Life detection on Europa from a lander: metabolic signatures

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Starting Hypothesis

• If Life exists on Europa
  – Living Entities are small-sized and not visible from an Orbiter
  – Living Entities are organized like Cells and have properties similar to living Cells on Earth
  – These Cell-like Entities carry out Carbon Chemistry in liquid Water
How to detect microbial Cells from an Orbiter

• We cannot look at them
• We cannot measure their metabolic activity
• We can search for Life Macromolecules, but there is a serious detection limit problem: a single cell dry weight is about $10^{-12}$ g.
• But we can search for metabolic signatures
Nutrients for biosynthesis

Anabolism (biosynthesis)

Energy for biosynthesis

Catabolism

Energy for motility, transport of nutrients, and so on

Macromolecules and other cell components

Chemicals, light (energy source)

Waste products (fermentation products; acids, alcohols, CO₂, and so on; reduced electron acceptors)
The best example

- To fix carbon dioxide via the Calvin cycle, oxygenic photosynthetic organisms need to reduce it into carbohydrates.
- The reducing power (electrons from **Hydrogen**) comes from photolysis of water.
- This photolysis also produces $O_2$, which accumulated in Earth’s atmosphere.
Diversity of metabolisms involved in energy production

- Phototrophy
- Chemotrophy
  - Aerobic respiration
    - Organic or inorganic electron donors
  - Anaerobic respiration
    - Organic or inorganic electron donors
    - Organic or inorganic electron acceptors
  - Fermentation of organic compounds
Phototrophy

- **Oxygenic photosynthesis**
  - $O_2$ detection
- **Anoxygenic photosynthesis**
- **Bacteriorhodopsin-like processes**
- In all cases: pigments
**Examples of reactions with H₂ as e⁻ donor**

- H₂ + fumarate²⁻ → succinate²⁻
  \[ \Delta G^0 = -86 \text{ kJ} \]

- H₂ + NO₃⁻ → NO₂⁻ + H₂O
  \[ \Delta G^0 = -163 \text{ kJ} \]

**Couple**

- CO₂/glucose (-0.43) 24 e⁻
- 2H⁺/H₂ (-0.42) 2 e⁻
- CO₂/methanol (-0.38) 6 e⁻
- NAD⁺/NADH (-0.32) 2 e⁻
- CO₂/acetate (-0.28) 8 e⁻
- S⁰/H₂S (-0.28) 2 e⁻
- SO₄²⁻/H₂S (-0.22) 8 e⁻
- Pyruvate/lactate (-0.19) 2 e⁻
- S₅O₃²⁻/S₂O₃²⁻ (+0.024) 2 e⁻
- Fumarate/succinate (+0.03) 2 e⁻
- Cytochrome \(b_{ox/red}\) (+0.035) 1 e⁻
- Ubiquinone \(b_{ox/red}\) (+0.11) 2 e⁻
- Cytochrome \(c_{ox/red}\) (+0.25) 1 e⁻
- Cytochrome \(d_{ox/red}\) (+0.39) 1 e⁻
- NO₃⁻/NO₂⁻ (+0.42) 2 e⁻
- NO₃⁻/N₂ (+0.74) 5 e⁻
- Fe³⁺/Fe²⁺ (+0.75) 1 e⁻
- \(\frac{1}{2}O₂/H₂O (+0.82) 2 e⁻\)
Hydrogen oxidation

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]

\[ \Delta G^\circ' = -237 \text{ kJ} \]
**Fe**

**Fe**

++ oxidation

\[
2\text{Fe}^{++} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{+++} + \text{H}_2\text{O}
\]

Non soluble iron hydroxide

\[
\text{FeCO}_3 + 10\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 3\text{HCO}_3^- + 3\text{H}^+
\]
Oxidation of reduced sulphur compounds

\[
\begin{align*}
H_2S + 2O_2 &\rightarrow SO_4^{2-} + 2 H^+ \\
HS^- + 1/2O_2 + H^+ &\rightarrow S^0 + H_2O \\
S^0 + H_2O + 1/2O_2 &\rightarrow SO_4^{2-} + 2 H^+ \\
S_2O_3^{2-} + H_2O + 2O_2 &\rightarrow 2SO_4^{2-} + 2 H^+ \\
\end{align*}
\]

Environment becomes acidic
Ammonium oxidation $\rightarrow$ Nitrite
Nitrite Oxidation $\Rightarrow$ Nitrate
Methane & C$_1$ compounds oxidation

$\text{CH}_4 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCOO}^- \rightarrow \text{CO}_2$
Nitrate respiration $\Rightarrow$ NO, N$_2$O, NO$_2$, N$_2$
Sulphate reduction $\Rightarrow$ H$_2$S

\[ 4 \text{H}_2 + \text{SO}_4^- + \text{H}^+ \Rightarrow \text{HS}^- + 4 \text{H}_2\text{O} \]

\[ \text{CH}_3\text{COO}^- + \text{SO}_4^- + 3 \text{H}^+ \Rightarrow 2 \text{CO}_2 + \text{H}_2\text{S} + 2 \text{H}_2\text{O} \]
CO$_2$: electron acceptor

Methanogenesis

CH$_4$ + 3 H$_2$O

HCO$_3^-$ + H$^+$

4 H$_2$

2 HCO$_3^-$ + H$^+$

Proton motive force

Proton motive force or sodium motive force

ATP

Acetogenesis

O

CH$_3$ – C – O$^-$

+4 H$_2$O
Other electron acceptors

• Chlorate (ClO$_3^-$) => Chloride
• Mn$^{4+}$ => Mn$^{2+}$
• Fe$^{3+}$ => Fe$^{2+}$
• Selenate => Selenite
• Arsenate => Arsenite
• DMSO => DMS
• Fumarate => Succinate
Fermentations

Organic compound (e⁻ donor) → Intermediate

Intermediate → Intermediate ~P

Intermediate ~P → ADP

ADP → Substrate-level phosphorylation

Substrate-level phosphorylation → ATP

ATP → Oxidized organic compound (e⁻ acceptor)

Oxidized organic compound (e⁻ acceptor) → Electron carriers

Electron carriers → Reduced organic compound (fermentation product)

Reduced organic compound (fermentation product) → ATP
Fermentation products (1)

Mixed acid fermentation, *e.g.*, *E. coli*

**Glycolysis**

- **Glucose** → **Pyruvate**

- **CO₂** → **Succinate**

- **Acetyl-CoA** + **Formate** → **Ethanol** → **Acetate**

- **CO₂** → **H₂**

**Typical products (molar amounts)**

- Acidic : neutral 4 : 1
- **CO₂** : **H₂** 1 : 1
Fermentation products (2)

**Butanediol fermentation, e.g., *Enterobacter***

- **Glycolysis**
  - Glucose → Pyruvate

  - **2,3-Butanediol + CO₂**
  - Ethanol
  - Lactate
  - Succinate
  - Acetate
  - CO₂ + H₂

**Typical products (molar amounts)**

- Acidic : neutral
  - 1 : 6
- CO₂ : H₂
  - 5 : 1
Conclusions (1)

There is a variety of compounds that cells (prokaryotic) may use to obtain energy.

This energy is used by cells to build macromolecules and biomass.

If the amount of energy produced by unit of substrate is low, then the amount of biomass produced may be undetectable.

But the quantity of metabolic products may be high.
Conclusions (2)

Some metabolic products are volatile and may accumulate in the atmosphere:
$\text{H}_2$, $\text{CO}_2$, $\text{CH}_4$, $\text{O}_2$, $\text{N}_2$, $\text{NO}$, $\text{N}_2\text{O}$, $\text{H}_2\text{S}$, organics, etc.

Some others may accumulate in the liquid phase, dissolved (nitrate, nitrite) or not (iron hydroxide), or change the pH of the environment (sulphuric acid).

Detection of concentration anomalies of such compounds may indicate the existence of life-mediated chemical reactions.