Observations of Europa’s surface materials with Subaru/IRCS and its comparison with laboratory experiments

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Europa: Possible Habitable Environment

- Icy covered surface
- Interior ocean

Image credit: NASA JPL
Why is Europa possible habitable?

- Water-Rock interaction
  - Geologically active surface
  - Material cycle
    - Redox disequilibrium = Energy for life
  - Oxidizing: $O_2$, $SO_4$, $ClO_4$
  - Reducing: $H_2$, $H_2S$

Topics:
1. Reducing?
2. Radiation
Outline of today’s talk

1. Europa’s observation

2. Topic 1: The cycle of sulfur in the interior
   - Laboratory experiments
     (Implications for observation)

3. Topic 2: Oxidation of chlorine on the surface
   - Observation with Subaru
   - Laboratory experiments
     
     \[\text{On-going}\]
Europa’s observation: Surface reflectance

Non-ice material: **Ocean composition?**

- NIR observation by Galileo spacecraft
  (e.g., McCord et al., 1999)
  - $\text{SO}_4$-bearing salt? (e.g., $\text{MgSO}_4$
  - Low resolution ($\delta\lambda \sim 25 \text{ nm}$)
  - No regional distribution

(Edited from Dalton et al., 2007)
Europa’s observation: Surface reflectance

- NIR Observation by telescope (Keck, VLT)
  - High resolution (δλ~0.5 nm) (e.g., Fischer et al., 2015)
  - Regional distribution

**H₂SO₄**

Trailing side; Sulfur from Io

**Cl-bearing salts? (e.g. NaCl)**

Geological active region

**Keck/OSIRIS data**

(Fischer et al., 2015)

SO₄-salt (sulfate)

Cl-salt (Chloride)

Reflectance

Major composition: Cl? Not SO₄
**Topic 1: Environment of Europa’s interior?**

- NIR Observation by telescope (Keck, VLT)
  - High resolution ($\delta\lambda \sim 0.5$ nm) (e.g., Fischer et al., 2015)
  - Regional distribution

H$_2$SO$_4$

Trailing side; Sulfur from Io

Cl-bearing salts? (e.g. NaCl)

Geological active region

SO$_4^{2-}$ supply into the ocean
$10^{-3}$-$10^{-2}$ mol/yr/m$^2$ (Hand et al., 2015)

$\leftrightarrow$ Earth’s ocean $10^{-2}$ mol/yr/m$^2$

$\rightarrow$ SO$_4^{2-}$ as the major component??

Where did SO$_4$ go in Europa’s ocean?

What process is responsible for sink of SO$_4$?
Sulfur sink: Hydrothermal sulfate reduction

Hydrothermal system:
Sink of 40% of $\text{SO}_4^{2-}$ in Earth’s ocean

$$\text{SO}_4^{2-} + 4\text{H}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}$$

(e.g., Charlson et al., 2000)

Previous experiments ~10 MPa
← Earth’s seafloor condition
(e.g., Truche et al., 2009)

How effective does sulfate reduction proceed under Europa’s conditions (~100 MPa)?
What condition would be suitable for sulfate reduction? (pH & rocks)
Measurement of reaction rates

- Dickson-type autoclave
  - Autoclave of Stainless Steel 630 max. 130 MPa → Europa, Mars, Super Earth
  - By pressurizing the flexible gold cell, we collect in-situ fluid samples without significant changes in P-T
Measurement of reaction rates

- Dickson-type autoclave
  - Autoclave of Stainless Steel 630 max. 130 MPa → Europa, Mars, Super Earth
  - By pressurizing the flexible gold cell, we collect in-situ fluid samples without significant changes in P-T

Applicable to simulate hydrothermal reactions beyond Earth
Sulfate reduction proceeds on Europa’s seafloor? (Tan et al., submitted)

- Small pressure dependence: Sulfate reduction proceeds effectively on Europa, as on Earth
- Strong pH dependence: inhibited at pH > 6

Graph showing the reaction rate log k/s vs pH at different pressures:
- ~10 MPa (Earth)
- 100 MPa (Europa)

Legend:
- 10MPa (This study)
- 100MPa (This study)
- 10 MPa (Truche et al., 2009)
- 50 MPa (Cross et al., 2004)
- 3.5-6.8 MPa (Thom & Anderson, 2008)
Hydrothermal fluid can be pH < 6

What decides pH and composition of hydrothermal fluid?
→ Water-rock interaction (e.g., Shibuya et al., 2015)

Europa’s possible seafloor rock: **Chondritic** / **Basaltic**

**Themodynamic calculation**

**Chondritic rock**

<table>
<thead>
<tr>
<th>Initial $\text{SO}_4^{2-}$ (mM)</th>
<th>Fluid pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>100</td>
<td>7</td>
</tr>
<tr>
<td>200</td>
<td>6</td>
</tr>
<tr>
<td>300</td>
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<tr>
<td>400</td>
<td>6</td>
</tr>
<tr>
<td>500</td>
<td>6</td>
</tr>
</tbody>
</table>

**Basaltic rock**

<table>
<thead>
<tr>
<th>Initial $\text{SO}_4^{2-}$ (mM)</th>
<th>Fluid pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>100</td>
<td>5.5</td>
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<td>200</td>
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<tr>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>500</td>
<td>5</td>
</tr>
</tbody>
</table>

Sulfate reduction **inhibited**

Sulfate reduction **proceeds**
The fate of exogenic $\text{SO}_4^{2-}$ in Europa

**Chondritic rock**
- $\text{CO}_2$, $\text{H}_2$
- $\text{Na}_2\text{SO}_4$, $\text{Na}_2\text{CO}_3$, $\text{NaCl}/\text{MgCl}_2$
- $\text{H}_2\text{SO}_4$
- $\text{SO}_4^{2-}$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{Cl}^-$, $\text{CO}_3^{2-}$
- $\text{pH} > 6$
- $\text{SO}_4$ accumulate

**Basaltic rock**
- $\text{H}_2\text{S}$, $\text{H}_2$
- $\text{NaCl}/\text{MgCl}_2$
- $\text{H}_2\text{SO}_4$
- $\text{SO}_4^{2-}$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Cl}^-$
- $\text{pH} < 6$
- Sink of $\text{SO}_4$
- FeS precipitate

Controlled by seafloor rock composition
The fate of exogenic $\text{SO}_4^{2-}$ in Europa

**Chondritic rock**
- $\text{CO}_2$, $\text{H}_2$
- $\text{Na}_2\text{SO}_4$, $\text{Na}_2\text{CO}_3$, $\text{NaCl/MgCl}_2$
- $\text{H}_2\text{SO}_4$
- $\text{SO}_4^{2-}$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{Cl}^-$, $\text{CO}_3^{2-}$
- $\text{pH} > 6$
- $\text{CaSO}_4$ accumulate

**Basaltic rock**
- $\text{H}_2\text{S}$
- $\text{NaCl/MgCl}_2$
- $\text{H}_2\text{SO}_4$
- $\text{SO}_4^{2-}$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Cl}^-$
- $\text{pH} < 6$
- $\text{Sink of SO}_4$
- FeS precipitate

**Consistent**
- $\text{NaCl/MgCl}_2$

**Controlled by seafloor rock composition**
Proxy indicator for observation

Experimental data provides proxy indicator for observation

Gas species in H$_2$O plume
H$_2$S, CO$_2$, H$_2$
→ ALMA,
Future spacecraft
(Europa Clipper)
Surface salts
→ Large telescopes (e.g., JWST)

(e.g., Roth et al., 2014)
Irradiation of high-energy particle (cf. electron) & UV (e.g., Paranicas et al., 2009)

- Oxidation of surface material (e.g. forming oxychlorines)

\[
\text{H}_2\text{O} \rightarrow \text{O}_2, \text{H}_2\text{O}_2, \text{O}_3
\]

- Redox disequilibrium
- Habitability?

\[
\text{NaCl/MgCl}_2 \\
\rightarrow \text{NaClO}_3/\text{Mg(ClO}_3)_2, \text{NaClO}_4/\text{Mg(ClO}_4)_2?
\]

(Ligier et al., 2016, Johnson et al., 2019)

Surface oxidation: Important for Europa’s geochemistry

Topic 2: Cl-bearing salts oxidation on Europa’s surface?

Eutectic point↓

➢ Habitability?

➢ Tectonics?

(Image by NASA JPL)
Current understanding of Cl-salt oxidation

**Surface observations**
(e.g., Fischer et al., 2015, Ligier et al., 2016)

- **Salt Cl? ClO₄?**

*Peaks of chlorine salts: ~1.0, 1.2, 1.4 μm*  
(Data of VLT/SINFONI, Ligier et al., 2016)

*Limited wavelength range*

**Oxychlorine: What? Where?**

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**Irradiation experiments**

- **Electron for chloride**  
  (e.g., Hand et al., 2015)  
  → Color changes

- **UV for NaCl + SiO₂**  
  (Carrier et al., 2015)

- **Electron for Cl₂ + CO₂**  
  (Kim et al., 2013)  
  → ClOₓ generated

*No research of H₂O ice + Cl-salt*

Generating thin film of ice + salt is challenging

**Oxidation mechanism?**
Europa’s surface observation with Subaru/IRCS

Grism spectroscopy

- Date: May 16, 17 (S19A-119)
  - 5/16: Leading side  
    (material from interior?)
  - 5/17: Trailing side (Exogenic sulfur)

- Angular resolution \(^\text{w/ AO188}\)  
  ~0.06 arcsec/pix (~300 km~Geological unit)

- Standard stars (G2V)  
  HD154805, HD160257

- Fix of telluric absorption,  
  calculation of reflectance \(R(\lambda)\):  
  \[ R(\lambda) = \frac{F_{\text{Europa}}(\lambda)}{F_{\text{G2V}}(\lambda)} \]

- EXP time: ~2 s (SNR > 10)

(Fischer et al., 2015)
Expected spectra

- Band: zJH (0.95–1.5 μm) ← First observation by telescope
- Spectral resolution: $R \sim 230$, $\delta \lambda \sim 2.3$ nm ← Higher than spacecraft data ($\delta \lambda \sim 25$ nm)
- Expected material from interior (5/16 area): Cl, ClO$_3$, ClO$_4$-salts
  ➢ Different peak position, shape? (hydrated waters $\sim 1.0, 1.2, 1.4$ μm)

![Reflectance spectra graph](Hanley et al., 2014)
• Similar spectrum to previous data of Galileo
• Strong telluric absorptions
  ➢ Better fix is necessary (time variation of atmospheric condition)

(Edited from McCord et al., 1999)
Preliminary results

Composition?
- Nearly H$_2$O ice spectrum
- Less specific features

Salts: < 40\% (Fischer et al., 2015)
 < 30\% (Ligier et al., 2016)

☐ Non-hydrated salt?
(NaCl, NaClO$_4$)

☐ De-hydrated salt?
(MgCl$_2$, Mg(ClO$_4$)$_2$)
← Dehydration by UV?
(e.g., Thomas et al., 2017)

Analysis of other area is on-going

**H$_2$O ice : salt = 60 : 40**
(Clark et al., 2007, Hanley et al., 2014)

- NaCl
- NaClO$_4$
- NaClO$_4$·2H$_2$O
- MgCl$_2$·2H$_2$O
- MgCl$_2$·4H$_2$O
- MgCl$_2$·6H$_2$O
- Mg(ClO$_4$)$_2$·6H$_2$O
- Mg(ClO$_3$)$_2$·6H$_2$O
Irradiation experiment

- Electron: 5–10 keV
- UV: 115–400 nm
- Temperature: 90–150 K
- Pressure: 10^{-6}–10^{-5} Pa

Thin film of Cl-salt + H₂O ice
(NaCl, MgCl₂·6H₂O)
Thickness ~100 μm

Electron/UV ~10 hours

Newly-constructed system

Electron gun
UV lamp
TMP
Sample
100 mm
Thin film of Cl-salt + H₂O ice (NaCl, MgCl₂·6H₂O)
Thickness ~100 μm

Analysis of compositional change:
ClO₄⁻ (Ion Chromatography)
Cl redox state (XAS)

Electron: 5–10 keV
UV: 115–400 nm
**Preliminary results of experiments**

IC analysis: No detection ClO$_4$ in all case
Detection limit: ClO$_4$/Cl > ~0.1–1%
Upper limit yield: $10^{-24}$ mol/e$^-$, $10^{-26}$ mol/photon

XAS analysis
Mg(ClO$_4$)$_2$?
Only 1 case: MgCl$_2$$\cdot$6H$_2$O, 100–120 K, 11 hours, electron, 5 keV, 1.7$\mu$A

No clear detection of oxychlorine generation

- Reaction proceeds in shallow depth?
  Penetration depth: e$^-$ (10keV: 1 $\mu$m), UV (0.1 $\mu$m)

- Short irradiation time?
e$^-$ /UV dose <100 yrs on Europa’s surface (~10 Ma)

Retry in same condition → No detection in IC

Too small scale in time & space is problem?
On-going and future study

1. Higher energy electron irradiation
   Energy of electron irradiated to Europa:
   ~10 keV−100 MeV
   (e.g., Paranicas et al., 2009)
   ~1 MeV electron: penetrating ~ 4 mm
   (Zombeck, 1982)

2. Analysis of observing data of Subaru
   - Better fix of atmospheric absorption
   - Analysis of wide area on the surface
Summary

- Europa’s interior ocean: Habitable?
  - Surface material: Seawater & Seafloor rock reflect?
    - Hydrothermal experiments
    - Proxy for observations: Cl-salts (surface), H$_2$S (plume)

- Irradiated Surface: Cl-bearing salt oxidized?
  - Surface observation with Subaru
  - Irradiation experiments
    \[\text{On-going program}\]