Metal Sulfides and their Relation to Atmospheric Sulfur on Venus

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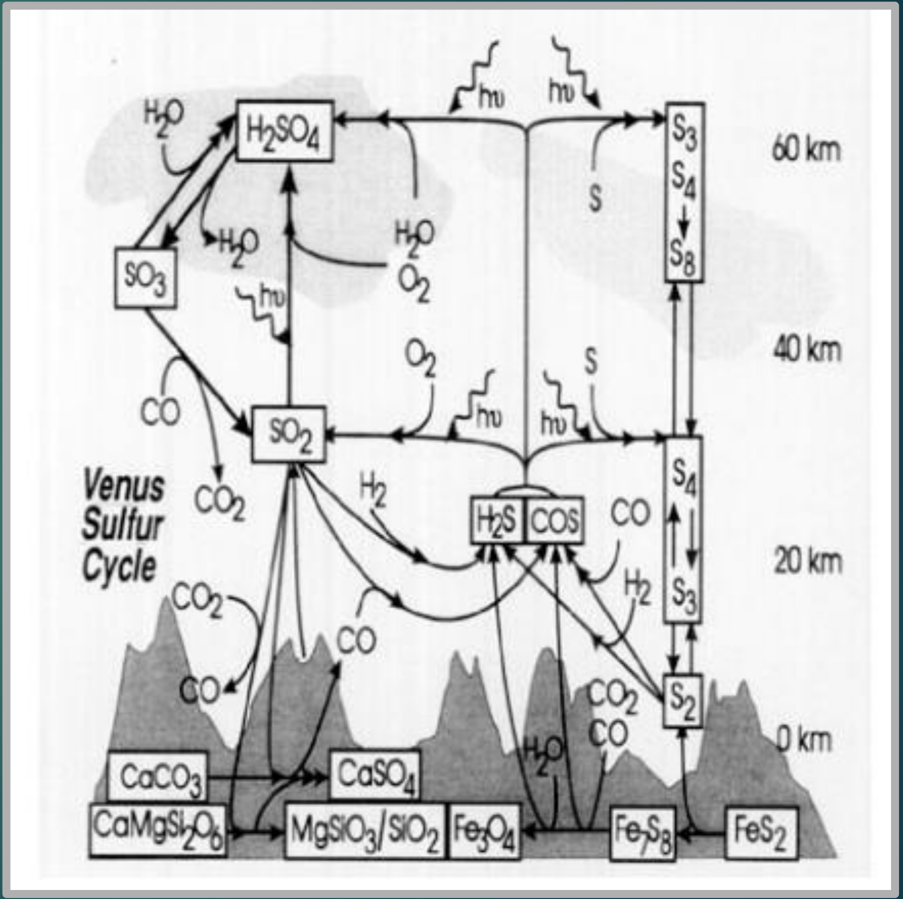
Introduction

- Sulfur is an important constituent in the atmosphere
  - SO_2
  - COS
  - H_2SO_4
- More abundant in atmosphere than on Earth
- Expect a complex Sulfur Cycle on Venus
- Little understanding of the surface composition
- Sources and sinks of sulfur?



Fegley, B., et al. (1995)

Objective

- **Determine possible sources and sinks for sulfur:**
  - **Venusian temperature and pressure**
  - **CO_2, SO_2, and COS**

Mineralogy

- **Galena (PbS)**
  - **SO_2 can be released via the oxidation** Abdel-Rehim, A.M., 2006
  - **Most common lead mineral on Earth** Nowak, P. et al., 2009
  - **On list of metal frost candidates** Schaefer, L., et al., 2004
- **Pyrrhotite (Fe_7S_8)**
  - **Speculated to be one of the most abundant sulfur minerals on Venus** Fegley, B., et al., 1992
  - **Decomposition can release COS** Fegley, B., et al., 1995
  - **On list of metal frost candidates** Fegley, B., et al., 1992
- **Metacinnabar (HgS)**
  - **Stable form of cinnabar at high temperatures** Ballirano, P., et al., 2013
  - **Temperature sensitive** Ballirano, P., et al., 2013
  - **Found near volcanic activity** Rytuba J.J. et al., 1992

Methods

- One gram of each mineral
- Two Scenarios:
  - 1. Oven
    - Lindberg Tube Oven
    - Temperature
      - 460°C (avg. lowland altitude)
      - 425°C (slightly above frost line)
      - 380°C (11 km)
    - Gases
      - CO_2
      - CO_2 100ppm SO_2
      - CO_2 100ppm COS

Methods

- 2. Chamber
  - UArk Cassiopeia Chamber
  - Temperature/Pressure
    - 460°C/95 bar
    - 425°C/75 bar
    - 380°C/45 bar
  - Gases
    - CO_2
    - CO_2 100ppm SO_2
    - CO_2 100ppm COS

- All experiments lasted 24 hours
- All samples were analyzed with the PANalytical X'Pert MRD

Results

- **Pyrrhotite: Untreated (left), 380°C in CO_2, 425°C in CO_2, 460°C in CO_2 (right)**

Pyrrhotite CO_2 Oven v. Chamber

	460°C/1 bar (lowlands)	425°C/1 bar (frost line)	380°C/1 bar (highlands)
Oven	Hematite (Fe_2O_3) Mikasaite ($Fe_2(SO_4)_3$)	Magnetite (Fe_3O_4) Pyrrhotite (Fe_7S_8)	Pyrrhotite (Fe_7S_8) Troilite (FeS)
	460°C/95 bar	425°C/75 bar	380°C/45 bar
Chamber	Pyrrhotite Troilite	-----	Pyrrhotite Troilite

Pyrrhotite SO_2 v. COS (Oven)

	460°C/1 bar (lowlands)	425°C/1 bar (frost line)	380°C/1 bar (highlands)
CO_2/SO_2	Pyrrhotite Troilite Hematite	----	Pyrite (FeS_2) Pyrrhotite Hematite Troilite Magnetite
	460°C/1 bar	425°C/1 bar	380°C/1 bar
CO_2/COS	Hematite Mikasaite	Hematite Maghemite Mikasaite	Pyrrhotite Pyrite Hematite

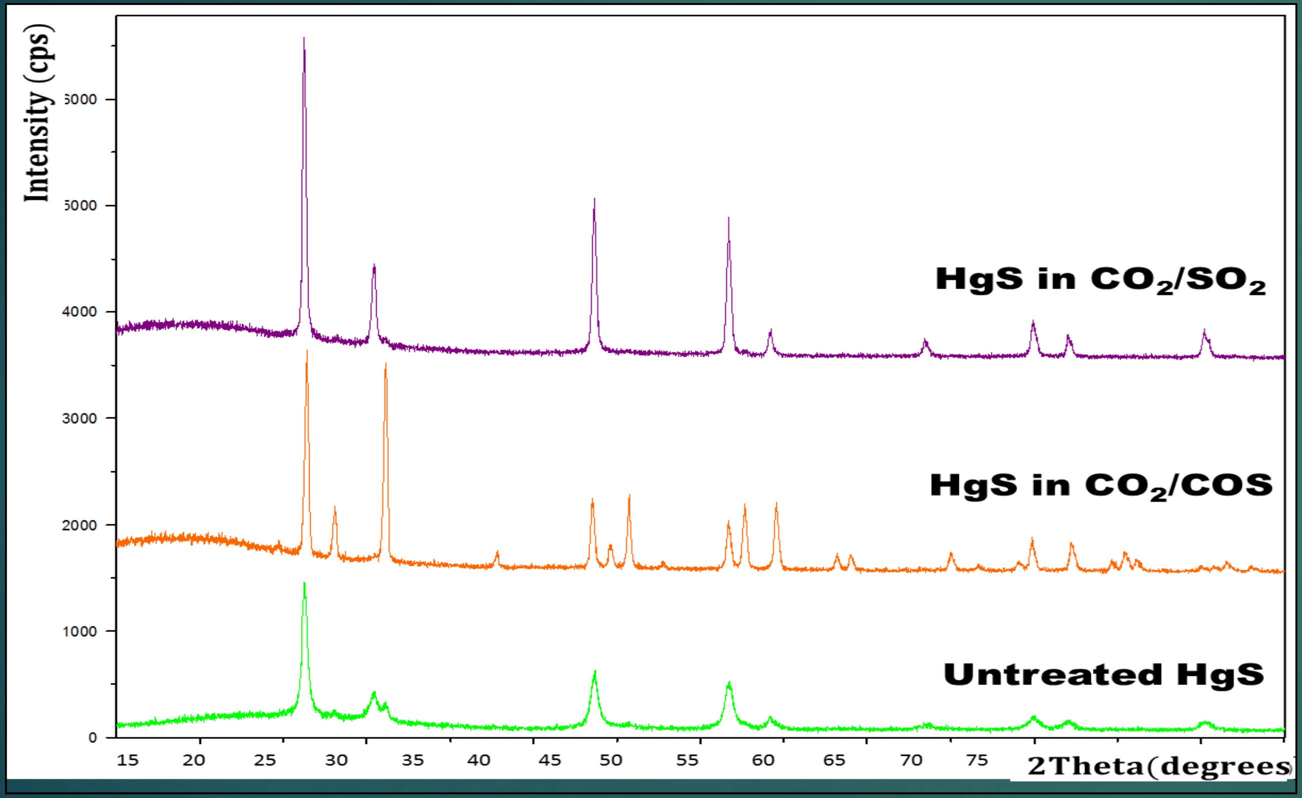
Galena CO_2 Oven v. Chamber

	460°C/1 bar (lowlands)	425°C/1 bar (frost line)	380°C/1 bar (highlands)
Oven	**Galena (PbS)** **Anglesite ($Pb(SO_4)$)** **Lanarkite ($Pb_2(SO_4)O$)**	**Galena (PbS)** **Anglesite ($Pb(SO_4)$)** **Lanarkite ($Pb_2(SO_4)O$)**	**Galena (PbS)** **Anglesite ($Pb(SO_4)$)**
	460°C/95 bar	425°C/75 bar	380°C/45 bar
Chamber	**Galena**	**------**	**Galena** **PbO (Litharge)**

Galena SO_2 v. COS (Oven)

	460°C/1 bar (lowlands)	425°C/1 bar (frost line)	380°C/1 bar (highlands)
CO_2/SO_2	Galena Anglesite Lanarkite	Galena Anglesite	Galena Anglesite
	460°C/1 bar	425°C/1 bar	380°C/1 bar
CO_2/COS	Galena Anglesite	Galena Anglesite	Galena Anglesite

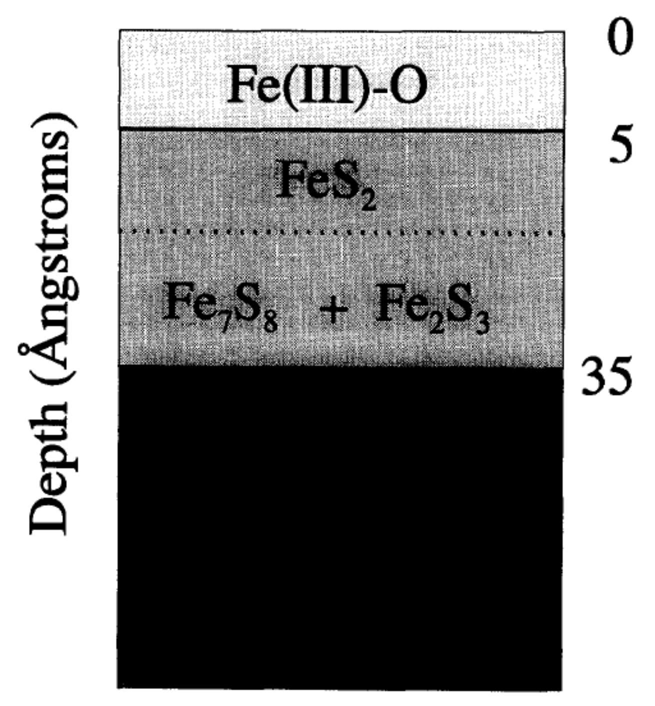
Metacinnabar



	380°C/1 bar (highlands)
CO_2/SO_2	Metacinnabar
	380°C/1 bar
CO_2/COS	Cinnabar

Pyrrhotite

- **Pyrrhotite → Magnetite → Maghemite → Hematite**
  Fegley, B., et al., 1995
- **Troilite: Vaporization of S increases the ratio of Fe to S**
- **Quicker oxidization in mixed gas experiments**
- **Pyrite formation in the low temperature, mixed gas experiments**
  - **Product of oxidation**
- **$3Fe_7S_8 + 28CO_2 \leftrightarrow 7Fe_3O_4 + 12S_2 + 28CO$**
  $S_2(g) + 2CO(g) \leftrightarrow 2COS(g)$ Fegley, B., et al., 1995
- **Unable to verify**



Mycroft, J. R., et al. (1994)

Galena

- Formation of Anglesite:
  - $3PbS + 5O_2 \rightarrow 2PbO + PbSO_4 + 2SO_2$
  - $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$
    $2PbO + 2SO_2 + O_2 \rightarrow 2PbSO_4$
- Formation of Lanarkite:
  - $PbS + 7PbSO_4 \rightarrow 4(PbSO_4 \cdot PbO) + 4SO_2$
- Formation of Lead Oxide (Litharge):
  - $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$
- SO_2 produced in all equations
- Currently unable to verify

Metacinnbar

- **Instability in all CO_2 experiments in the oven**
- **Cinnabar is a low T/P version of metacinnabar**
- **Heating and cooling of metacinnabar can form cinnabar**
  Ballirano, P., et al., 2013
- **Stability in CO_2 in the chamber at lowland and highland conditions**

Future Work

- **Gas Chromatograph**
- **Gas Mixture Experiments in the Chamber**
- **In situ Studies with RAMAN**
- **Longer Experiments (48-72h)**

Conclusion

- Pyrrhotite
  - Unstable in oven
  - Stable in chamber
  - More rapid oxidation in mixed gases

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- Galena
  - Minor instability in oven
  - Better stability in chamber
  - Mixed gases had no effect

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- Metacinnabar
  - Unstable in high temperatures in oven
  - May show better stability in chamber

Conclusion

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  - More rapid oxidation in mixed gases
- Galena
  - Minor instability in oven
  - Better stability in chamber
  - Mixed gases had no effect
- Metacinnabar
  - Unstable in high temperatures in oven
  - May show better stability in chamber
- Mixed gas experiments need to be completed in the chamber
- Currently cannot determine what gases are released during reactions
  - Source/Sink?