Last Time (on line)

Sulfides and Sulfosalts

1. Properties of select sulfides/sulfosalts
2. Occurrences and Associations
3. Economics (resources, reserves, extraction)

Featured minerals: Copper-sulfides
### Sulfides, Sulfosalts and Arsenides

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>System</th>
<th>Specimen Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentite</td>
<td>Ag₂S</td>
<td>Isometric</td>
<td>g,g,g</td>
</tr>
<tr>
<td>*Arsenopyrite</td>
<td>FeAsS</td>
<td>Monoclinic</td>
<td>p,f,g,g</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu₅FeS₄</td>
<td>Orthorhombic</td>
<td>f(x3), g(x7)</td>
</tr>
<tr>
<td>Boulangerite</td>
<td>Pb₅Sb₄S₁₁</td>
<td>Orthorhombic</td>
<td>f,g</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu₂S</td>
<td>Monoclinic</td>
<td>g(x5)</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>Tetragonal</td>
<td>f,f,g,g</td>
</tr>
<tr>
<td>Cinnabar</td>
<td>HgS</td>
<td>Hexagonal</td>
<td>f,g</td>
</tr>
<tr>
<td>Cobaltite</td>
<td>CoAsS</td>
<td>Orthorhombic</td>
<td>g,g</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>Hexagonal</td>
<td>g,g,g</td>
</tr>
<tr>
<td>*Domeykite</td>
<td>Cu₃As</td>
<td>Isometric</td>
<td>g</td>
</tr>
<tr>
<td>*Digenite</td>
<td>Cu₉S₃</td>
<td>Hexagonal (trigonal)</td>
<td>g</td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu₃AsS₄</td>
<td>Orthorhombic</td>
<td>g(x5)</td>
</tr>
<tr>
<td>*Galena</td>
<td>PbS</td>
<td>Isometric</td>
<td>g,g,g</td>
</tr>
<tr>
<td>Jamesonite</td>
<td>Pb₄FeSb₆S₁₄</td>
<td>Monoclinic</td>
<td>g,g,g</td>
</tr>
<tr>
<td>*Marcasite</td>
<td>FeS₂</td>
<td>Orthorhombic</td>
<td>g,g</td>
</tr>
<tr>
<td>*Millerite</td>
<td>NiS</td>
<td>Hexagonal</td>
<td>p</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS₂</td>
<td>Hexagonal</td>
<td>f(x6),g(x4)</td>
</tr>
<tr>
<td>Nickel/Bnicolite</td>
<td>NiAs</td>
<td>Hexagonal</td>
<td>g,g,g</td>
</tr>
<tr>
<td>Orpiment</td>
<td>As₂S₃</td>
<td>Monoclinic</td>
<td>g(x7)</td>
</tr>
<tr>
<td>*Pararammelsbergite</td>
<td>NiAs₂</td>
<td>Orthorhombic</td>
<td>g</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>Isometric</td>
<td>g(x5)</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe₁₋ₓS</td>
<td>Variable</td>
<td>g,g,g</td>
</tr>
<tr>
<td>*Realgar</td>
<td>AsS</td>
<td>Monoclinic (combined with orpiment)</td>
<td>g,g,g</td>
</tr>
<tr>
<td>Skutterudite/smaltite</td>
<td>(Co,Ni)As₂₋₃/(Co,Ni)As₃ₓ</td>
<td>Isometric</td>
<td>g,g,g</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>Isometric</td>
<td>g(x4)</td>
</tr>
<tr>
<td>Stibnite</td>
<td>Sb₂S₃</td>
<td>Orthorhombic</td>
<td>f,g,g,g</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>(Cu, Fe)₁₂Sb₄S₁₃</td>
<td>Isometric</td>
<td>f(x4),g(x3)</td>
</tr>
</tbody>
</table>

※ p-poor, f-fair, g-good
Sulfides etc.

Sulfides phase diagram

Sulfides Assemblages Plot

Mineral assemblages found in ore deposits

Covellite/digenite/bornite assemblage
Porphyry Copper Ores

1) Primary mineralization (hypothermal fluids ~400°C)

http://reynolds.asu.edu/sierra_cobre/p_formation.htm
Porphyry Copper Ores

2) Supergene mineralization (epithermal fluids ~25°C)

Erosion removes the stratovolcano and top of the original copper deposit. Rainwater and weathering cause copper to be leached from the top of the deposit and redeposited as the downward-moving groundwater reaches the water table. The resulting enriched zone is commonly high grade and fairly flat.
Copper sulfide precipitation is controlled by
1) temperature (high to medium)
2) pH (acidity promotes Cu$^+$ solution)
3) Sulfur content (as S$^{2-}$ or SO$_2$)

$$4\text{Cu}^+ + 4\text{Fe}^{2+} + 8\text{H}_2\text{S} + \text{O}_2 \rightarrow 4\text{CuFeS}_2 + 12 \text{H}^+ + 2\text{H}_2\text{O}$$
Sulfide Chemistry

Other considerations:

1) Production of sericite \([\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH, F})_2]\) is accelerated in acidic solutions and this lowers temperature of CuFeS\(_2\) formation

2) Hornblende alters to biotite releasing more Fe\(^{2+}\) and promoting precipitation of CuFeS\(_2\)

3) at high temperatures, SO\(_2\) content is higher than H\(_2\)S content, but this changes as the temperature decreases to 400 °C:

\[
4\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{SO}_4 + \text{H}_2\text{S}
\]
By the way.....

Gold can also be precipitated in porphyry copper assemblages: Gold transported as: \( \text{AuS}_x^{x^+} \)

\[
\text{AuS}_x^{x^+} + x\text{H}^+ \rightarrow \text{Au}^0 + \text{XH}_2\text{S}
\]

\[
\text{AuS}_x^{x^+} + 4\text{Cu}^+ + 4\text{Fe}^{2+} + (x-1)\text{H}_2\text{S} + \text{O}_2 \rightarrow \\
\text{Au}^0 + 4\text{CuFeS}_2 + (12-x) \text{H}^+ + 2\text{H}_2\text{O}
\]
Today’s Agenda

Sulfides and Sulfosalts

1. Properties of more sulfides/sulfosalts
2. Economics (resources, reserves, extraction)

Featured minerals: Molybdenite, Cinnabar
Molybdenite (MoS$_2$)

Crystal: Hexagonal
Pt. Group: 6/m 2/m 2/m
Habit: hexagonal plates, scales
SG: 4.7
H: 1-1.5
L: metallic
Col: silver to lead grey
Str: green-grey
Clev: perfect basal (001)

Name derivation: from the Greek *molybdos* meaning “lead”
Sulfide Minerals

Molybdenite ($\text{MoS}_2$)
Occurrence: accessory mineral in granite pegmatites and in porphyry copper deposits

Associated Mins: scheelite, cassiterite, wolframite, fluorite

Related Mins:

May be confused with: graphite (but only once!)
Molybdenum Emplacement

http://minerals.cr.usgs.gov/gips/images/porphlrg.gif
Molybdnenite Emplacement

The Climax Mine near Leadville, Co. was started during WWI and was, until the mid 1990’s, the major producer of Mo in the world. It is currently in shutdown.

City of Leadville, Colorado
Molybdenite Emplacement

The current owners (Phillips Dodge) are doing environmental work on the mine, the tailings and the surrounding area.
Cinnabar (HgS)
Crystal: Hexagonal (trigonal)
Pt. Group: 32
Habit: massive, rarely rhombohedral
SG: 8.1
H: 2.5
L: dull to adamantine
Col: scarlet red
Str: scarlet
Clev: perfect (100)

Name derivation: from the Persian zinjifrah meaning red resin
Cinnabar (HgS)

Occurrence: volcanic and sedimentary rocks as veins or disseminated grains.

Associated Mins: native mercury, realgar, stibnite, pyrite, marcasite, calcite, quartz and opal

Related Mins: pseudomorphic with metacinnabar (iso) and hypercinnabar (hex). Coloradoite (HgTe), Tiemannite (HgSe)

May be confused with: hematite, cuprite and realgar
Cinnabar Mineralization

Fig. 5. Schema of localization of main gold-mercury ore districts of the world (tectonic scheme by [11])
Cinnabar Mineralization

Fig. 2. Relationship between Au-As-Hg and other types of gold mineralization for Au-As-Hg-Sb-Tl ore-forming systems.
Mining (Copper)

City of Butte

Berkley Pit (1 mile wide, 900 feet deep)
Copper Mining

And since it’s closure in 1982, filling up with acidic water
Copper Mining

And since it’s closure in 1982, filling up with acidic water (pH=2.5)

140 million litres of acidic water
Sulfide Refining

Extraction → Processing → Smelting → Conversion

Blasting
Extraction
Transport
Crushing
Concentration
Slurried
Roasting in an oxidizing furnace
Roasting in an reducing furnace

CuFeS₂ (1%) → CuFeS₂ (30%) → CuO + slag + SO₂ → Cu + slag + SO₂

Blister Copper
Electrolysis
99% pure Cu
Fire Refining
Final removal of S and O
Today’s Stuff To Do

1. Learn your Native and Sulfide minerals! (first mineral test Tuesday or Thursday)

Next Time

1. Oxides and hydroxides
2. Choose a mineral for your posters
GY 302: Crystallography and Mineralogy

Lecture 10: Sulfides Part 2

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