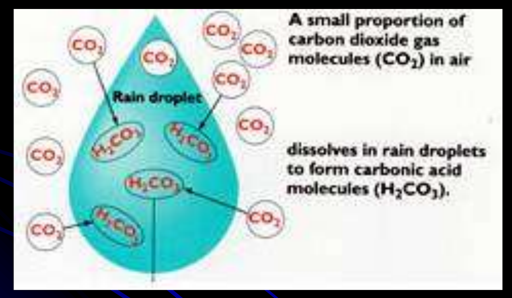
Oxidation and Reduction:
Chemical Weathering and Smelting

How do we produce metals from minerals?

Chemical Weathering

- Dissolution
  - $H_2CO_3 + CaCO_3 \rightarrow Ca^{2+}_{(aq)} + 2HCO_3^{-}{}_{(aq)}$
    - Dissolution of calcite in carbonic acid
    - All rainwater is a weak carbonic acid solution
      - $CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+_{\,(aq)} + HCO_{3-\,(aq)}$



Chemical Weathering

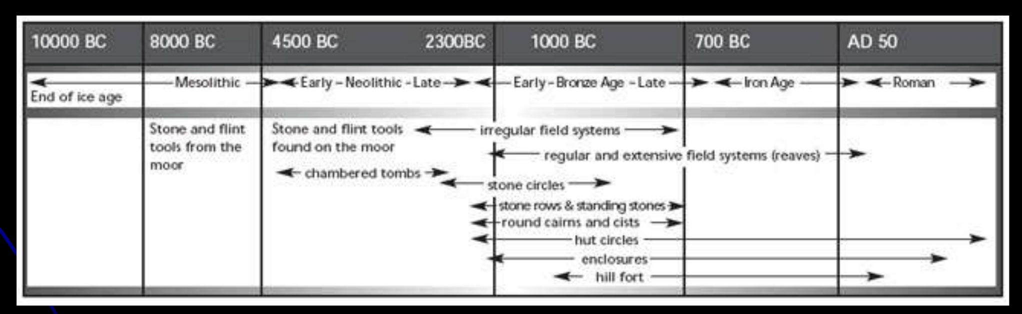
- Hydrolysis
  - In hydrolysis a molecule is split into two parts by reacting with water. One product includes an OH^- from the water molecule, whereas H^+ is added to another
  - $Mg_2SiO_4 + H_2O \rightleftharpoons 2Mg^{2+}_{(aq)} + 4OH^- + 4H_4SiO_{4\,(aq)}$ Silicic Acid (Dissolved Silica)
    - Hydrolysis of olivine produces a solution (mineral dissolves)
  - $2KAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightleftharpoons Al_2Si_2O_5(OH)_4 + 4H_4SiO_{4\,(aq)} + 2K^+ + 2HCO_3^-$
    - Hydrolysis of K-feldspar produces kaolinite (clay product)

Chemical Weathering

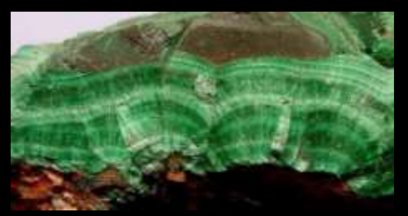
- Oxidation
  - $4FeS_2 + 15O_2 + 22H_2O \longrightarrow 4FeO(OH) + 8SO_4^{2-} + 16H^+$
    - Oxidation of pyrite to form limonite
  - $4\ FeSiO_{3(s)} + O_{2(g)} + 8H_2O \rightarrow 2Fe_2O_{3(s)} + 4H_4SiO_{4(aq)}$
    - Oxidation and hydrolysis of pyroxene to form hematite

Archeological Periods

- Stone Age (Neolithic): absence of metals tools
- Bronze Age: copper alloys tools
  - Copper Age (Chalcolithic)
  - earliest Bronze Age; copper tools
- Iron Age



Copper Minerals

- Native Copper (Element) 
- Cuprite (Oxide) 
- Malachite and Azurite (Carbonates) 
- Chalcocite, Covellite, Bornite, Chalcopyrite (Sulfides)  
- Tetrahedrite, Tennantite (Sulfosalts) 

Native Copper

- Copper can occur as a native element
- Commonly associated with volcanic rocks
- Hardness = 2.5-3
- Malleable
- Melting T = 1095°C

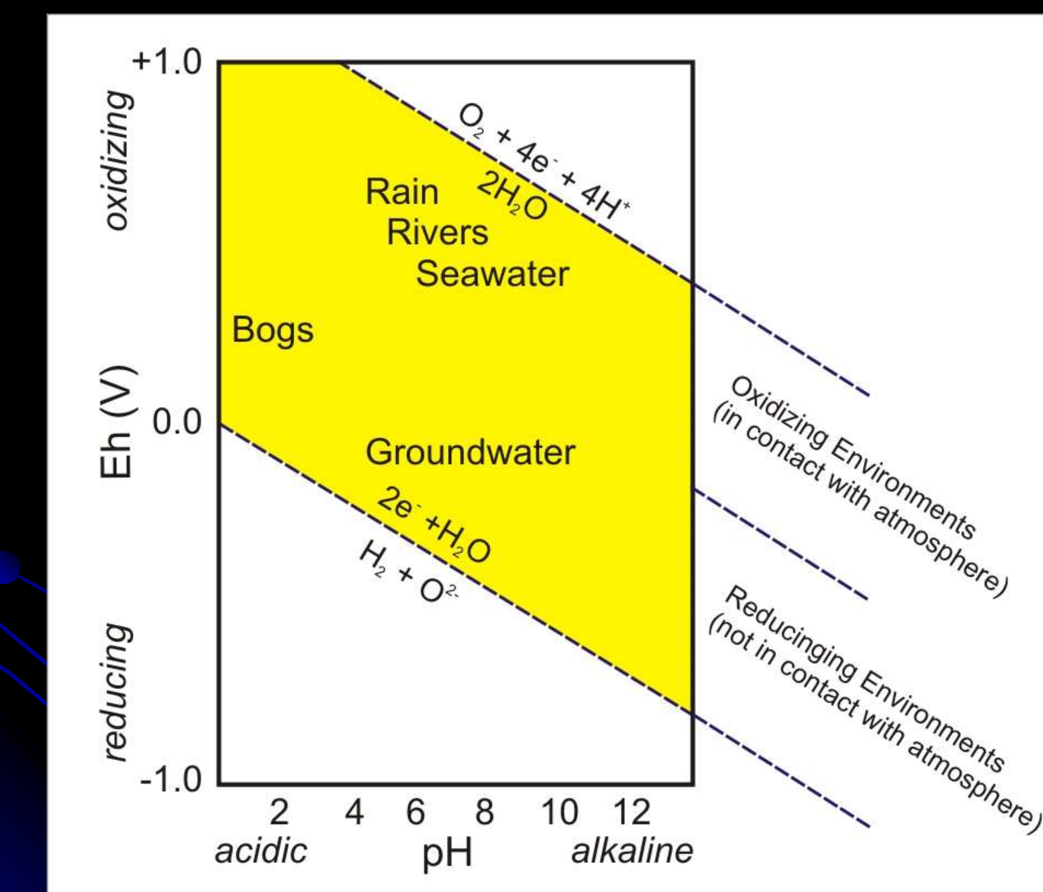
Early Copper Use

- Native copper too soft for effective tools
- Initially native copper used for ornaments
  - Beads, disks, plates, headdresses

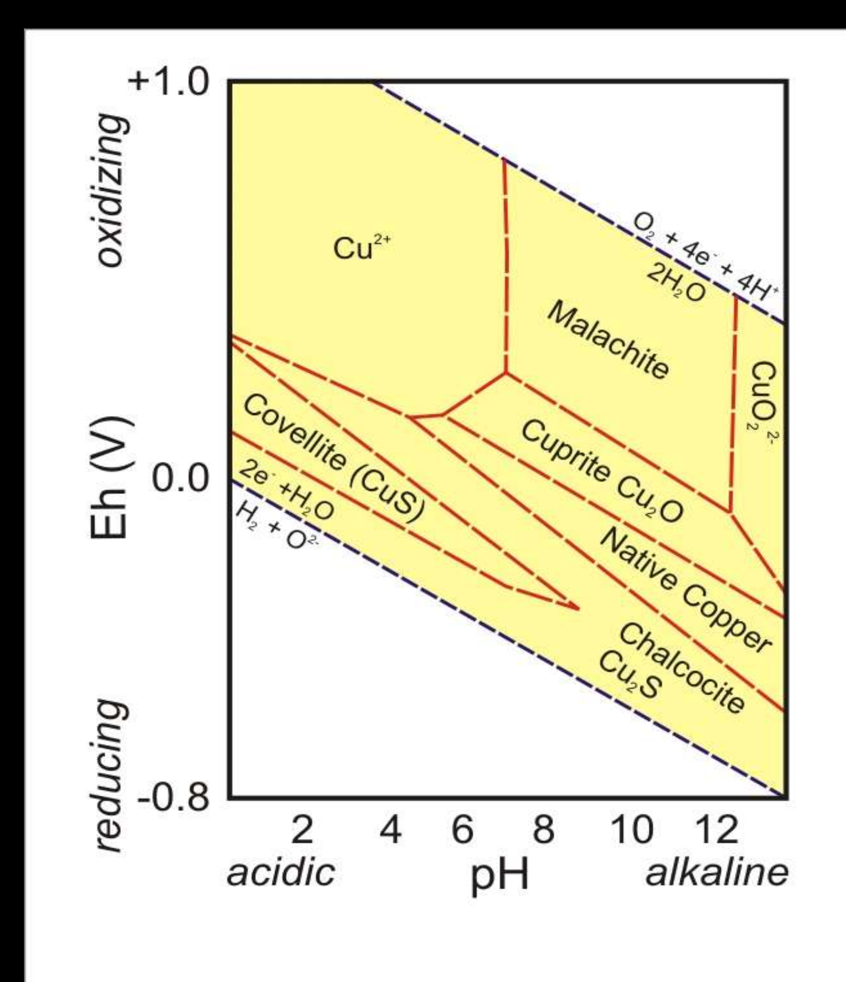
Copper Smelting

- Of the copper minerals only native Cu has the malleable properties of a metal
- Other copper minerals need to be treated in order to extract native copper
  - Smelting is the separation of metals from ore by heating the ore in a reducing environment

Eh-pH Diagrams

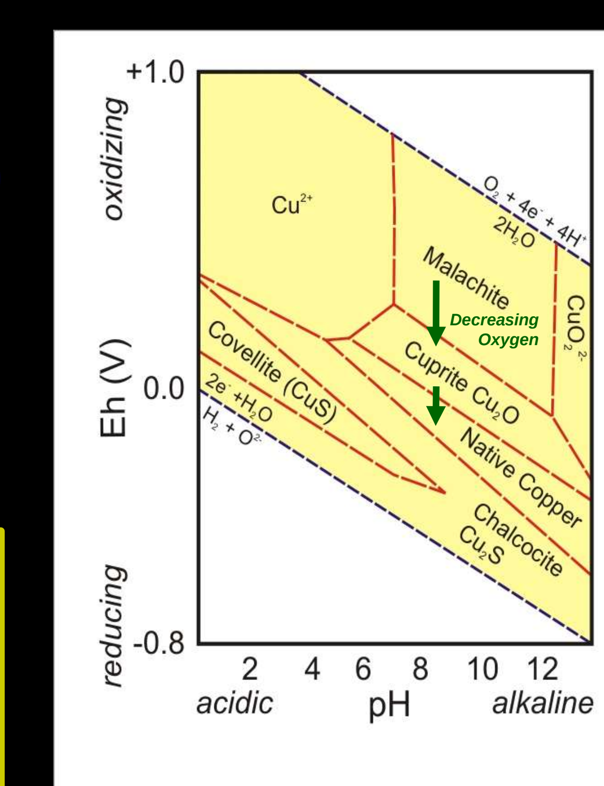


Eh-pH Diagram for Copper Minerals



Smelting from Malachite Ore

- Heating of malachite in a fire or furnace produces copper oxide
  - $Cu_2(CO_3)(OH)_2 = 2CuO + CO_2 + H_2O$
- Heating copper oxide to 1100°C under low-oxygen conditions produces molten copper
  - $CuO + CO = Cu + CO_2$



Copper Smelting

Crucible Smelting

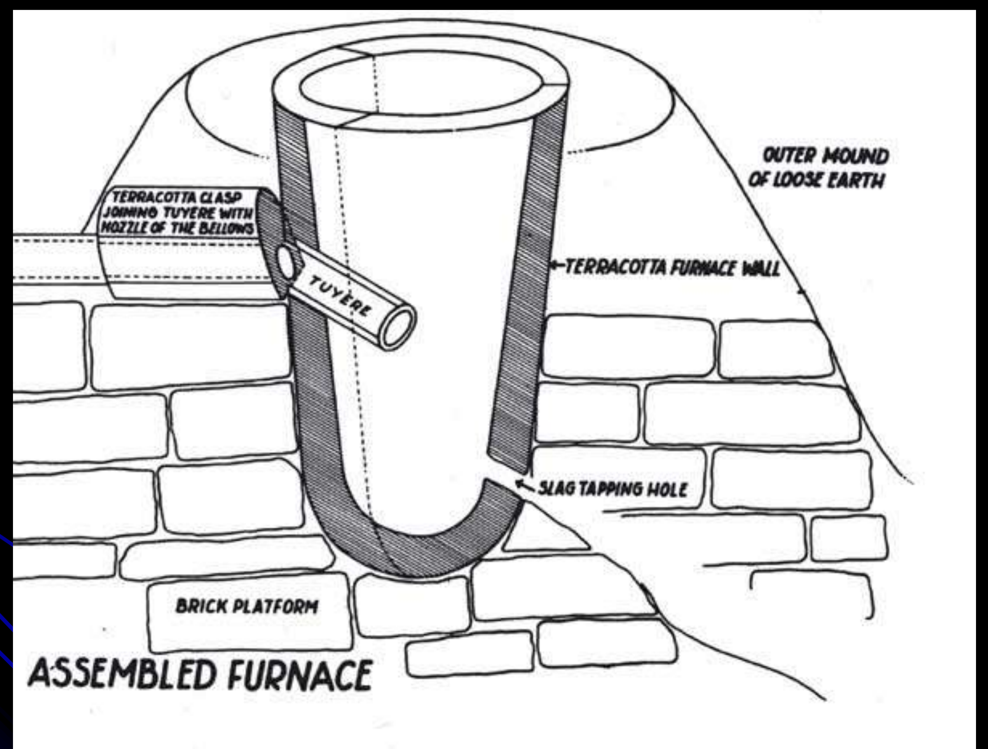


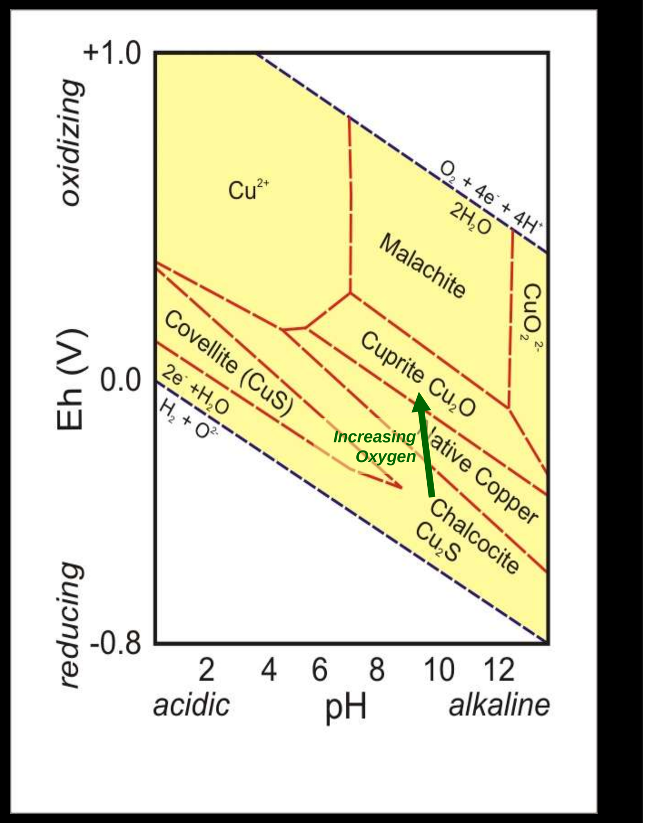
Fig. 3

Copper from Sulfide Minerals

- As surface deposits of Cu-carbonates were depleted, people turned to the more abundant Cu-sulfide minerals
- Requires an extra step to produce copper metal

Roasting of Sulfidic Ores

- Sulfidic ores are roasted in an oxygen-rich furnace to oxidize the ore
  - $2\ Cu_2S + 4\ O_2 = 4\ CuO + 2\ SO_2$
- The oxidized ore can then be smelted



Bronze

- Bronze is an alloy that contains 85-95% copper
- Earliest bronze was an alloy of copper and arsenic
  - Arsenical copper
    - Harder than copper
    - Stays hard when heated
    - Lower melting temperature
    - Can be brittle

Arsenical Copper

- Arsenic-bearing minerals commonly occur in epithermal copper deposits
- First arsenical copper probably produced accidentally by smelting As-bearing copper ore

Tennantite ($Cu_{12}As_4S_{13}$) is a copper ore mineral that is common in epithermal deposits and contains substantial amounts of arsenic

Arsenic Poisoning

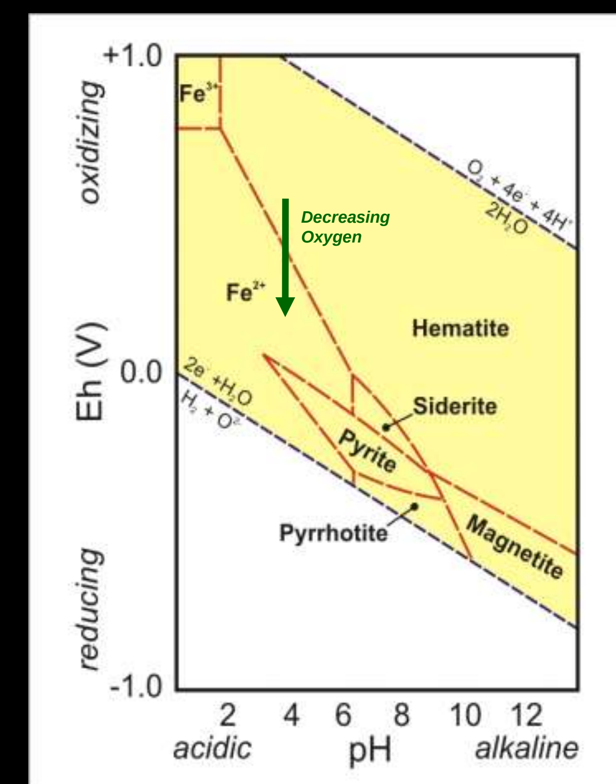
- Working with arsenical copper would have resulted in arsenic poisoning (arsenicosis)
- Symptoms include lividity of the limbs and skin cancers
- Hephaestus (Greek god of blacksmiths) and Vulcan (Roman god of blacksmiths) were both lame and disfigured
  - Likely a reflection of arsenicosis which would have afflicted blacksmiths who worked with arsenical copper

Tin Bronze

- Alloy of copper with tin
  - Sn ore is much rarer than As ore
- First used in Turkey ~3000 BC
  - May have been an accidental discovery because the tin-bearing mineral stannite looks similar to the Cu-As-bearing mineral tennantite
- In broad use by ~2000 BC
  - Harder and less brittle than arsenical copper
  - Not toxic
  - Melting temperature of 950°C

Iron Smelting

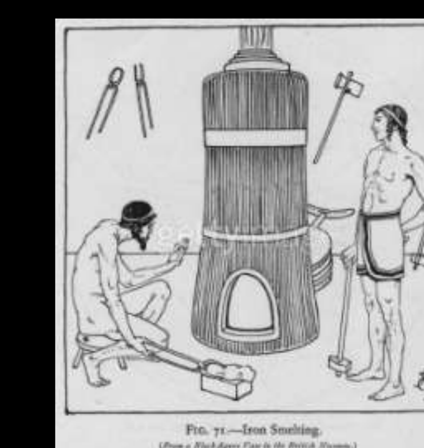
- In principle, Fe smelting is similar to that of Cu smelting
  - Reduce iron oxides to iron metal in a low-oxygen furnace
  - $Fe_3O_4 + 4\ CO = 3\ Fe + 4\ CO_2$



History of Smelting

- Iron has a melting temperature of ~1500°C (compared to ~1100°C for copper)
- Iron ore is much more common than copper ore
- Iron could not be melted in primitive furnaces, and so iron could not be produced until technology was sufficiently advanced
  - Beginning of Bronze Age: ~3300 BC
  - Beginning of Iron Age: ~1800-1200 BC

Copper Smelting



Wrought Iron

- Iron from smelting of iron ore forms a spongy mass called iron bloom
- Holes in bloom contain impurities and slag
- If the iron bloom is reheated and hammered, then the molten impurities in the bubbles can be worked out
- Requires repeated heating and working
- The pure iron product is called wrought iron