Geomicrobiology of Ore Deposits: Genesis and Exploration

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- High T: “Quick” abiotic thermodynamic equilibrium
- Low T: Redox reactions are very sluggish at low temperature (≈≤150°C)
- Only biological processes can catalyze them: energy needed for living

- Life needs **liquid** water, temperatures below ≈ 121°C and chemical disequilibrium (electron donors = **nutrients**)

- Do not have direct control on fluid chemistry but can modify the environment: local, regional and global (bio) geochemical cycles

- High capability of duplication and high surface ratio: extremelly effective
• Winogradsky (1888): Pyrite oxidized by bacteria

• Discovery in Yellowstone of a bacteria (Thermus aquaticus) with an enzime that makes it able to survive at high T (50-80°C) (Brock, 1969): **Bacteria in hydrothermal systems**

1979: (Dark) **Deep Biosphere** (Corliss et al., 1979)
No light/no oxygen

Anderson et al. (2007)
The deep biosphere

- A large biomass (>55%; ~10^{30} individuals; 75-94% prokaryotes) – 95% unknown

- Anaerobic & extremophiles
  - Oxigen is toxic: Obtain energy from different electron donors (H_2, CH_4, CH_3COOH, …)
  - Environment with low energy and nutrients
  - Mostly (meso)thermophilic
  - Thick membranes
  - Special enzimatic evolution

- Ore deposits: The perfect place
  - Water, heat and nutrients

**Heterotrophic:** Organic carbon $\rightarrow$ CO_2 + reduction inorganic aqueous species/minerals

$[\text{CH}_2\text{O}] + \text{SO}_4^{2-} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S} + 6\text{H}^+$

**Autotrophic/chemolithoautotrophic:** Inorganic compounds (Fe, Mn, H_2S)

$\text{CO}_2 + 4\text{H}_2\text{S} + \text{O}_2 \rightarrow [\text{CH}_2\text{O}] + 3\text{S}^0 + 3\text{H}_2\text{O}$
**Redox environment**

- **Aerobic-oxic**
  - Oxidation: \(4Fe^{2+} + O_2 + 4H^+ \rightleftharpoons 4Fe^{3+} + 2H_2O + 4e^-\)
  - \(SO_4^{=} + 2H^+ \rightleftharpoons H_2S + 2O_2 + 2e^-\)

- **Anoxic**
  - Reduction \(O_2: O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O\) (0.812)
  - Reduction \(NO_3^-: NO_3^- + 6H^+ + 6e^- \rightleftharpoons N_2 + 3H_2O\) (0.747)
  - Reduction \(Mn^{4+}: MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{++} + 2H_2O\) (0.526)
  - Reduction of \(Fe^{3+}: Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{++} + 3H_2O\) (-0.047)

- **Euxinic**
  - Reduction of \(SO_4^{=}=: SO_4^{=} + 10H^+ + 8e^- \rightleftharpoons H_2S + 4H_2O\) (-0.221)
  - Reduction of \(S^0: S^0 + 2H^+ + 2e^- \rightleftharpoons H_2S\)

- **Methanogenic**
  - Reduction of \(CO_2: CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O\) (-0.244)

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Microbes are facultative:
Electron acceptors are reduced and can become e-donors

Highest chemical and biological activity at the interfaces (presence of electron donors and acceptors)
Geothermal systems

Waimangu (New Zealand)
Microbes need minerals

Microbes \( \Delta \log Q/K \) inside or within the membrane to precipitate minerals

Microbes precipitate toxic metals
• The products of the reaction change the environment
• $\Delta \log Q/K$ outside the cell with minerals nucleating on minerals, bounding the cell (chemical reactive sites) and extracellular polymers
Ore deposits and the origin of life

Ueno et al (2007)

Control the surface 3.5 My ago

\[ \delta^{34}\text{S}_{\text{py}} \text{ -5 to +5}\% \]

\[ \delta^{34}\text{S}_{\text{ba}} \text{ -17 to +5}\% \]

\[ \delta^{13}\text{C}_{\text{CH}_4} \text{ <-56}\% \]

Pilbara (3550 Ma)
Euxinic brine pools/euxinic bottoms
Abundance of sulfate-reducers coexisting with methanotrophs

- $2[\text{CH}_2\text{O}] + \text{SO}_4^{=} \rightarrow \text{H}_2\text{S} + \text{HCO}_3^-$
- $\text{CH}_4 + \text{SO}_4^{=} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{CO}_2 + 2\text{H}_2\text{O}$
- $\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$
- If electron donors present => large amounts of sulfides
- Increase of pCO$_2$: carbonates?
- sedex and VMS deposits

$\delta^{34}\text{S}: -45 \text{ to } +10\%$
Photosynthetic bacteria produce ATP
\[
\text{CO}_2 + \text{H}_2\text{O} + \text{ATP} \rightarrow [\text{CH}_2\text{O}] + \text{O}_2
\]
\[
\text{Fe}^{2+} + 0.5\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.5\text{H}_2\text{O}
\]
\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+
\]
Carbonates stable
Seasonal
60 times faster than abiotic oxidations

Anoxic photosynthesis
\[
4\text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow [\text{CH}_2\text{O}] + \text{Fe(OH)}_3 + 8\text{H}^+
\]
Aerobic systems: supergene profiles/laterites

Host a large consortium of microorganisms

*Acidithiobacillus ferrooxidans* oxidizes S and Fe and \( \nabla \text{pH} \)

\[
\text{FeS}_2 + 8\text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{SO}_4^{=} + 16\text{H}^+ \\
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ = 4\text{Fe}^{3+} + 2\text{H}_2\text{O}
\]

Accelerate the weathering of aluminosilicates and precipitation of iron oxyhydroxides

1/3 total sulfate in the crust

10^5 faster than abiotic processes
Aerobic systems: iron oxidation

- Funghii and bacteria are able to change the redox state of the environment (increase Eh) and oxidize (toxic) Fe$_{2+}$

- BCM jarosite precipitates in the micro-organisms coating and entombing the cells (Oggerin et al., 2014)

\[ \Sigma Fe \quad SO_4^{2-} \quad K^+ \rightarrow \text{jar} \]

Tharsis (Spain)
Aerobic systems: supergene and alluvial gold

- Microbes (α-proteobacteria) are critical for gold mobilization/precipitation
- $2Au^0 + O_2 + 4H^+ \rightarrow 2Au^+ + 2H_2O$
- $FeS_2 + 3H_2O \rightarrow Fe^{3+} + S_2O_3^{2-} + 6H^+$
- $Au^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-}$
- $AuCl_2^- & AuCl_4^- in chloride-rich settings$
- Aqueous gold is toxic for another bacteria

- Biodegradation of plants
- $Au(S_2S_3)_2^{3-} + 2CH_3COOH \rightarrow Au^+ + 4HS^- + 4CO_2 + 2H_2O$
- $HS^- + 2Au^+ \rightarrow 2Au^0 + S^0 + H^+$
- Precipitation as nanoparticles on gold surfaces (BIC) or in bacteria (BCM)

Reith et al (2009)

Cupriavidus metallidurans
Some of largest copper producers

Related to bacterial activity? (Sillitoe et al. 1996)

Very few bacteria in cementation zones of porphyry copper deposits (Enders et al. 2006)

Reduced sulphur inherited from the host sulphides
Las Cruces: geology

- Niebla-Posadas aquifer
  - Alkaline (pH=8-9) bicarbonate Ca-(Na) waters
  - T: 25-30°C

- Deep reservoir
  - Alkaline (pH=8-9) Na chloride waters
  - T: 35-40°C
  - $T_{reser} : 107-146°C$

- Niebla Posadas

- Biogenic Zone
  - 1.83 Mt @ 1.88% Pb, 2.3 g/t Au, 40 g/t Ag

- Cementation Zone
  - 17 Mt @ 6% Cu
  - 2 Mt @ 20% Cu

- Biogenic Zone
  - High grade secondary deposit on a VMS
  - Secondary alteration formed by the same processes
Las Cruces: the Biogenic Zone

Post-burial (7 Ma) replacement of a previous sub-aerial gossan

The process implies:

- Reduction of Fe$^{3+}$ to Fe$^{2+}$
- Increase of fCO$_2$ and fS$_2$
- Concentration of gold and silver
- A biogenic origin? → Giant bioreactor

The biologic activity has produced ca. 3.1 x 10$^9$ moles H$_2$S, 10$^{10}$ moles of CO$_2$, 1.19 Mt of carbonates, 114,000 t of galena, 638 t of Ag (sulfides) and 6.5 t of gold plus a significant proportion of the secondary copper sulfides in 7 My
Morphologies (BCM) are seldomly a proof
Quick recrystallization (metastable textures)
Supersaturation (framboids)
TEM is definitive
Detecting life: biomarkers

$\delta^{13}C_{\text{DIC}} = -9$ to $-6\%$

$\delta^{13}C_{\text{CO}_2} < -60\%$

CO$_2$ derived from mixing of DIC in aquifer and a deep one derived from the biogenic oxidation of methane

- Remnants of lipids
- Carbon (quite) definitive: Extreme negative $\delta^{13}C$ values ($\Delta^{13}C_{\text{CH}_4-\text{CO}_2} < -40\%$) trace organic oxidation of methane
- Sulphur problematic
- Other?: Cu, Fe,…
Search for deep life: Las Cruces

- Microbial activity has been present at Las Cruces in the last 11 Ma: does it continue today?
- Water sampling: abundant living prokaryotes
- Drillholes: Living mesophillic (lithotrophic) archea & bacteria in the biogenic and cementation zones
- Much more complex than expected
Detecting PRESENT DAY life

- Cultives
- Fluorescent In Situ Hybridation (FISH)
- Genoma replicates
- RNA extraction: Problem with sulphides
- Problem of contamination
Future in exploration

- Microbes mobilize (dissolve) and redistribute (organic complexes) of As, Se, Mo, Sn, Sb, Te, Hg, W, Cd, Hg, Pb, U, Ag, Cu & Au in regolith
- Increase kinetics of oxidation
- Dispersion halo: microbes create a reduced column with metals concentrating in the top
- Precipitation of (toxic) metals in soil
- Soil enrichment is dominantly microbial
  - In situ composition and microbial activity (few identified, Bacillus cereus)
  - Metal specific bacterial sensors
- Released gases with specific isotope composition
- Isotope geochemistry of water (sulphate reducers/methanotrophes)

Some important messages

- Extremophille microbes are abundant below the surface: deep (and ignote) biosphere
- They can form large ecosystems in the presence of water & electron donors/acceptors
- Ore deposits are one of the best environments for the deep biosphere
- They change the mineralogy of the host rock and form/modify a wide variety of ore deposits

Frontier in R & D
- Origin of life
- Ore forming processes
- Bioleaching (Cu, Au)
- In situ deep biomining (Cu–(Zn-Ni-Pb-Co))
- Soil remediation (bacteria accept large amounts of metals)
- Prevention of corrosion
- Energy (Bioaccumulators)
- Biotechnologies (Pharmacy)
- Nanotechnologies
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