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

\[ \text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+} \]

Mn (oxyhydr)oxides

- Oxidation in solution → very slow (years)
- Mineral-surface-catalyzed oxidation → faster (5-2800 d)
- Microbe mediated oxidation → orders of magnitude faster
Structure of biogenic Mn oxides – limited

Layered

Hexagonal Birnessite
Triclinic Birnessite

Tunnel

Todorokite

More than 30 known Mn oxide minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolusite</td>
<td>MnO₂</td>
</tr>
<tr>
<td>Rammelsellite</td>
<td>MnO₂</td>
</tr>
<tr>
<td>Natrite</td>
<td>Mn(OH)₂</td>
</tr>
<tr>
<td>Hollandite</td>
<td>Ba₅(Mn⁴⁺,Mn³⁺)₆O₁₆</td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>K₆(Mn⁴⁺,Mn³⁺)₆O₁₆</td>
</tr>
<tr>
<td>Manjroite</td>
<td>Na₆(Mn⁴⁺,Mn³⁺)₆O₁₆</td>
</tr>
<tr>
<td>Coronadite</td>
<td>Pb₆(Mn⁴⁺,Mn³⁺)₆O₁₆</td>
</tr>
<tr>
<td>Romanechite</td>
<td>Ba₆(Mn⁴⁺,Mn³⁺)₆O₁₆·1.3H₂O</td>
</tr>
<tr>
<td>Todorokite</td>
<td>(Ca,Na,K)₆(Mn⁴⁺,Mn³⁺)₆O₁₆·3.5H₂O</td>
</tr>
<tr>
<td>Lithiophorite</td>
<td>Li₆(Mn⁴⁺,Mn³⁺)₆O₁₆(OH)₆</td>
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<tr>
<td>Chalcophanite</td>
<td>ZnMnO₂·3H₂O</td>
</tr>
<tr>
<td>Birnessite</td>
<td>(Na,Ca)MnO₁₄·2.8H₂O</td>
</tr>
<tr>
<td>VERNADITE</td>
<td>MnO₂·nH₂O</td>
</tr>
<tr>
<td>Manganese</td>
<td>MnOOH</td>
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<tr>
<td>Gouellite</td>
<td>MnO₃</td>
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<tr>
<td>Feiklincehteite</td>
<td>Mn(OH)₃</td>
</tr>
<tr>
<td>Hausmannite</td>
<td>Mn⁷⁺·Mn³⁺·O₄</td>
</tr>
<tr>
<td>Biopyrite</td>
<td>Mn₂O₇</td>
</tr>
<tr>
<td>Pyrochorite</td>
<td>Mn(OH)₂</td>
</tr>
<tr>
<td>Manganosite</td>
<td>MnO</td>
</tr>
</tbody>
</table>

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


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?

Debates about the structure
- Existence of tetrahedral Fe
- Structural organization

Tang et al. Chem Mater 2010
Michel et al. Chem Mater 2007

Michel et al. Science 2007
Goethite $\alpha$-FeOOH

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

Hematite

- Hematite ($\text{Fe}_2\text{O}_3$) – can form directly or via ferrihydrite $\rightarrow$ goethite $\rightarrow$ hematite
- Red-brown mineral is very common in soils and weathering iron-bearing rocks
Corundum structure: HCP, 2/3 octahedral sites filled

- Face shared octahedra from layers 1 and 2
- Layer 1 octahedra sharing a face with a lower layer 0
- Layer 2 octahedra sharing a face with a higher layer 3

Magnetite
- Magnetite (Fe₃O₄) – Magnetic mineral of mixed valence → must contain both Fe²⁺ and Fe³⁺ → how many of each??
- ‘Spinel’ structure – 2/3 of the cation sites are octahedral, 1/3 are tetrahedral

Spinel structure:
- A⁴⁺B⁶⁺₂O₄ (normal)
- B⁶⁺[B⁶⁺A⁶⁺]O₄ (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$_2$O$_3$ – 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$_2$O$_4$ – High-P metamorphic mineral

Sulfides
Sulfide Minerals

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

Substitution into sulfides is very common
- As and Se substitute for S very easily
- Au can substitute in cation sites (auriferrous 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\textsubscript{x}S\textsubscript{y}
- Pyrite – FeS\textsubscript{2} (cubic)
- Marcasite – FeS\textsubscript{2} (orthorhombic)
- Troilite – FeS end member
- Pyrrhotite – Fe\textsubscript{1-x}S (slightly deficient in iron)
- Arsenopyrite – FeAsS
- Chalcopyrite – CuFeS\textsubscript{2}

Other important sulfides

- Galena – PbS
- Sphalerite/wurtzite – ZnS
- Cinnabar – HgS
- Molybdenite – MoS
- Covellite – CuS
- Chalcocite – Cu\textsubscript{2}S
- Acanthite or Argenite – AgS
- Stibnite – Sb\textsubscript{2}S\textsubscript{3}
- Orpiment – As\textsubscript{2}S\textsubscript{3}; Realgar – AsS
When sulfides meet oxygen

- Abandoned sub-surface mines
- Exposure to air/water causes the oxidation of metal sulfides (often pyrite FeS₂)
- Increased acidity

Pyrite oxidation

**Initial oxidation**
- FeS₂ + 3.5 O₂ + H₂O → Fe²⁺ + 2 SO₄²⁻ + 2 H⁺

**Secondary oxidation**
- Fe²⁺ + 0.25 O₂ + H⁺ → Fe³⁺ + 0.5 H₂O

At ~pH 4, Fe³⁺ hydrolyze (take on water) and precipitate
- Fe³⁺ + 3H₂O → Fe(OH)₃ + 3H⁺

1 mole FeS₂ → 4 mole H⁺
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 $\text{Cu}_2\text{CO}_3(\text{OH})_2$

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 \( \text{CaCO}_3 \)
- Stable at elevated pressures
- Adopted by carbonates of cations larger than \( \text{Ca} \)
  - Witherite (Ba)
  - Cerussite (Pb)

Speleotherm
(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/cm³); Ca CN = 6
- Aragonite: density = 2.95 gm/cm³; Ca CN = 9

"top" view
Carbonates – (3) dolomite structure

- Dolomite: $\text{CaMg(CO}_3\text{)}_2$
- 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

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

**Calcite Group**  
(Hexagonal; $R3c$)  
- Calcite: $\text{CaCO}_3$  
- Magnesite: $\text{MgCO}_3$  
- Siderite: $\text{FeCO}_3$  
- Rhodochrosite: $\text{MnCO}_3$  
- Smithsonite: $\text{ZnCO}_3$

**Aragonite Group**  
(Orthorhombic; $Pmcn$)  
- Aragonite: $\text{CaCO}_3$  
- Witherite: $\text{BaCO}_3$  
- Strotianite: $\text{SrCO}_3$  
- Cerussite: $\text{PbCO}_3$

**Dolomite Group**  
(Hexagonal; $R3$)  
- Dolomite: $\text{CaMg(CO}_3\text{)}_2$  
- Ankerite: $\text{CaFe(CO}_3\text{)}_2$

**Monoclinic Carbonates with (OH)**  
- Malachite: $\text{Cu}_2\text{CO}_3(\text{OH})_2$  
- Azurite: $\text{Cu}_3(\text{CO}_3\text{)}_2(\text{OH})_2$

Carbonates and their solid solution in the system $\text{CaO-MgO-FeO-CO}_2$
Sulfates

- Gypsum (CaSO$_4$·2H$_2$O)
- Compare with
  - Anhydrite (CaSO$_4$
  - Barite (BaSO$_4$)

Dessert Rose

Gypsum CaSO$_4$·2H$_2$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): $\text{Ca}_5(\text{PO}_4)_3(\text{OH, F})$

- 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