Last Time

Oxides and Hydroxides

1) Properties of select minerals
2) Economics (resources, reserves, extraction)
   3) The chemistry of oxides/hydroxides
4) Banded Iron Formation (Chalk Board)

Featured minerals: Iron
# Oxides and Hydroxides

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>System</th>
<th>Specimen Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatas</td>
<td>TiO$_2$</td>
<td>Tetragonal</td>
<td>f, f, g</td>
</tr>
<tr>
<td>Bauxite</td>
<td>Al$_2$O$_3$</td>
<td>aggregate</td>
<td>f, g(x6)</td>
</tr>
<tr>
<td>Cassiterite</td>
<td>SnO$_2$</td>
<td>Tetragonal</td>
<td>f(x3), g, g</td>
</tr>
<tr>
<td>Chromite</td>
<td>FeCr$_2$O$_4$</td>
<td>Isometric</td>
<td>g(x6)</td>
</tr>
<tr>
<td>Chrysoberyl</td>
<td>BeAl$_2$O$_4$</td>
<td>Orthorhombic</td>
<td>g</td>
</tr>
<tr>
<td>Columbite</td>
<td>(Fe, Mn)Nb$_2$O$_4$</td>
<td>Orthorhombic</td>
<td>g</td>
</tr>
<tr>
<td>Corundum</td>
<td>Al$_2$O$_3$</td>
<td>Hexagonal</td>
<td>g, g, g</td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu$_3$O$_2$</td>
<td>Isometric</td>
<td>p, f, g, g</td>
</tr>
<tr>
<td>Franklinite</td>
<td>(Zn, Mn$^{2+}$, Fe$^{3+}$)(Fe$^{3+}$, Mn$^{2+}$)O$_4$</td>
<td>Isometric</td>
<td>g(x3)</td>
</tr>
<tr>
<td>*Hematite (v. BIF)</td>
<td>Fe$_2$O$_3$</td>
<td>Hexagonal</td>
<td>g</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>Hexagonal</td>
<td>g, g, g</td>
</tr>
<tr>
<td><strong>Hydroxides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Bindheimite</td>
<td>Pb$_2$Sb$_2$O$_5$(OH)$_2$</td>
<td>Isometric</td>
<td>g, g</td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)$_2$</td>
<td>Hexagonal</td>
<td>g, g, g</td>
</tr>
<tr>
<td>Diaspore</td>
<td>AlO(OH)</td>
<td>Orthorhombic</td>
<td>g</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al(OH)$_3$</td>
<td>Monoclinic</td>
<td>g, g, g</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeO(OH)</td>
<td>Orthorhombic</td>
<td>f, g, g</td>
</tr>
<tr>
<td>Limonite</td>
<td>FeO(OH)</td>
<td>aggregate</td>
<td>f, g(x4)</td>
</tr>
<tr>
<td>Manganite</td>
<td>MnO(OH)</td>
<td>Monoclinic</td>
<td>f, g(x4)</td>
</tr>
</tbody>
</table>

© p-poor, f-fair, g-good
Oxides

- Oxides involve a strong Ionic bond between metal cations and $O^{2-}$.
- Classification is done on the basis of valancey (AX types).

$A_2X$: e.g., $Cu_2O$ (cuprite)

$AX$: e.g., $MgO$ (periclase)

$AB_2X_4$: e.g., $FeCrO_4$ (chromite)
$Fe_3O_4$ ($FeO \cdot Fe_2O_3$) (magnetite)

(Spinel Group = spinel, magnetite, chromite, etc.)

Isostructural (exhibits solid solution)
Oxides

- Oxides involve a strong Ionic bond between metal cations and $O^{2-}$.
- Classification is done on the basis of valancey (AX types).

$A_2X_3$: e.g., $Al_2O_3$ (corundum)
(Hematite Group = corundum, hematite, ilmenite, etc.)

$AX_2$: e.g., $SnO_2$ (Cassiterite)
(Rutile Group = cassiterite, rutile, pyrolusite, uraninite etc.)
Hydroxides

- Hydroxides involve a weaker ionic bond between metal cations and OH\(^-\) (softish)
- No real attempt to classify (many have variable chemistry, poor crystal structure)

\[ \text{AlO(OH): diaspore, boehmite} \]
\[ \text{Al (OH)}_3: \text{ gibbsite} \]

Typically mixed up with bauxite
Iron Formation

Three major types of iron deposits.

1) Replacement of limestone (Red Mountain Formation, Alabama); most are Jurassic in age
   Clinton Type Fe Deposits

2) Primary hydrothermal deposits (deep sea vents); most are PreCambrian (Algoma Type Fe Deposits)

3) Banded Iron Formations (hematite + jasper); most are Archean in age (Superior Type Fe Deposits)
BIFs

BIFs are thought to have been formed through oxygenation of sea water containing Fe$^{2+}$ (reduced iron).
Iron (Fe) and Human Uses

- Earth crust ~5% by weight (very abundant)

- \(^1\)Steel consumption (world per capita, 1990): \(\sim 150 \text{ kg/yr}\)

\[ \Sigma \text{world population steel consumption} = 6 \times 10^9 \text{ people} \times 1.5 \times 10^{-1} \text{ T/yr} = 9 \times 10^8 \text{ T/yr} \]

- \(^2\)Reserves of Fe ore (1990): \(2.2 \times 10^{11} \text{ T}\)

- Years of supply: \(\frac{2.2 \times 10^{11} \text{ T}}{9 \times 10^8 \text{ T/yr}} = 2.4 \times 10^2 \text{ yrs}\)

- Banded Fe formations (global): \(5 \times 10^{14} \text{ T} \times 0.2 \approx 1 \times 10^{14} \text{ T}\)

\[ \therefore \frac{\text{Global Resources}}{\text{Global Reserves}} = \frac{10^{14} \text{ T}}{2.2 \times 10^{11} \text{ T}} \approx 5 \times 10^2 \]

\[ \frac{\text{Global Resources}}{\text{Annual Fe Use}} = \frac{10^{14} \text{ T}}{10^9 \text{ T/yr}} \approx 10^5 \text{ yrs} \]

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1 Murck et al., 1996, p. 324.  

http://www.ldeo.columbia.edu/edu/dees/U4735/lectures/03.html
Iron Formation

Banded Iron Formations (very low $O_2$ in atm)

$10^{14}$ Tons of banded iron formations

Millions of years before present

Very Large Fe Deposits

<table>
<thead>
<tr>
<th>Continent</th>
<th>Area</th>
<th>Age ($10^6$ yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>Transvaal, S.A.</td>
<td>2100–2600</td>
</tr>
<tr>
<td>Australia</td>
<td>Hamersley Range</td>
<td>2400–2700</td>
</tr>
<tr>
<td>Eurasia</td>
<td>Krivoi Rog, Ukraine</td>
<td>1900–2000</td>
</tr>
<tr>
<td>North America</td>
<td>Labrador Trough, Canada</td>
<td>1900–2500</td>
</tr>
<tr>
<td>South America</td>
<td>Minas Gerais, Brazil</td>
<td>2000–2700</td>
</tr>
</tbody>
</table>

http://www.ldeo.columbia.edu/edu/dees/U4735/lectures/03.html
Iron Extraction

Mt. Whaleback open pit iron mine at Newman, Western Australia.
Today’s Agenda

More Oxides

1. Chromite (and Chromium)
2. Uraninite (and Uranium)
3. Chromite formation (ultramafic intrusions)
4. Uraninite formation (sedimentary, placer)
5. Supergene enrichment (recap of hydrothermal emplacement)
Chromite ($\text{FeCr}_2\text{O}_4$)

Crystal: Isometric  
Pt. Group: $4/m \overline{3} 2/m$  
Habit: octahedral, sucrosic  
SG: 5.10  
H: 5.5  
L: metallic  
Col: black (brownish)  
Str: black (brown)  
Clev: none; twinning on $\{111\}$; concoidal fracture

Name derivation: From its elemental composition containing chromium
**Chromite (FeCr$_2$O$_4$)**

**Occurrence:** Ultramafic intrusive rocks; placer deposits

**Associated Mins:** olivine, pyroxene, spinel, magnetite

**May be confused with:** magnetite and especially ilmenite. Beware: it may be magnetic (isostructural with magnetite)

**Uses:** principle ore of chromium; stainless steel
Arguably, the most important chromite deposits are found in the Bushveld Complex of South Africa (along with major deposits of platinum) and the Great Dyke of Zimbabwe.
Oxide Minerals

2000 degrees C

A bad cartoon of a pluton
Oxide Minerals

A bad cartoon of a pluton

2000 degrees C
Oxide Minerals

A bad cartoon of a pluton

2000 degrees C
Oxide Minerals

2000 degrees C

A bad cartoon of a pluton
Oxide Minerals

Layered olivine (dunite)
Oxide Minerals

Layered olivine (dunite) +/- chromite
Oxide Minerals

Uraninite (UO₂)

Crystal: Isometric
Pt. Group: 4/m 3 2/m
Habit: massive, botryoidal
SG: 7.0-9.5
H: 5.5
L: submetallic to dull
Col: black
Str: brown to black
Clev: none; concoidal fracture

Name derivation: From its elemental composition containing uranium

http://www.treasuremountainmining.com/eb56uran1M.jpg
Uraninite (UO$_2$)


Associated Mins: monazite, cassiterite, tourmaline, zircon (granite pegmatites)

May be confused with: not much (radioactivity gives it away)

Uses: source of Uranium (nuclear fuel, spent Uranium munitions)

Name derivation: From its elemental composition containing uranium
Oxide Minerals

Carnotite (a vanadate: VO$_4$)
$\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot3(\text{H}_2\text{O})$

Occurrence: a secondary mineral in sandstone (meteoric water alteration)

Related Mins:
Tyuyamunite Ca(\text{UO}_2)_2\text{V}_2\text{O}_8\cdot n\text{H}_2\text{O},
Torbernite Cu(\text{UO}_2)_2(\text{PO}_4)_2\cdot n\text{H}_2\text{O},
Autunite Ca(\text{UO}_2)_2(\text{PO}_4)_2\cdot 10\text{H}_2\text{O}

May be confused with: any of the above minerals

Named after the French chemist, M. A. Carnot (1839-1920)
Figure 8 Location map for the world’s major primary uranium deposits, showing regions characterized by disseminated magmatic deposits and pegmatites (hatched), vein-type deposits (light grey) and vein-type deposits related to Proterozoic unconformities (dark grey). Named localities are those mentioned in the text.
USA Uranium

Cross section of a solution-collapse breccia pipe in the Grand Canyon region, showing the general distribution of uranium ore within the pipe.
More Terms...

**Hydrothermal**: a process involving “hot” water (usually groundwater under confining pressure).

Epithermal: <200°C (50°C and above)
Mesothermal: 200-300°C
Hypothermal: >300°C
More Terms...

**Hydrothermal:** a process involving “hot” water (usually groundwater under confining pressure).

Epithermal: <200°C (50°C and above)
Mesothermal: 200-300°C
Hypothermal: >300°C

**Supergene enrichment** involves *meteoric water* (“cold”)
Supergene enrichment occurs when oxidizing acids dissolve metal ions from the primary ore zone and redeposit them in more reducing, alkaline areas below the water table. This results in an oxidized zone on top (gossan), a supergene zone beneath and the primary zone (hypogene) beneath that.
Supergene enrichment

Leaching reactions

\[ 2 \text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 (\text{aq}) + 2\text{H}_2\text{SO}_4 \]

\[ 2\text{FeSO}_4 (\text{aq}) + \text{H}_2\text{SO}_4 + 0.5 \text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 (\text{aq}) \]

\[ 2 \text{FeS}_2 + 7.5 \text{O}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 \]

\[ 2 \text{Fe}^{+2} + \frac{1}{2} \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}^+ \]

\[ 2 \text{CuFeS}_2 + 8.5 \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{Cu}^{+2} + 4\text{SO}_4^{-2} + 4\text{H}^+ \]

or

\[ 2 \text{CuFeS}_2 + 8 \text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 17 \text{FeSO}_4 + 8 \text{H}_2\text{SO}_4 \]
Supergene enrichment

Precipitation reactions

$5 \text{FeS}_2 + 14 \text{Cu}^{+2} + 14 \text{SO}_4^{-2} + 12 \text{H}_2\text{O} \rightarrow 7 \text{Cu}_2\text{S} + 5 \text{Fe}^{+2} + 24 \text{H}^+ + 17 \text{SO}_4^{-2}$

Chalcocite is enriched

http://webmineral.com
Today’s Stuff To Do

1. Oxides/hydroxides
2. Mineral note book examination next Tuesday

Next Time

Thursday: Ore Assessment; assignment 7