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Primordial Sulfur and the Origin of Life

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Why Study Sulfur

- Roles in biology:
  - It forms part of two essential amino acids: cysteine and methionine
  - It plays a key role in the central metabolism of cells
  - It can act as a bioenzyme
  - Some bacteria rely on it as an energy source
- Life as we know it would not be possible without sulfur's presence in the primordial soup
  - Carbonaceous chondrites may have made a contribution to the reservoir of prebiotic molecules available on the Earth at the time of life's origin
- Proof that the cosmos have delivered exogenous organic material (including S-bearing molecules) to the Earth is provided by the content of carbonaceous chondrites

Goals for Study

- An understanding of the thermal history of the parent body
  - Chemical evolution of the sulfur-bearing species in the meteorite (i.e. have any aqueous oxidation reactions taken place)
  - How prebiotic molecules were synthesized within the parent body
- The fractionation and distribution of sulfur among the primitive bodies in the early solar system
  - How the nature, isotopic signatures, abundances, and distributions of the organic species in meteorites impose bounds on the solar system's formation and evolution (i.e. positive isotope ratios indicate a nebular origin)
- If there are reasonable differences in the S isotope ratio numbers for different classes of carbonaceous chondrites

Carbonaceous Chondrites

- Minimal amounts of heating, melting, and planetary formation → primitive meteorites
- High bulk S content
  - S^0, organic sulfur, sulfates, and sulfides

Murchison

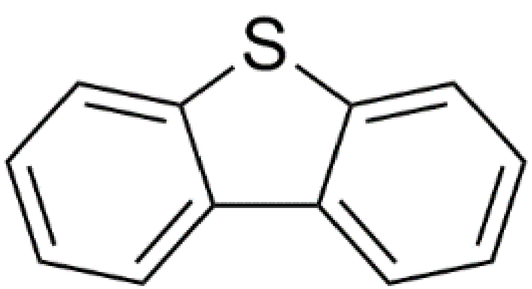
NWA 1180

Sulfur Species

SO_4^{2-} — S^0 — S^{2-}

Most oxidized ⟷ Most Reduced

- Organic sulfur compounds: dibenzothiophene, thiophene, methionine, and cysteine



Dibenzothiophene

S_8

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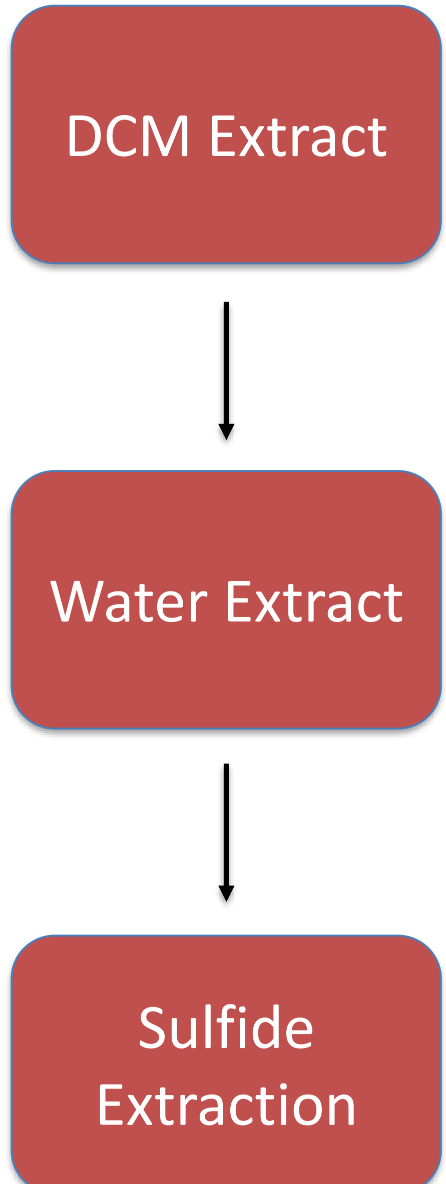

Labidi et al., 2017

Simulant

Species	SO_4^{2-}	S_8	Dibenzothiophene	Thiophene	S^{-2}
Concentration (ppm)	718	1402	300	3705	87

- Water-soluble: SO_4^{2-}
- DCM-soluble: S_8, dibenzothiophene, thiophene
- FeS is not soluble in water or DCM

Montmorillonite Simulant

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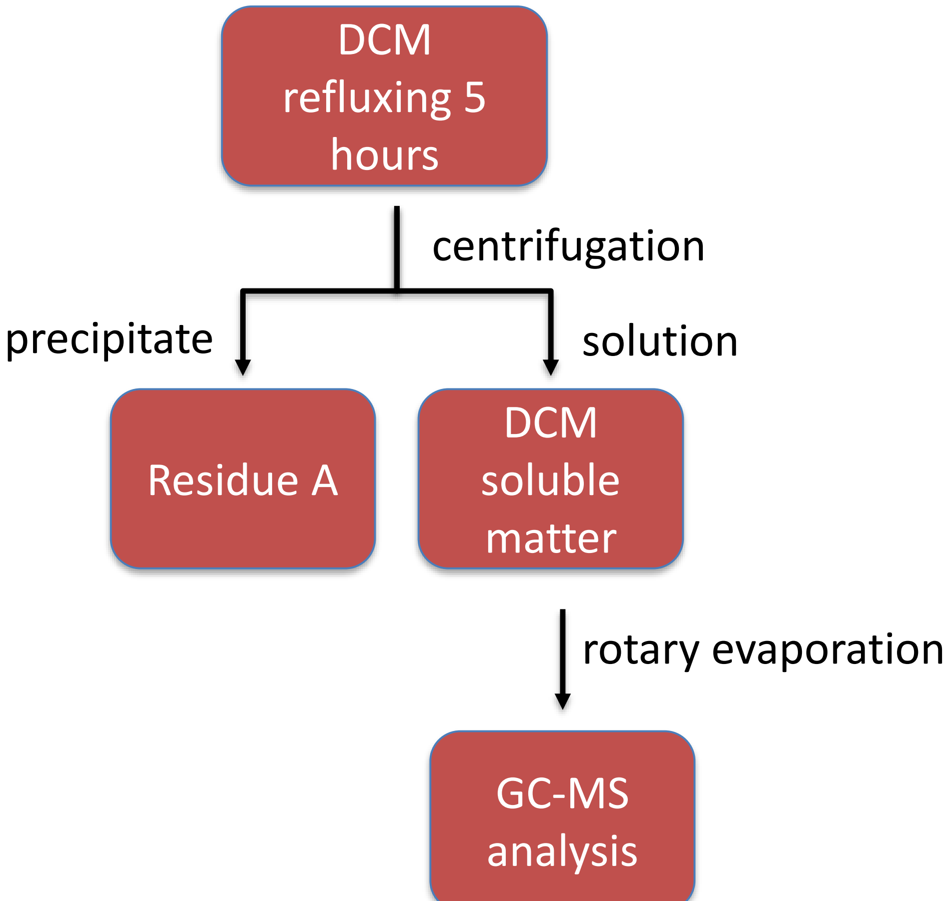
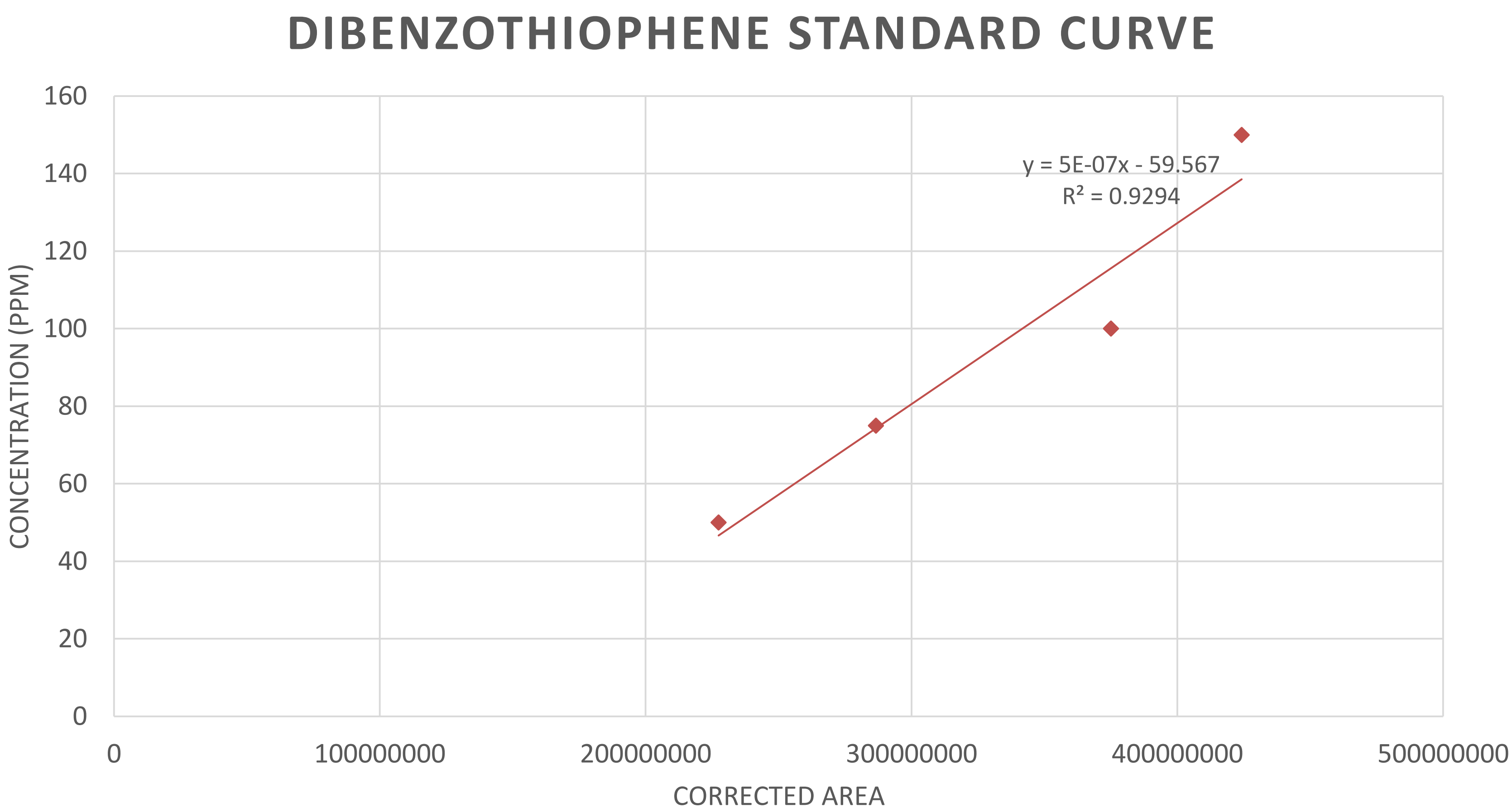
DCM Extract

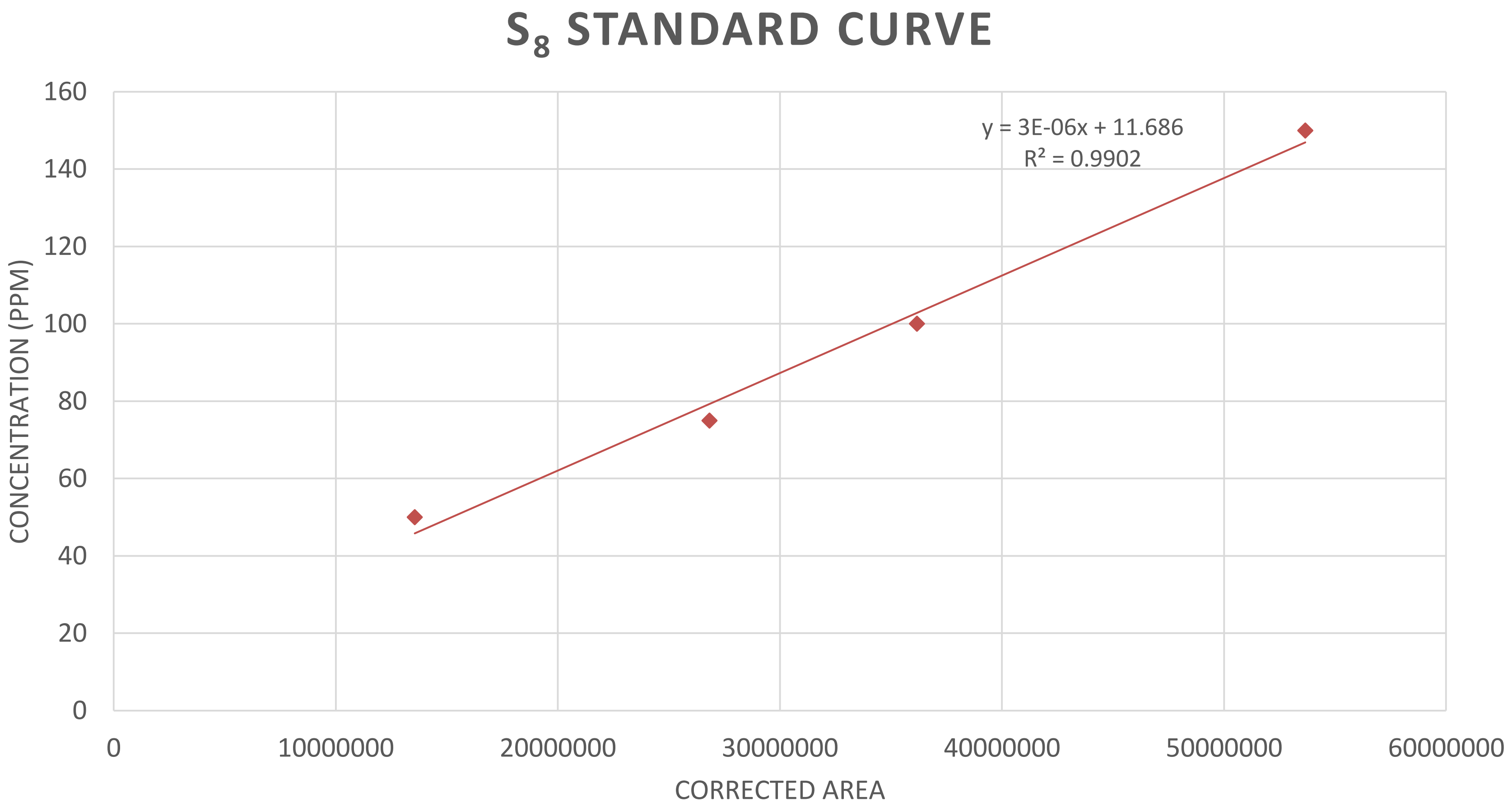


Simulant refluxing in DCM

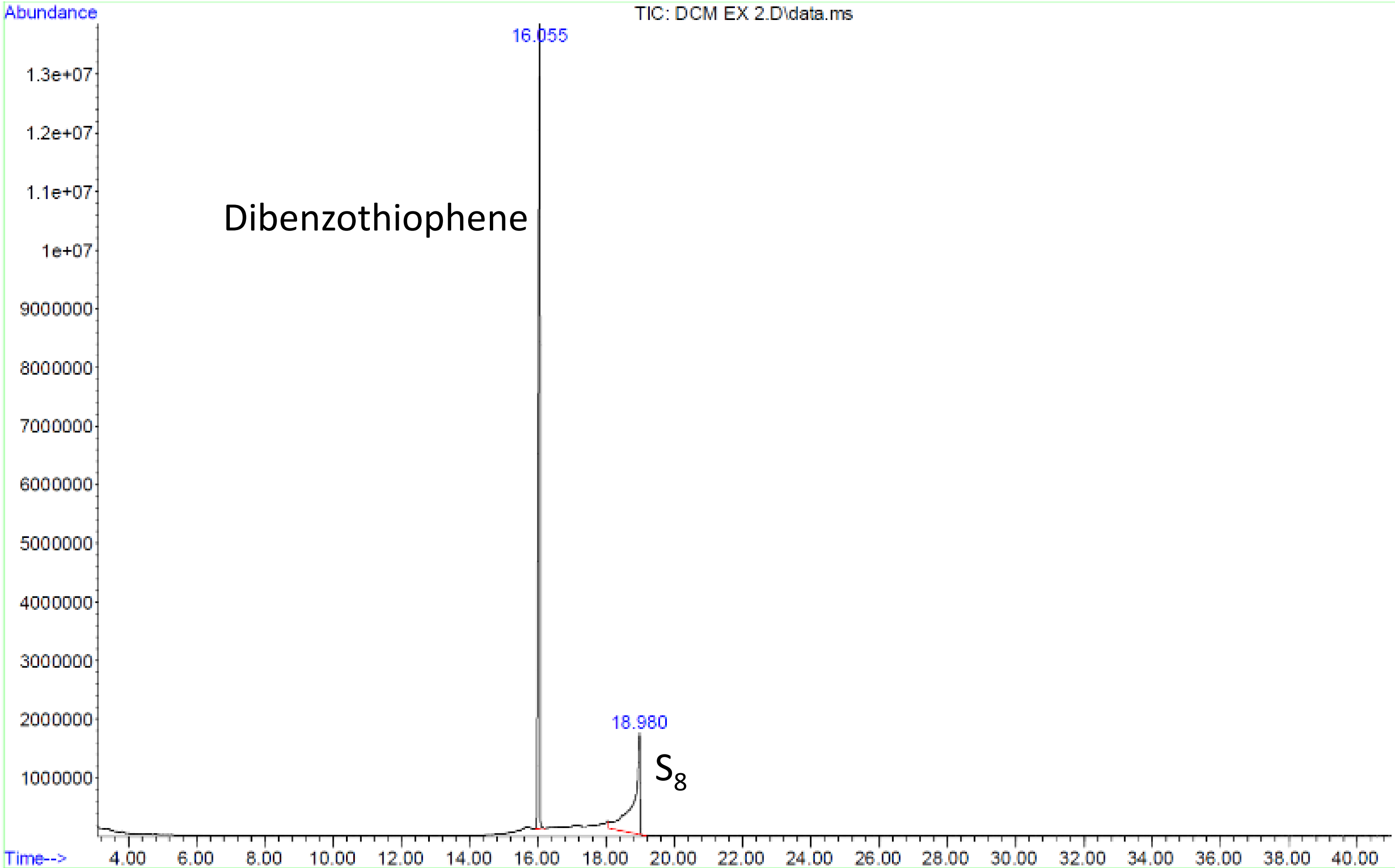
Standard Curves



Standard Curves



DCM Extract: GC-MS



DCM Extract: Results

Sample Calculation: Dibenzothiophene

Extract:

Average corrected area = 434925014.5

Concentration (ppm) = 157.9 ppm (from standard curve)

$1 \text{ ppm} = \frac{1\ \mu g}{1\ mL}$ $\quad$ $157.9 \text{ ppm} = \frac{x\ \mu g}{2.5\ mL}$ $\quad$ $x = 394.74\ \mu g$

Theoretical:

$1 \text{ ppm} = \frac{1\ \mu g}{1\ g}$ $\quad$ $300 \text{ ppm} = \frac{x\ \mu g}{2.86\ g}$ $\quad$ $x = 858\ \mu g$

Percent Yield:

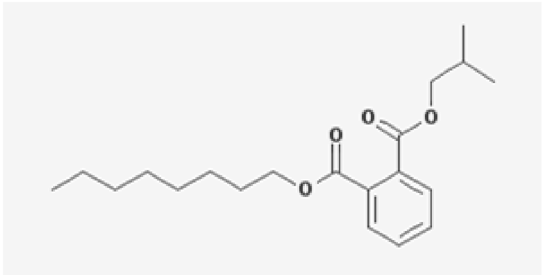
$$\frac{394.75 \mu g}{858\ \mu g} \bullet 100\% = \boxed{46.00\%}$$

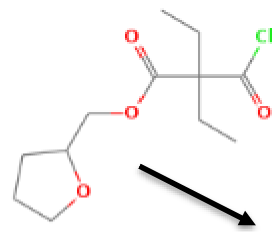
S_8 percent yield: $\boxed{45.12\%}$

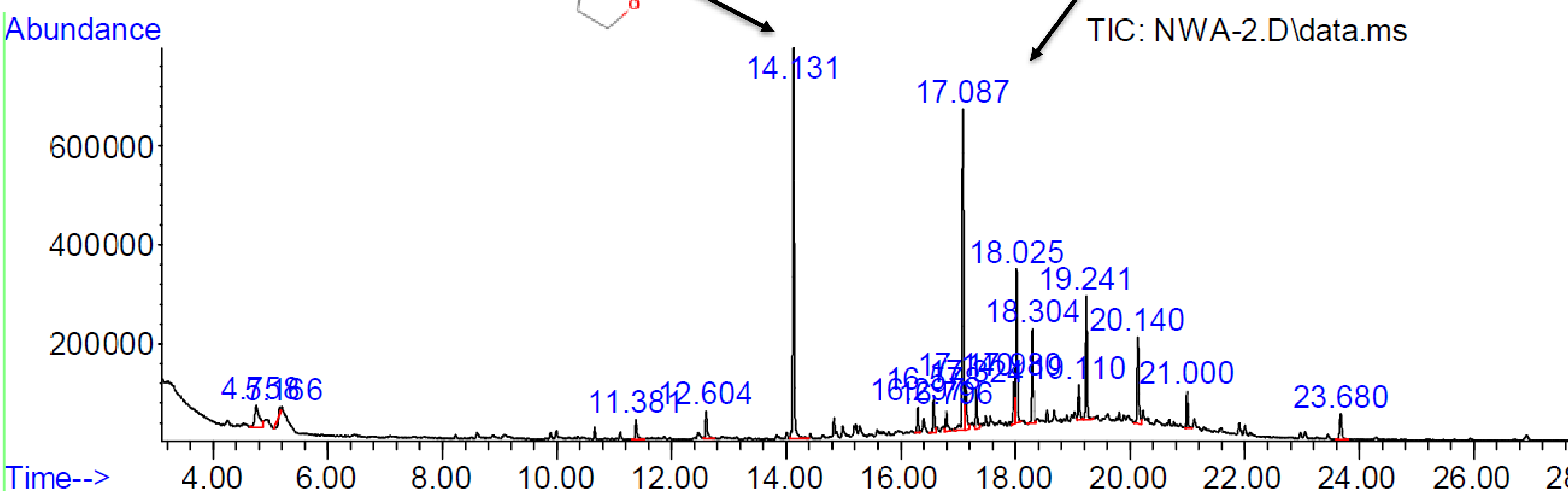
DCM Extract: NWA 1180

- S oxidized to sulfate in desert

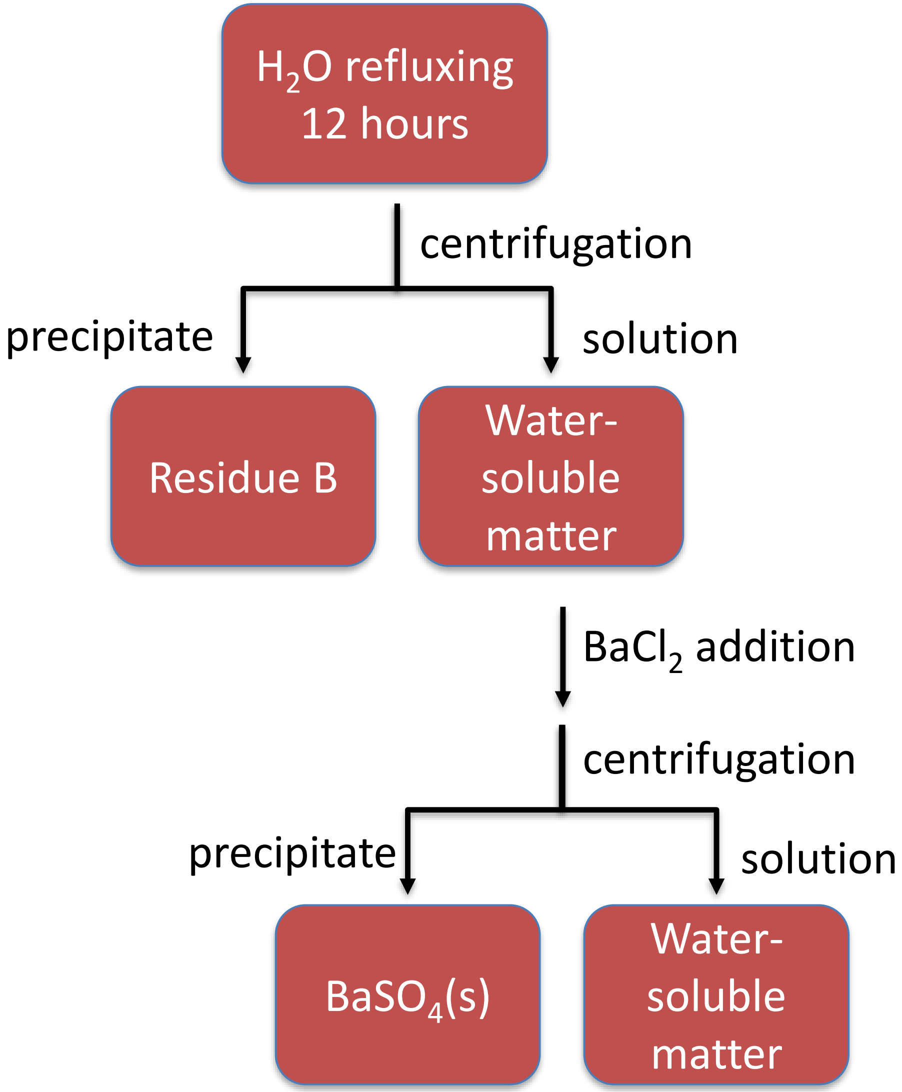
DCM blank

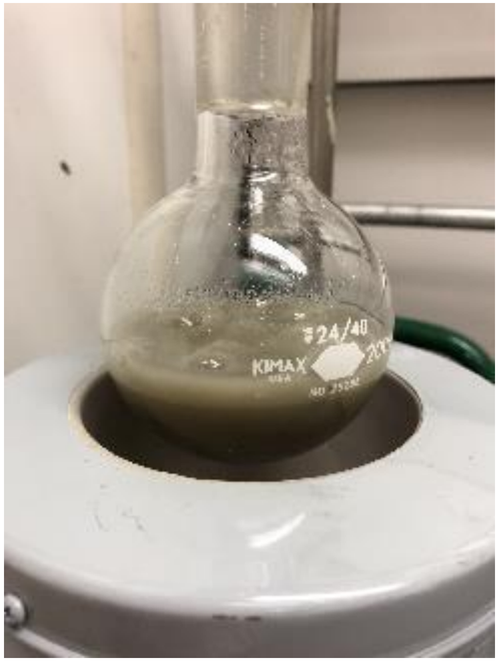






Water Extract





Simulant refluxing in H_2O

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

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Water Extract: Results

Sample Calculation: Extraction 1

Theoretical:

$$1\ \text{ppm} = \frac{1\ \mu\text{g}}{1\ \text{g}} \quad 718\ \text{ppm} = \frac{x\ \mu\text{g}}{4.51\ \text{g}} \quad x = 0.00324\ \text{g}$$

Percent Yield:

$$\frac{0.00288\ \text{g}}{0.00324\ \text{g}} \bullet 100\% = 86.42\%$$

Extraction 2 percent yield: 2829.35%

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Water Extract: NWA 1180

- Mass of sulfate recovered: 0.02519 g
- Calculated sulfate concentration in NWA 1180: 4646 ppm

NWA 1180 refluxing in H_2O

$BaSO_4$(s) in solution

$BaSO_4$(s) after centrifugation and drying

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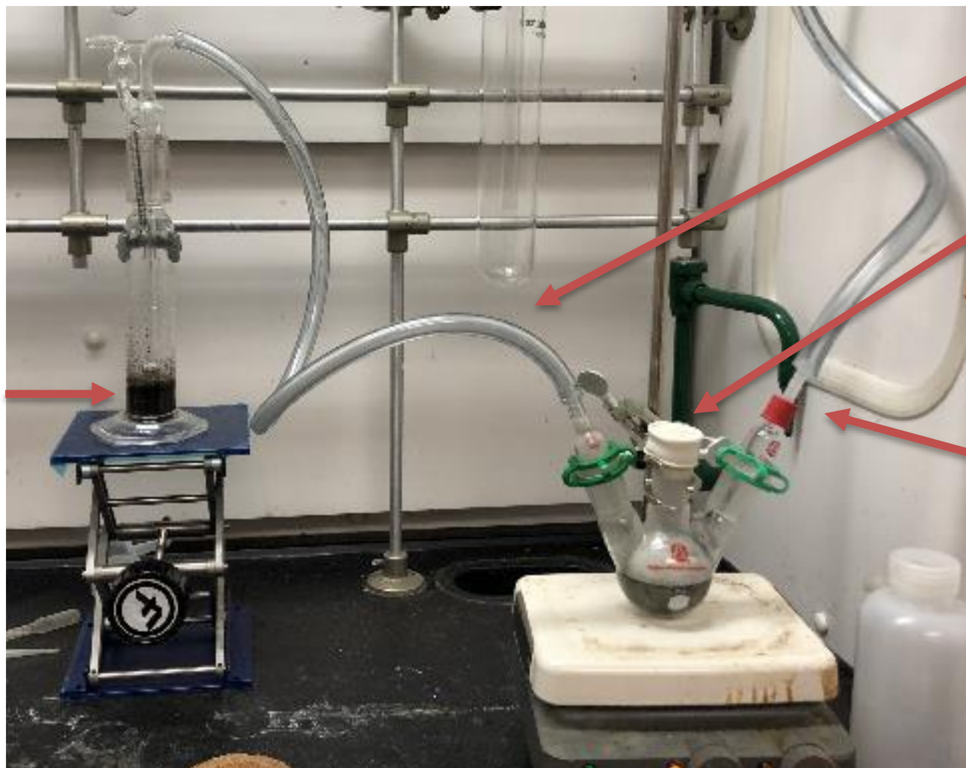
Sulfide Extraction

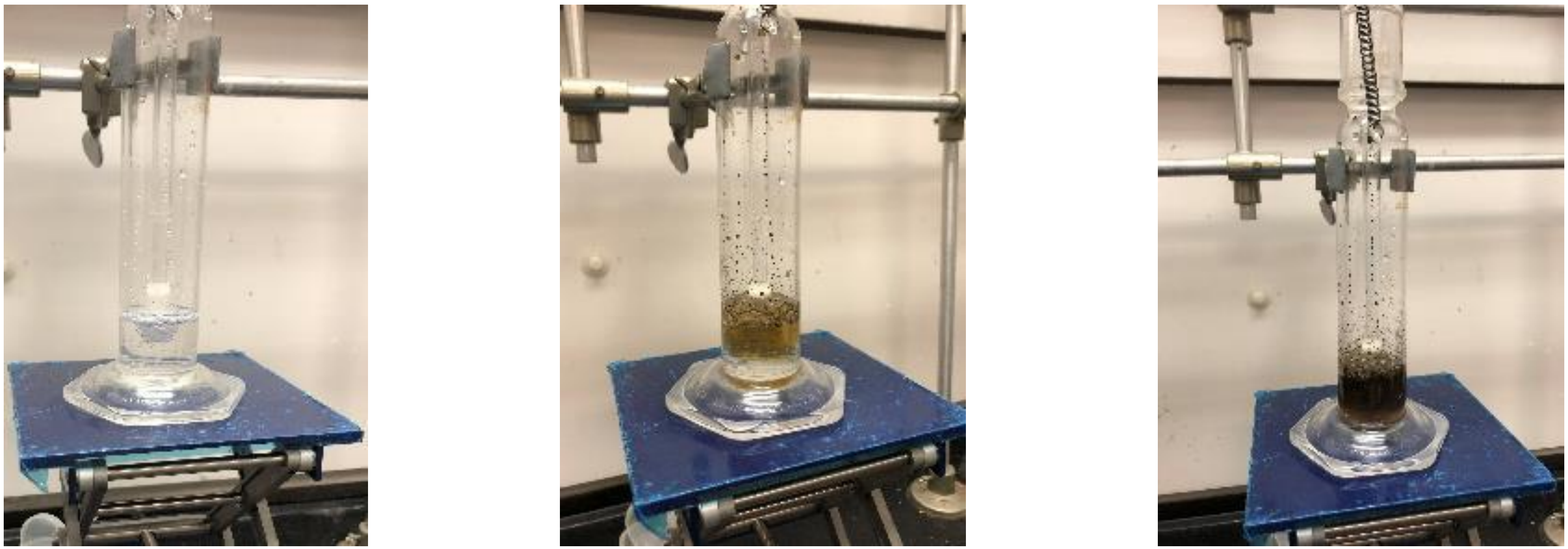
$$S^{2-}(aq) + 2\ H^{+}(aq) \rightarrow H_2S(g)$$

$$H_2S(g) + 2\ Ag^{+}(aq) \rightarrow Ag_2S(s) + 2\ H^{+}(aq)$$



Sulfide extraction apparatus

Sulfide Extraction: Results



Time

Accumulation of $Ag_2S(s)$ in $AgNO_3(aq)$ solution

Future

- Extract sulfur from the remaining meteorites in the MacEwan Collection
  - Isotope ratio determination (Dr. James Farquhar from the University of Maryland)
- Apply techniques to extract sulfur from the Tagish Lake meteorite at the University of Alberta

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