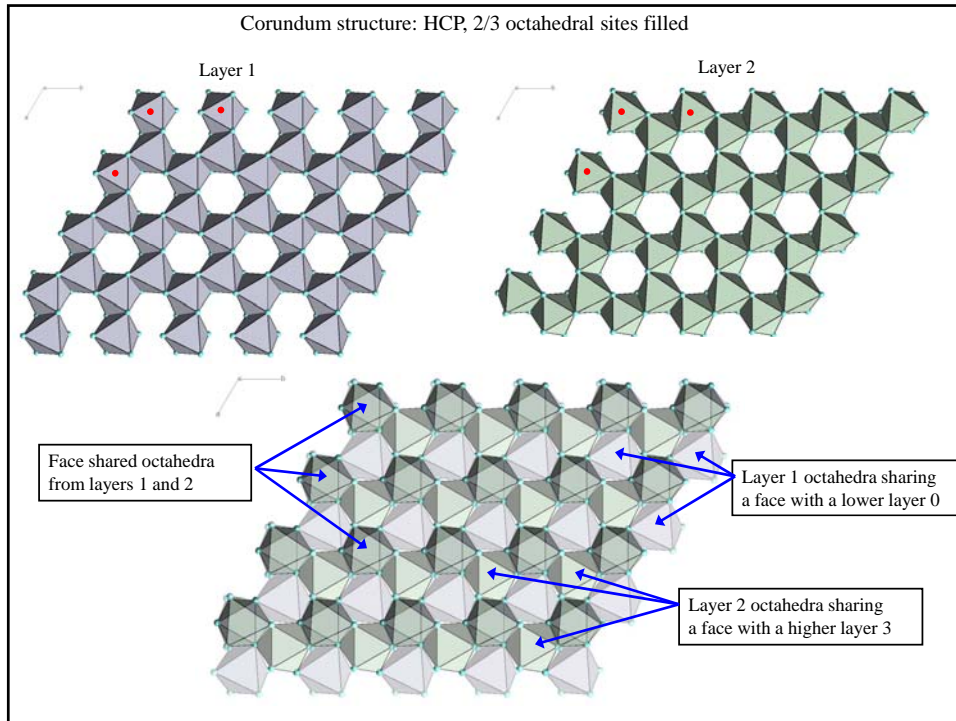
- Ferrihydrite \rightarrow goethite (α -FeOOH) etc
- Other polymorphs
 - Lepidocrocite g-FeOOH
 - Akaganeite b-FeOOH



Hematite

- Hematite (Fe_2O_3) – can form directly or via ferrihydrite \rightarrow goethite \rightarrow hematite
- Red-brown mineral is very common in soils and weathering iron-bearing rocks





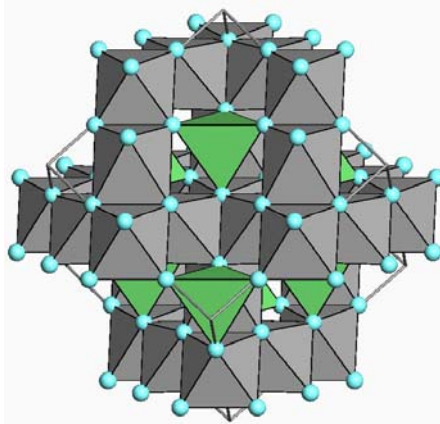
Magnetite

- Magnetite (Fe_3O_4) – Magnetic mineral of mixed valence → must contain both Fe^{2+} and Fe^{3+} → how many of each??
- ‘Spinel’ structure – 2/3 of the cation sites are octahedral, 1/3 are tetrahedral

Spinel structure:

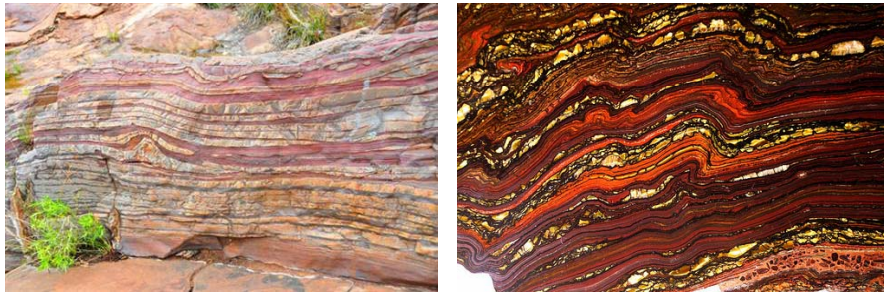
$\text{A}^{(4)}\text{B}^{(6)}_2\text{O}_4$ (normal)

$\text{B}^{(4)}[\text{B}^{(6)}\text{A}^{(6)}]\text{O}_4$ (inverse)



Banded Iron Formations (BIFs)

- Huge Precambrian formations composed of Fe-rich vs Fe-poor bands: magnetite, hematite, Fe-silicates, Fe-carbonates, chert
- Account for ~90% of the world's iron supply
- Occur only 1.9 – 3.8 billion years ago @ many sites around the world



BIFs and microbial activity

- Early earth did not have free O_2
- Microbial activity became widespread and photosynthetic organisms started generating O_2
- Deep ocean hydrothermal input \rightarrow mix with sea water \rightarrow reduced Fe species oxidized \rightarrow Fe oxide minerals



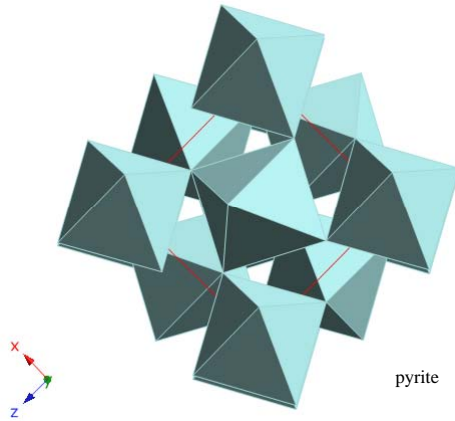
Other important oxides

- Periclase MgO
- Brucite Mg(OH)_2
- Rutile, anatase, brooksite – TiO_2 polymorphs
- Corundum Al_2O_3 – sapphire and ruby
- Ilmenite, FeTiO_3 – common in igneous and metamorphic rocks
- Cuprite, Malachite, Azurite – copper oxides
- Uraninite UO_2 – important U ore
- Spinel MgAl_2O_4 – High-P metamorphic mineral

Sulfides

Sulfide Minerals

- Minerals with S^{2-} or S_2^{2-} (monosulfides) or S_2^{2-} (disulfides) as anionic group
- Transition metals bonded with sulfide anion groups



Sulfide Minerals

- Substitution into sulfides is very common
- As and Se substitute for S very easily
- Au can substitute in cation sites (auriferous minerals)
- Different metals swap in and out pretty easily → Cu and Fe for instance have a wide range of solid solution materials

Iron Sulfides

- Mackinawite – FeS
- Greigite – Fe_xS_y
- Pyrite – FeS_2 (cubic)
- Marcasite – FeS_2 (orthorhombic)
- Troilite – FeS end member
- Pyrrhotite – Fe_{1-x}S (slightly deficient in iron)
- Arsenopyrite – FeAsS
- Chalcopyrite – CuFeS_2

Other important sulfides

- Galena – PbS
- Sphalerite/wurtzite – ZnS
- Cinnabar – HgS
- Molybdenite – MoS
- Covellite – CuS
- Chalcocite – Cu_2S
- Acanthite or Argenite – AgS
- Stibnite – Sb_2S_3
- Orpiment – As_2S_3 ; Realgar – AsS

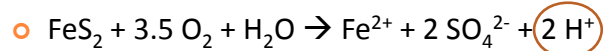
When sulfides meet oxygen

- Abandoned sub-surface mines
- Exposure to air/water causes the oxidation of metal sulfides (often pyrite FeS_2)
- Increased acidity

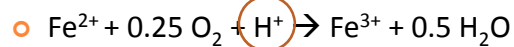


Pyrite oxidation

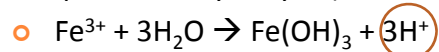
Initial oxidation



Secondary oxidation



At ~pH 4, Fe^{3+} hydrolyze (take on water) and precipitate



Minerals of oxyanions

Carbonates
Sulfates
Phosphates

Oxyanions

- The salts of oxyanions forms a large mineral group
- An oxyanion is an anion formed by oxygen covalently bonded to another atom

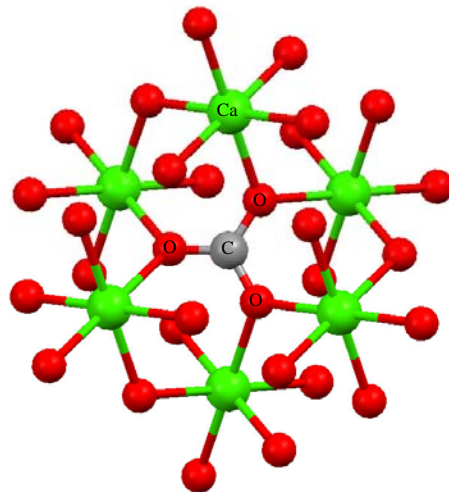
Examples

- carbonate (CO_3)⁻
- sulfate (SO_4)²⁻
- phosphate (PO_4)³⁻
- chromate (CrO_4)²⁻

- tungstate, arsenate, vanadate...

Typically more than one type of bonding

- strong covalent bonds within the oxyanion
- weaker ionic bonds between the cation and oxyanion



Carbonates

- Most abundant, especially in sedimentary rocks
- 3 main sub-groups: calcite, aragonite, dolomite
- More complex hydroxy-carbonates, e.g.
 - Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
 - Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$

azurite and malachite



azurite and malachite



malachite



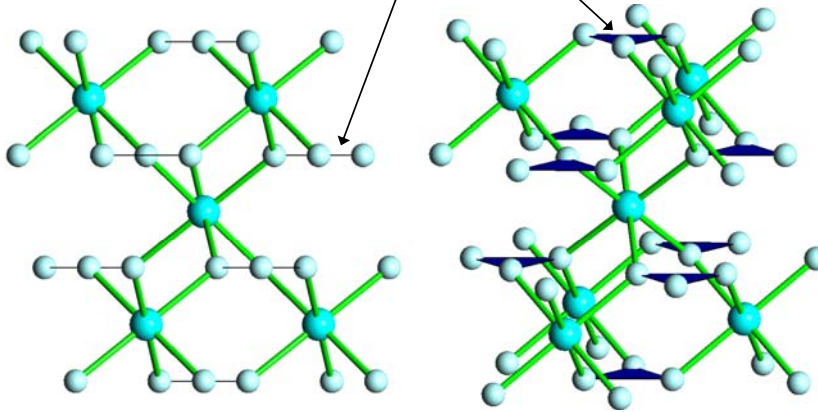
Carbonates – (1) calcite structure

- adopted by carbonates with ionic size of Ca and smaller
- calcite (Ca)
magnesite (Mg)
siderite (Fe)
complete solid solution between magnesite and siderite
- Cation CN = 6
- Each carbonate oxygen bonded to two cations

Carbonates – (1) calcite structure

side view
approximate CCP array of carbonate

triangular $(\text{CO}_3)^{2-}$ groups



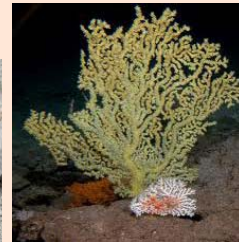
Carbonates – (2) aragonite structure

- Polymorph of CaCO_3
- Stable at elevated pressures
- Adopted by carbonates of cations larger than Ca
 - Witherite (Ba)
 - Cerussite (Pb)

speleothem
(calcite, aragonite, or gypsum)



Coral (aragonite)

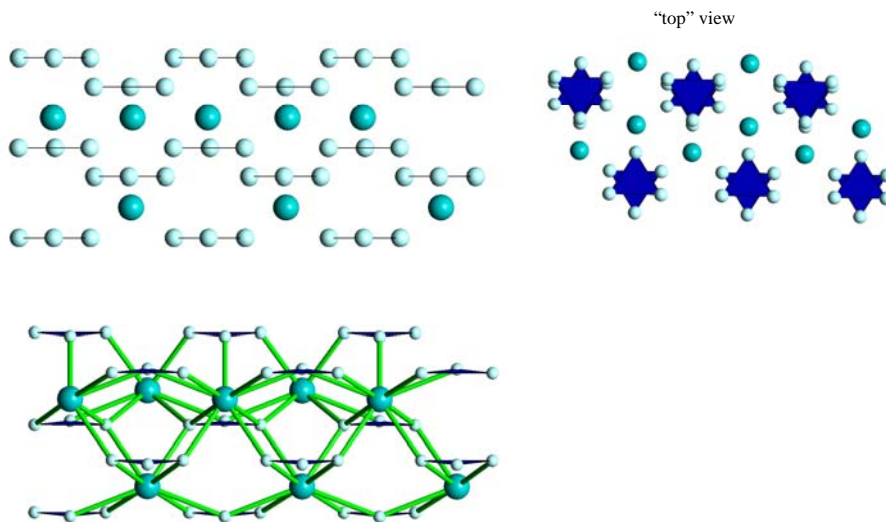


Carbonates – (2) aragonite structure

- Pearly layer of many shells, pearl
- Cation CN = 9: higher coordination results in denser material
- Dense materials are more stable at high-pressure than less dense material

- Calcite: density = 2.71 grams per cubic cm (gm/cm^3); Ca CN = 6
- Aragonite: density = 2.95 gm/cm^3 ; Ca CN = 9

Carbonates – (2) aragonite structure



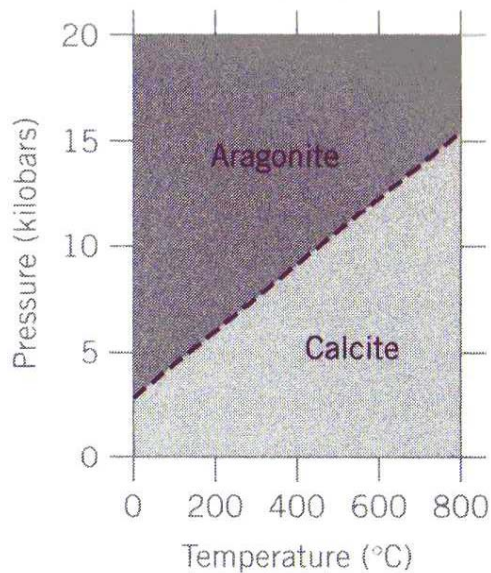


FIG. 17.4 The approximate location of the experimentally determined stability fields of calcite and aragonite.

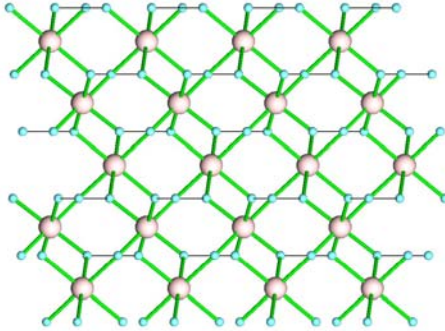
Carbonates – (3) dolomite structure

- Dolomite: $\text{CaMg}(\text{CO}_3)_2$
- Based on the calcite structure
- Ca and Mg in alternate layers

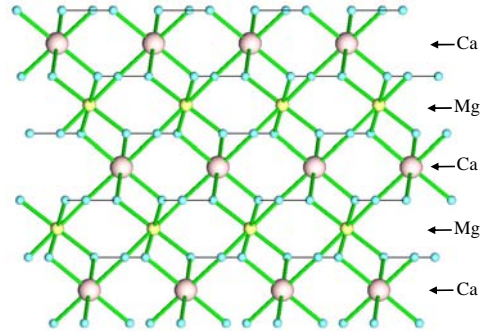
- Ca is too big for solid solution with Mg!
- Ca and Mg ordered into distinct layers

Carbonates – (3) dolomite structure

calcite CaCO_3



dolomite $\text{CaMg}(\text{CO}_3)_2$



The “dolomite problem”

- Found extensively in ancient rocks in the Earth’s crust
- Typically a sedimentary mineral
- Yet the mechanism of its growth under sedimentary conditions is unknown
- No geologic evidence indicating that its formation took place under unusual conditions of T or P
- Sedimentary dolomite does not form in the normal present-day marine environment (typically saturated with respect to dolomite)
- Notoriously difficult to crystallize under laboratory conditions unless high T, extreme supersaturation, high pH etc.

Geological record



Modern environments

Laboratory experiments

Common carbonate minerals

Calcite Group

(Hexagonal; $R\bar{3}c$)

Calcite	CaCO_3
Magnesite	MgCO_3
Siderite	FeCO_3
Rhodochrosite	MnCO_3
Smithsonite	ZnCO_3

Aragonite Group

(Orthorhombic; $Pm\bar{c}n$)

Aragonite	CaCO_3
Witherite	BaCO_3
Strontianite	SrCO_3
Cerussite	PbCO_3

Dolomite Group

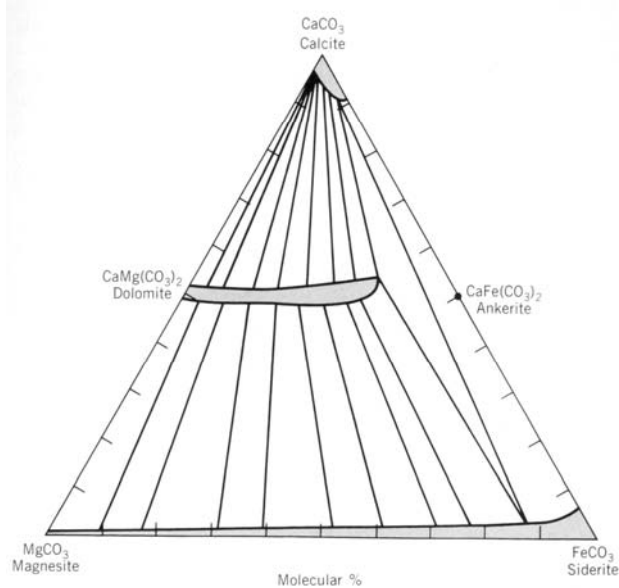
(Hexagonal; $R\bar{3}$)

Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Ankerite	$\text{CaFe}(\text{CO}_3)_2$

Monoclinic Carbonates with (OH)

Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Carbonates and their solid solution in the system CaO-MgO-FeO-CO₂



Sulfates

- Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
- Compare with
 - Anhydrite (CaSO_4)
 - Barite (BaSO_4)

Dessert Rose



Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

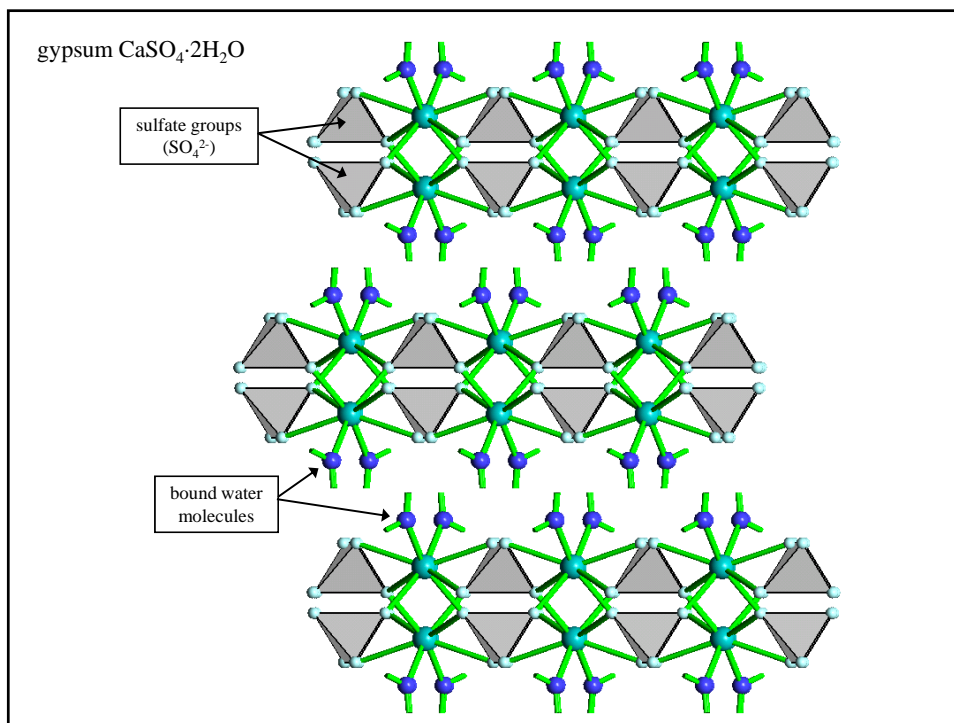
- The water molecules in gypsum are bound to the Ca ions and are an essential part of the structure.
- Virtually all wallboard used in modern residential construction is gypsum
- Removing the water results in a denser, harder mineral - anhydrite

Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Structure of gypsum

- Layers of Ca and sulfate
- Linked by weak van der Waals and hydrogen bonding interactions

- Gives rise to the perfect cleavage



Phosphates

- Principal rock forming phosphate is apatite (calcium phosphate): $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$
- Phosphate does not ordinarily substitute into silicates, so phosphates generally occurs in a separate mineral phase in rocks - commonly apatite.
- Many rare-earth elements (REE) and other large cations can substitute for Ca in apatite.

Apatite

