Alkaline Glycine Systems as Alternatives Reagents for Copper Deposits of Complex Mineralogy

Jacques Eksteen, Elsayed Oraby, Bennson Tanda

Western Australian School of Mines
Curtin University
Introduction

- Copper deposits are often complex (e.g. porphyries) with significant mineralogical variation in depth.
- Grades are declining - milling & flotation becoming less economic
- Acid consuming gangue in oxide zone
- Altered silicates often lead to silica gel formation during acid leach processes.
- Native copper often problematic.
- Gold often associated with copper and copper significant problem during cyanidation.
- Elemental sulfur problematic during acid leaching of Cu-sulfides.
- pH (acid-base swing for Cu-Au ore leaching)

Copper-Gold Oxide Ore from Utah, USA
Common Copper Minerals

• Copper ores have a complex mix of many different copper-bearing minerals and gangue minerals

• Copper oxides include: carbonates, silicates and chlorides
  Malachite \((\text{CuCO}_3\cdot\text{Cu(OH)}_2)\);  Azurite \((2\text{CuCO}_3\cdot\text{Cu(OH)}_2)\);
  Cuprite \((\text{Cu}_2\text{O})\);  Chrysocolla \((\text{CuO}\cdot\text{SiO}_2\cdot2\text{H}_2\text{O})\)

• Copper sulphides include: Chalcopyrite \((\text{CuFeS}_2)\). Bornite \((\text{Cu}_5\text{FeS}_4)\), Covellite \((\text{CuS})\), Chalcocite \((\text{Cu}_2\text{S})\) , Enargite \((\text{Cu}_3\text{AsS}_4)\)

• Native Copper \((\text{Cu metal})\)
What is an Amino Acid?

- Building block of all proteins
- About 500 different types.
- Simpler amino acids are produced in bulk quantities and available at low prices.
- Glycine is simplest amino acid (amino acetic acid).
- Sweet tasting, non-toxic, occurs in human body.

- Glycine has the following structure:

Black: Carbon  
White-grey: Hydrogen  
Blue: Nitrogen  
Red: Oxygen
Amino-acids as lixiviant

- Amino acids, *and glycine in particular*, satisfy most of the target attributes of lixiviants.
- Glycine in a mild alkaline environment was found to be able to leach copper minerals.
- Air, oxygen or dilute hydrogen peroxide may be used as oxidants.
- Key aspect is the ease of recovery and recycle-ability of glycine / glycinate salts in aqueous solution.
- No special equipment or high temperatures or pressures required.
- Low safety, health and environmental impacts.
The alkaline-glycine system

- Glycine has a FOB price of $1,800-$2,400 per ton (2014).
- Caustic or Lime can be used to adjust the leach pH.
- Optimal leach pH is between 10 – 12.
- Glycine is readily available in bulk quantities: Food grade glycine of around 488,000 tonnes was produced in 2010.
- The copper glycinate complex is stable over a wide pH-Eh range.
Advantages of Glycine Leach Systems at Alkaline pH

- Low cost, mass produced, available in bulk.
- Not toxic & environmentally benign.
- Simple chemistry and ease of control.
- Selectivity of Cu, Au and Ag over most typical gangue and iron minerals.
- Ease of recovery and reuse.
- Process simplicity and ease of Cu recovery.
- No transport and trade restriction.
- Stability over wide acid-base and redox range.
- Thermally stable and non-volatile.
Alkaline System For Cu-ores Why?
Challenges in Acidic leaching

- Many copper porphyries, Cu-Au deposits and some Au deposits have significant amounts of calcite, dolomite, siderite, magnesite, etc.
- For acid leaching, each 1% \( \text{CaCO}_3 \) requires about 1% \( \text{H}_2\text{SO}_4 \).
- pH shift to >3 precipitates/removes ferric oxidant.
- For economic acid leaching, carbonates (as \( \text{CO}_2 \)) should be <2%.
- Elemental sulfur produced during the leaching of copper sulfide can deposit and block pores.
- Special materials of construction are required
<table>
<thead>
<tr>
<th>Minerals</th>
<th>Formula</th>
<th>Specific acid consumption, kg/t</th>
<th>Time for complete dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 day</td>
<td>250 days</td>
</tr>
<tr>
<td>Albite</td>
<td>Na[AlSi₃O₈]</td>
<td>0.3</td>
<td>100–150 years</td>
</tr>
<tr>
<td>Microcline</td>
<td>K[AlSi₃O₈]</td>
<td>0.6</td>
<td>100–150 years</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl₂(OH)₂[AlSi₃O₁₀]</td>
<td>1.6</td>
<td>about 100 years</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg, Fe)₃[AlSi₃O₁₀]·(OH,F)₂</td>
<td>20.1</td>
<td>2–8 years</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>(Mg, Al, Fe)₃·(OH)₂[Si, Al]₄O₁₀·4H₂O</td>
<td>39.3</td>
<td>2–8 years</td>
</tr>
<tr>
<td>(hydromica)</td>
<td></td>
<td>247.2</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₄(OH)₈[Si₄O₁₀]</td>
<td>2.6</td>
<td>30–50 years</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>(Ca, Na)(Mg, Al, Fe)₂·(Si, Al)₄O₁₀·nh₂O</td>
<td>15.7</td>
<td>10–20 years</td>
</tr>
<tr>
<td>Chlorite</td>
<td>(Mg, Fe)₃ₙ(Al, Fe³⁺)ₙ/⁴AlₙSi₂ₙO₅(n=0.3–1)</td>
<td>18.9</td>
<td>from 1 day to 7–8 years</td>
</tr>
<tr>
<td>Carbonized organics</td>
<td>FeS₂</td>
<td>33.6</td>
<td>over 10 years</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>930</td>
<td>1–10 days</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Ca, Mg[CO₃]₂</td>
<td>980</td>
<td>up to 10 days</td>
</tr>
<tr>
<td>Ankerite</td>
<td>Ca(Mg, Fe)[CO₃]₂</td>
<td>940</td>
<td>3–8 days</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>262</td>
<td>8–10 days</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO₃</td>
<td>114</td>
<td>3–4 months</td>
</tr>
<tr>
<td>Limonite</td>
<td>Fe₂O₃·nh₂O(n = 1–4)</td>
<td>1149</td>
<td>1–7 months</td>
</tr>
</tbody>
</table>
Alkaline Vs Acidic leaching

• Alkaline leaching of copper is:
  ✓ More selective.
  ✓ Less corrosive.
  ✓ Lowering reagent consumption.
  ✓ No special materials of construction are required.
  ✓ No sulfur, gels and jarosite precipitation.
  ✓ Particularly useful when followed by alkaline gold or silver leaching (cyanide or glycine based).
  ✓ Does not passivate gold in a subsequent leach.
  ✓ Convenience of using NaSH in alkaline domain and high SX extraction selectivity.
Current alkaline lixiviant systems

- Ammonia leaching
  - Limited ability to recover efficiently and reuse.
  - Partial decomposition with cheaper oxidants.
  - Ammonia is not inherently benign
  - Lower capacity of leaching of acidic compounds
  - The use of ammonia is limited due to its high evaporation
  - May have potential at hydrostatic pressures associated with ISL.
  - Difficulty in maintaining high concentrations of dissolved NH$_3$.
  - Extractors used for copper recovery from ammonia medium do not have high efficiency.
Cu-NH₃ vs Cu-Glycine
Experimental

• All experiments were carried out using solutions prepared from analytical grade reagents and Millipore water.

• The particle size of the minerals used in the leaching experiments was 100% -75μm.

• Leaching of copper sources was conducted in a 2.5L Winchester bottle using a bottle roller at a speed of 150 rpm.

• Leaching at different Temperature, DO levels was conducted in controlled DO leaching system.

• Solution was analysed for copper using Atomic Absorption Spectrophotometry (AAS).
Use of glycine for Cu leaching in alkaline region

Copper extractions from Cu-Au concentrate after two-stages leaching: Stage 2 starts at zero time after stage 1. (Leaching conditions: two-stages, 0.3 M glycine, 1% peroxide, ambient, pH 11, 48 hours)

Effect of leaching solution pH on copper dissolution: 0.3M glycine, 1% H₂O₂, pH 11, at ambient temperature.
Results

1. Copper Oxides
## Quantitative XRD of Minerals Used

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Azurite</td>
</tr>
<tr>
<td>Azurite</td>
<td>65.0</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>-</td>
</tr>
<tr>
<td>Cuprite</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite</td>
<td>-</td>
</tr>
<tr>
<td>Goethite</td>
<td>-</td>
</tr>
<tr>
<td>Kaolinite-1A</td>
<td>3.4</td>
</tr>
<tr>
<td>Malachite</td>
<td>-</td>
</tr>
<tr>
<td>Muscovite-1M</td>
<td>-</td>
</tr>
<tr>
<td>Muscovite-2M1</td>
<td>6.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>7.4</td>
</tr>
<tr>
<td>Rutile</td>
<td>-</td>
</tr>
<tr>
<td>Amorphous Content</td>
<td>18</td>
</tr>
<tr>
<td>Mineral/element</td>
<td>Cu (%)</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>24.0</td>
</tr>
<tr>
<td>Malachite</td>
<td>41.55</td>
</tr>
<tr>
<td>Azurite</td>
<td>42.1</td>
</tr>
<tr>
<td>Cuprite</td>
<td>20.09</td>
</tr>
</tbody>
</table>
Comparison of Cu oxide mineral leaching

Copper Extraction from copper oxide minerals:
Gly: Cu=4:1, pH=11, H2O2=0.5%
Copper Extraction from Azurite: Gly:Cu, pH=11, H2O2=0.5%
Effect of glycine concentration on Malachite leaching

Copper Extraction from Malachite: Gly:Cu, pH=11, H2O2=0.5%
Effect of glycine concentration on Cuprite leaching

Copper Extraction from Cuprite: Gly:Cu, pH=11, H2O2=0.5%
Oxide Mineral Cu Extraction using alkaline glycine/glycinate

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Copper extracted, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hours</td>
</tr>
<tr>
<td>Azurite</td>
<td>94.2</td>
</tr>
<tr>
<td>Malachite</td>
<td>91.7</td>
</tr>
<tr>
<td>Cuprite</td>
<td>84.5</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>18.70</td>
</tr>
</tbody>
</table>
Results

2. Copper Sulphides - Chalcopyrite
## Chalcopryite sample mineralogy and assay

### Quantitative XRD analysis

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chabazite</th>
<th>Chalcopryite</th>
<th>Clinochlore</th>
<th>Pyrite</th>
<th>Quartz</th>
<th>Rutile</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight, %</td>
<td>0.8</td>
<td>35.0</td>
<td>1.5</td>
<td>29.4</td>
<td>0.9</td>
<td>0.4</td>
<td>32.0</td>
</tr>
</tbody>
</table>

### Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>As</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Pb</th>
<th>Si</th>
<th>S</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.71</td>
<td>0.31</td>
<td>14.8</td>
<td>30.9</td>
<td>1.08</td>
<td>0.29</td>
<td>3.64</td>
<td>32.4</td>
<td>4.95</td>
</tr>
</tbody>
</table>
Effect of glycine concentration - Results

Copper Extraction from Chalcopyrite: Gly:Cu, pH=11, H2O2=0.5%

Copper Extraction from Chalcopyrite: Gly:Cu, pH=11, H2O2=0.5%
Effect of pH - Results

Copper Extraction from Chalcopyrite: Gly:Cu, 4:1, pH, H2O2 0.5%.
Sulfur speciation during/after chalcopyrite leaching with alkaline glycine

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>mg/L</th>
<th>% of total S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>1142</td>
<td>89.8</td>
</tr>
<tr>
<td>Sulfite</td>
<td>74.0</td>
<td>7.2</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>22.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulfide</td>
<td>&lt; 0.1</td>
<td>-</td>
</tr>
</tbody>
</table>
Chalcopyrite leaching at ambient temp.

Leaching conditions: Bottle Roll
### Impurity dissolution under various conditions (Chalcopyrite bottle roll leach with alkaline glycine)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Concentration/element</th>
<th>As</th>
<th>Ca</th>
<th>Fe</th>
<th>Mg</th>
<th>Pb</th>
<th>Si</th>
<th>S</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 % peroxide</td>
<td>Expected conc in soln, mg/L</td>
<td>210.01</td>
<td>90.93</td>
<td>9143.69</td>
<td>319.60</td>
<td>85.60</td>
<td>1078.46</td>
<td>9596.88</td>
<td>1466.19</td>
</tr>
<tr>
<td>pH 11, Gly:Cu 4:1</td>
<td>Con after 600 hours (mg/L)</td>
<td>39.3</td>
<td>7.43</td>
<td>484</td>
<td>0.246</td>
<td>4.35</td>
<td>1.27</td>
<td>3379</td>
<td>716</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>18.72</strong></td>
<td><strong>8.17</strong></td>
<td><strong>5.29</strong></td>
<td>0.08</td>
<td><strong>5.09</strong></td>
<td>0.12</td>
<td><strong>35.21</strong></td>
<td><strong>48.82</strong></td>
</tr>
<tr>
<td>0.1 % peroxide</td>
<td>Con after 600 hours (mg/L)</td>
<td>35.4</td>
<td>7.23</td>
<td>435</td>
<td>0.382</td>
<td>4.22</td>
<td>1.11</td>
<td>2859</td>
<td>714</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>16.84</strong></td>
<td><strong>7.96</strong></td>
<td><strong>4.76</strong></td>
<td>0.12</td>
<td><strong>4.93</strong></td>
<td>0.10</td>
<td><strong>29.79</strong></td>
<td><strong>48.73</strong></td>
</tr>
<tr>
<td>0.5 % peroxide</td>
<td>Con after 600 hours (mg/L)</td>
<td>39.3</td>
<td>7.45</td>
<td>469</td>
<td>0.331</td>
<td>4.88</td>
<td>1.27</td>
<td>3224</td>
<td>720</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>18.73</strong></td>
<td><strong>8.19</strong></td>
<td><strong>5.13</strong></td>
<td>0.10</td>
<td><strong>5.70</strong></td>
<td>0.12</td>
<td><strong>33.59</strong></td>
<td><strong>49.09</strong></td>
</tr>
<tr>
<td>1 % peroxide</td>
<td>Con after 600 hours (mg/L)</td>
<td>30.0</td>
<td>6.70</td>
<td>353</td>
<td>0.240</td>
<td>3.84</td>
<td>0.940</td>
<td>3268</td>
<td>723</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>14.28</strong></td>
<td><strong>7.37</strong></td>
<td><strong>3.86</strong></td>
<td>0.08</td>
<td><strong>4.49</strong></td>
<td>0.09</td>
<td><strong>34.05</strong></td>
<td><strong>49.31</strong></td>
</tr>
<tr>
<td>Gly:Cu 2:1</td>
<td>pH 11, 0.5% H2O2</td>
<td>Con after 600 hours (mg/L)</td>
<td>5.72</td>
<td>4.79</td>
<td>58.0</td>
<td>0.448</td>
<td>0.708</td>
<td>0.351</td>
<td>2225</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>2.73</strong></td>
<td><strong>5.27</strong></td>
<td><strong>0.63</strong></td>
<td>0.14</td>
<td><strong>0.83</strong></td>
<td>0.03</td>
<td><strong>23.19</strong></td>
<td><strong>21.00</strong></td>
</tr>
<tr>
<td>Gly:Cu 8:1</td>
<td>pH 11, 0.5% H2O2</td>
<td>Con after 600 hours (mg/L)</td>
<td>38.7</td>
<td>7.67</td>
<td>593</td>
<td>0.266</td>
<td>4.47</td>
<td>1.40</td>
<td>3992</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>18.45</strong></td>
<td><strong>8.43</strong></td>
<td><strong>6.49</strong></td>
<td>0.08</td>
<td><strong>5.22</strong></td>
<td>0.13</td>
<td><strong>41.60</strong></td>
<td><strong>60.72</strong></td>
</tr>
<tr>
<td>Gly:Cu 4:1, pH 9, 0.5% H2O2</td>
<td>Con after 600 hours (mg/L)</td>
<td>105</td>
<td>41.1</td>
<td>578</td>
<td>2.59</td>
<td>24.3</td>
<td>3.49</td>
<td>1144</td>
<td>303</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>50.17</strong></td>
<td><strong>45.24</strong></td>
<td><strong>6.32</strong></td>
<td>0.81</td>
<td><strong>28.37</strong></td>
<td>0.32</td>
<td><strong>11.92</strong></td>
<td><strong>20.63</strong></td>
</tr>
<tr>
<td>pH 10, 0.5% H2O2</td>
<td>Con after 600 hours (mg/L)</td>
<td>120</td>
<td>17.44</td>
<td>1188</td>
<td>1.68</td>
<td>24.7</td>
<td>4.69</td>
<td>2190</td>
<td>522</td>
</tr>
<tr>
<td>% metal extracted</td>
<td></td>
<td><strong>56.97</strong></td>
<td><strong>19.18</strong></td>
<td><strong>12.99</strong></td>
<td>0.53</td>
<td><strong>28.89</strong></td>
<td>0.43</td>
<td><strong>22.82</strong></td>
<td><strong>35.61</strong></td>
</tr>
</tbody>
</table>
Results

Copper leaching from chalcopyrite concentrate

Cu Extraction, %

- 9.1% at 5 h
- 16.9% at 24 h
- 31.6% at 96 h
- 42.6% at 192 h
- 50.2% at 288 h
- 54.1% at 360 h
- 60.2% at 500 h

Time, h

205 mg/L
381 mg/L
715 mg/L
963 mg/L
1135 mg/L
1222 mg/L
1360 mg/L

Copper leaching from chalcopyrite concentrate
Alkaline Glycine leaching of Chalcopyrite: Controlled DO Experiment
Chalcopryrite leaching: Effect of dissolved $O_2$

Leaching conditions: 0.1 M Glycine, Ambient Temperature, pH 10.5, controlled DO level.
Chalcopyrite concentrate leaching: Effect of glycine concentration

Leaching conditions: 60°C pH 10.5, DO 25 ppm.
Chalcopyrite concentrate leaching:
Effect of temperature

Leaching conditions: 0.2 M glycine, DO 25 ppm, pH 11.5, °C.
COPPER RECOVERY
Copper recovery from alkaline glycinate solution: NaSH precipitation

Sulfide ions were added to the pregnant liquor at different Cu:S\textsuperscript{2-} molar ratios in order to recover copper from the glycine solution.

The copper recovery was up to 99.1% as copper sulfide, Covelite (CuS) at Cu:S\textsuperscript{2-} molar ratio of 1:0.70 in 10 minutes contact time.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Cu, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before precipitation</td>
<td>1243</td>
</tr>
<tr>
<td>After precipitation Cu:S\textsuperscript{2-} 1:0.70</td>
<td>11</td>
</tr>
<tr>
<td>After precipitation Cu:S\textsuperscript{2-} 1:0.5</td>
<td>226</td>
</tr>
</tbody>
</table>
XRD pattern of the copper sulfide (Covellite) precipitate
Particle size distribution of CuS precipitate

- $d(0.1)$: 8.8 µm
- $d(0.5)$: 33.1 µm
- P80: 67.0 µm
- $d(0.9)$: 89.4 µm

CuS as precipitated from alkaline copper glycinate solutions
Solvent extraction (SX) experiments show that copper glycinate can be easily extracted from the alkaline aqueous medium. Extractant: LIX 84

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Equip. pH</th>
<th>Cu</th>
<th>Extraction, (%)</th>
<th>Stripping, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>11.5</td>
<td>3596</td>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>Test 1</td>
<td>8.8</td>
<td>43.9</td>
<td>98.8</td>
<td>-</td>
</tr>
<tr>
<td>Test 2</td>
<td>9.4</td>
<td>65.6</td>
<td>98.2</td>
<td>100</td>
</tr>
<tr>
<td>Test 3</td>
<td>10</td>
<td>22.3</td>
<td>99.4</td>
<td>100</td>
</tr>
</tbody>
</table>
Conclusions

• 2 Patents pending (One PCT another Provisional)
• Amino acids, or their salts, with a suitable oxidant (O₂, H₂O₂, Air) opens up a range of leaching options (ISL VL, HL) feasible at alkaline pH.
• Results show high potential for the use of alkaline amino acids at moderately elevated temperatures (40-60 °C) as copper lixiviant for:
  - Heap/Vat leach operations
  - Tank leach operations
  - Possible in-situ leaching
Conclusions (Cont’d)

- Glycine shows much promise due to bulk availability and low cost.
- Many Cu or Au-Cu deposits have too much alkaline gangue to make either acid or bioleaching feasible, but which are amenable to amino-acid based leaching.
- High copper extraction from copper oxides was achieved in 24 hours.
- Higher copper extraction were achieved at 4:1 Gly:Cu
- Very low Fe co-dissolution
- Carbonate minerals are not decomposed.
- Precipitation of elemental sulfur, gypsum, jarosite eliminated.
Conclusions (Cont’d)

• In the presence of an air, oxygen or hydrogen peroxide or a mixture thereof, glycine can dissolve copper from chalcopyrite at either an elevated (40-70 °C) or ambient temperature.

• Pyrite remained unreacted during leaching of chalcopyrite and iron concentration in the final pregnant solution was less than 20 mg/L.

• Recovery and reuse potential of lixiviants after SX, electrowinning and NaSH precipitation.

• Sulfides are oxidised to sulfates.

• Applicable to wide range of Cu-minerals (oxide, sulfide, native copper).