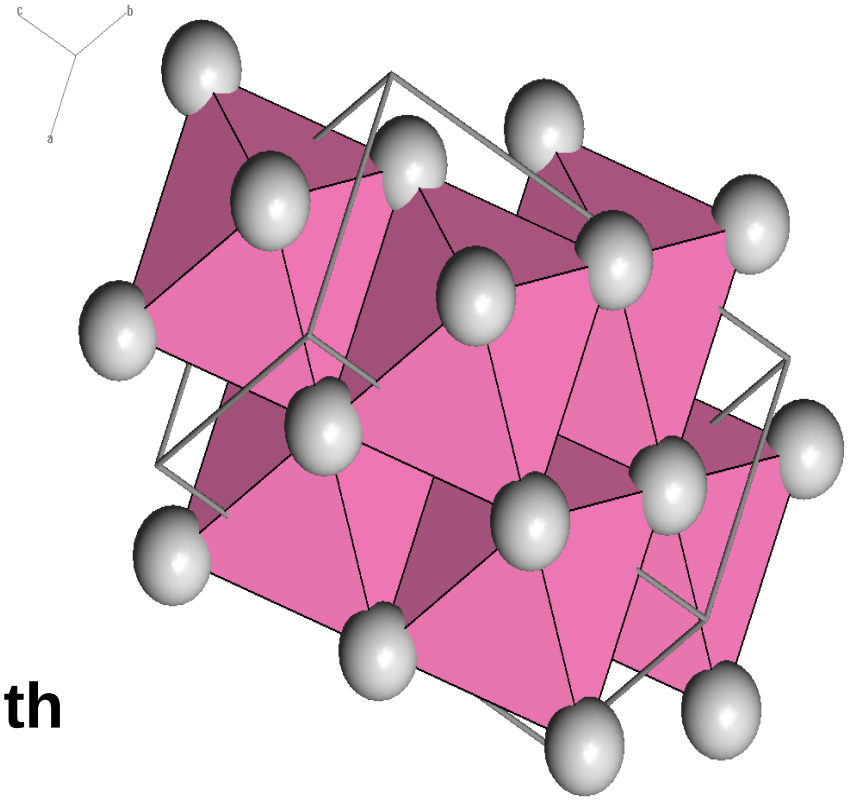
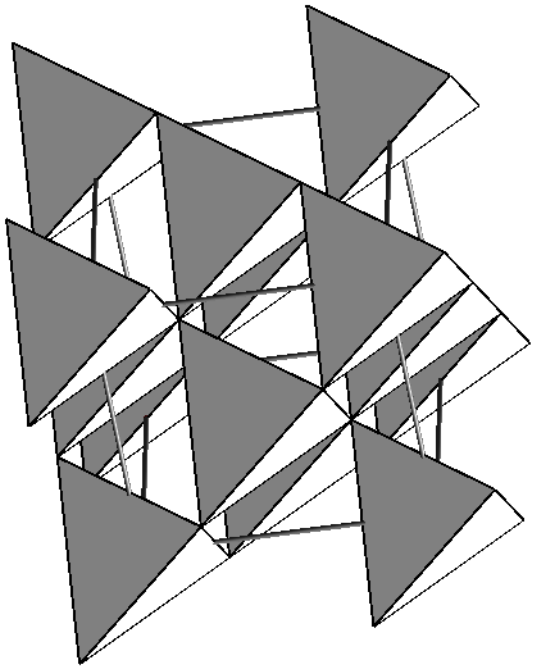
What is cinnabar?

- Found 2 structures for cinnabar HgS in the AMC
- Auvray (1973), CN=2!
  - **Hg^{2+}:S^{2-} 0.9/1.8 = 0.5**
  - **Pauling's radius ratio rule predicts CN = 6 to 8**
  - **Hg-S bond length = 2.37**
- BUT Ramsdell (1925) is different (shown to the right):
  - Sulfur: grey spheres
  - Hg polyhedra: pink
  - **CN=6**
  - **Hg-S average bond length = 2.87 Å**



Metacinnabar, HgS

- A polymorph of cinnabar
- CN=4
- Wyckoff (1963)
- Metacinnabar:
    - Hg-S Ave. bond length
      = 2.53 Å



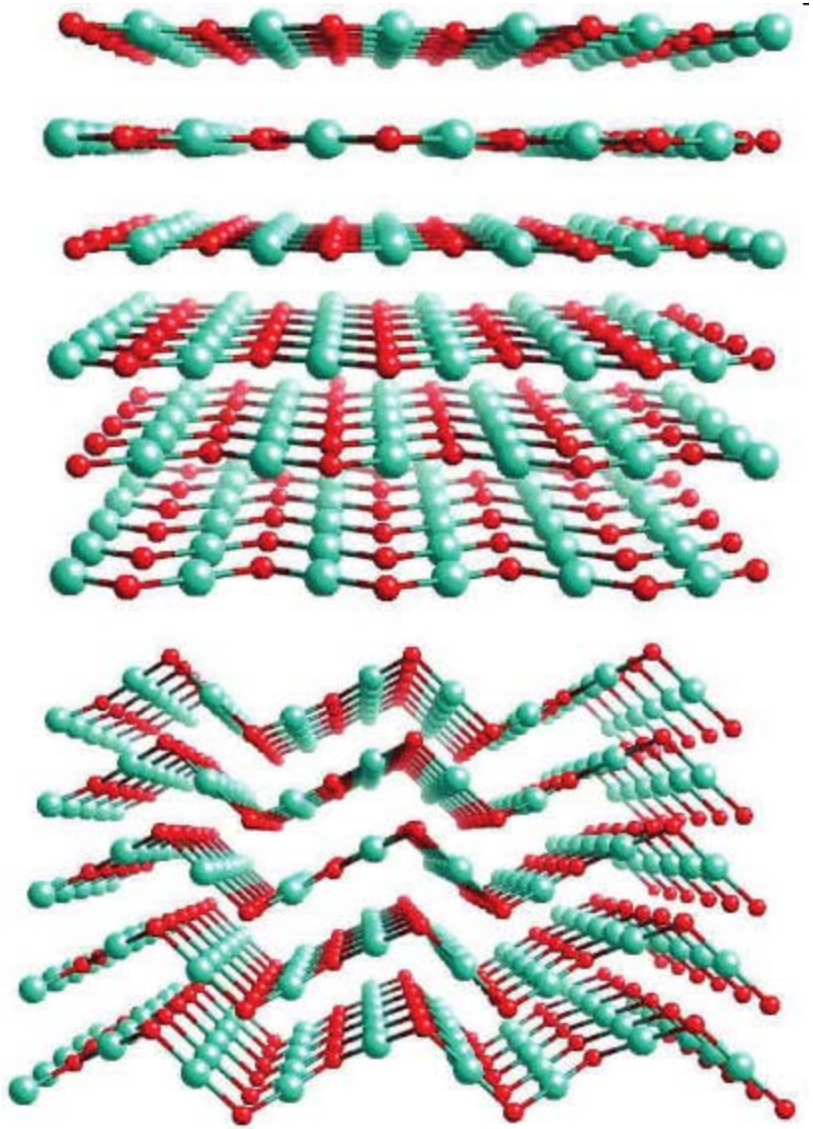
At atmospheric pressure → HgO exists as two main phases

- **Top right: HgO, Montroydite (orthorhombic)**
- **Bottom right: HgO, cinnabar-like structure (hexagonal) with CN = 2**
- Ionic radii of these ions in crystals structures (from Shannon,1976)
- O^{2-} (green): ~ 1.4Å
- Hg^{2+} (red): ~ 0.9 for CN 2 (?)

  radii values only given for

  CN 4: 0.96; CN 6: 1.02; and

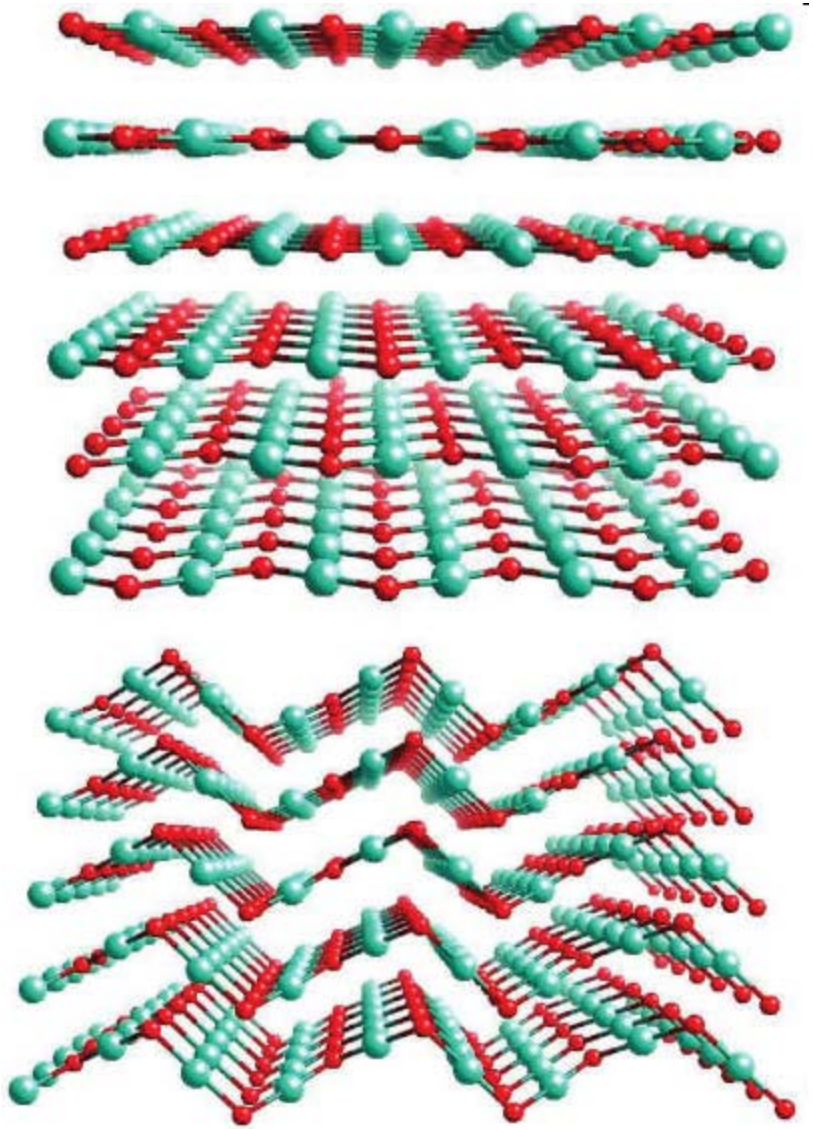
  CN 8: 1.14



- **According to Pauling's radius ratio rule…**
- **The radius ratio (Hg^{2+}:O^{2-}) 0.9/1.4 = 0.64**
- **should correspond to CN = 6 to 8**
- In reality: CN=2!
- Reason? Lack of ionic bond character due to "relativistic" effects
- Many more orbitals, with overlapping energy levels

NOTE:

- HgO → Hg^{2+} + O^{2-} (dissociates easily, unlike HgS…)
  - Weak Hg-O bond = 0.17eV



Pyrite: FeS_6 Corner Sharing

- Sulfur: grey spheres
- Fe octahedra (CN=6): yellow
- Fe^{2+} = 0.78 Å
- Radius ratio with S^{2-}:
  0.78/1.8 = 0.43 should correspond to CN=6
- Fe-S Ave. bond length:
  - 2.2636 Å
- **Compare to Hg-S bond length = 2.37 (Auvray, CN=2)**

Bond strength does not predict solubility (a thermodynamic property), but bond density and strength is expected to correlate to "ease of weathering"