CHONS Isotopes in the Search for Extraterrestrial Life

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Outline

- Background
- Case study: Sulfate-reducing microbes
- Case study: Identifying abiotic methane on Earth
- Up and coming measurements
- Analytical tools and techniques
- Recommendations for the next decade

Background

$$\delta^{13}\mathrm{C} = \left(\frac{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{\mathrm{sample}}}{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{\mathrm{standard}}} - 1 \right) \times 1000\ ‰$$

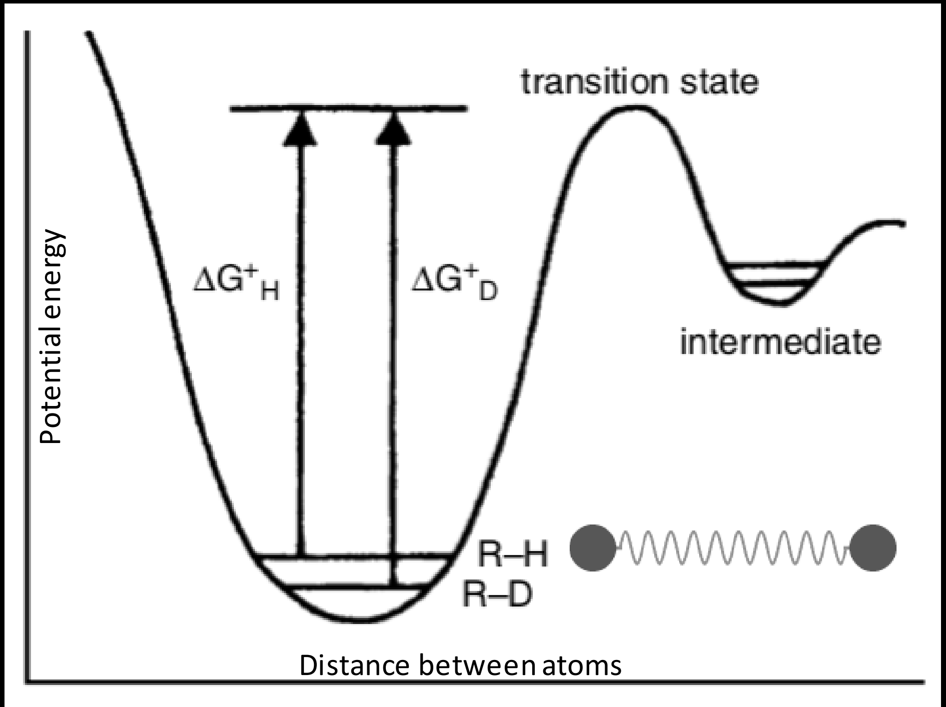


Image: Khalfina+Vlasov, 2011; Chemistry LibreTexts

- Light isotopes form bonds that are less stable
  - More reactive, easier to break bonds
- Basis of the kinetic isotope effect
- Isotopic deviations within the solar system are small but measurable
  - Use of delta notation

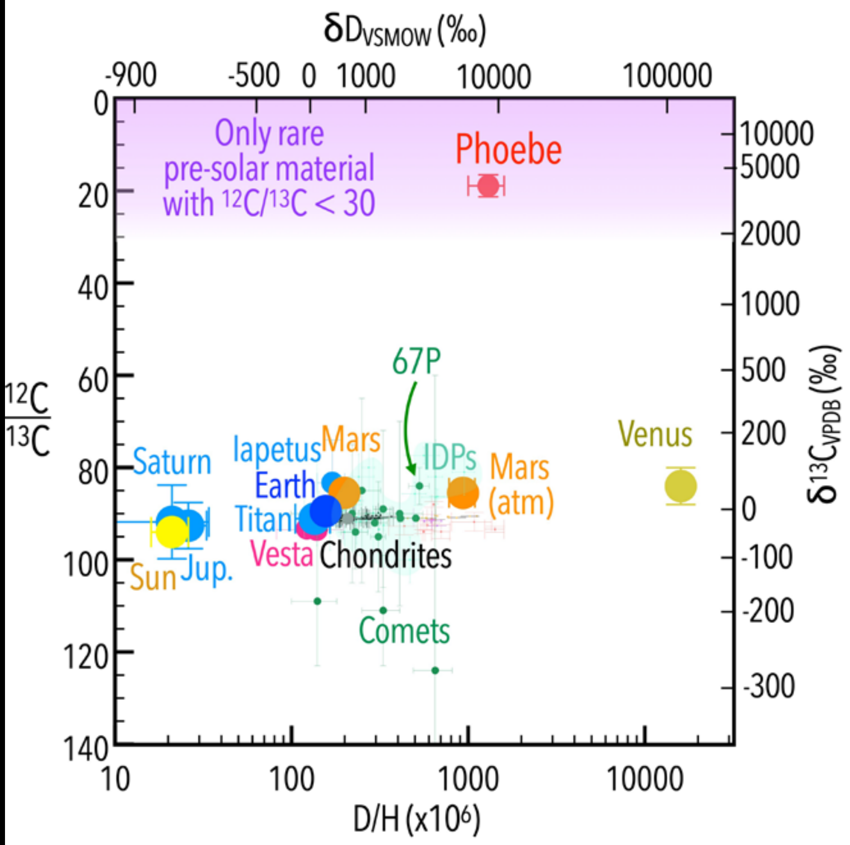
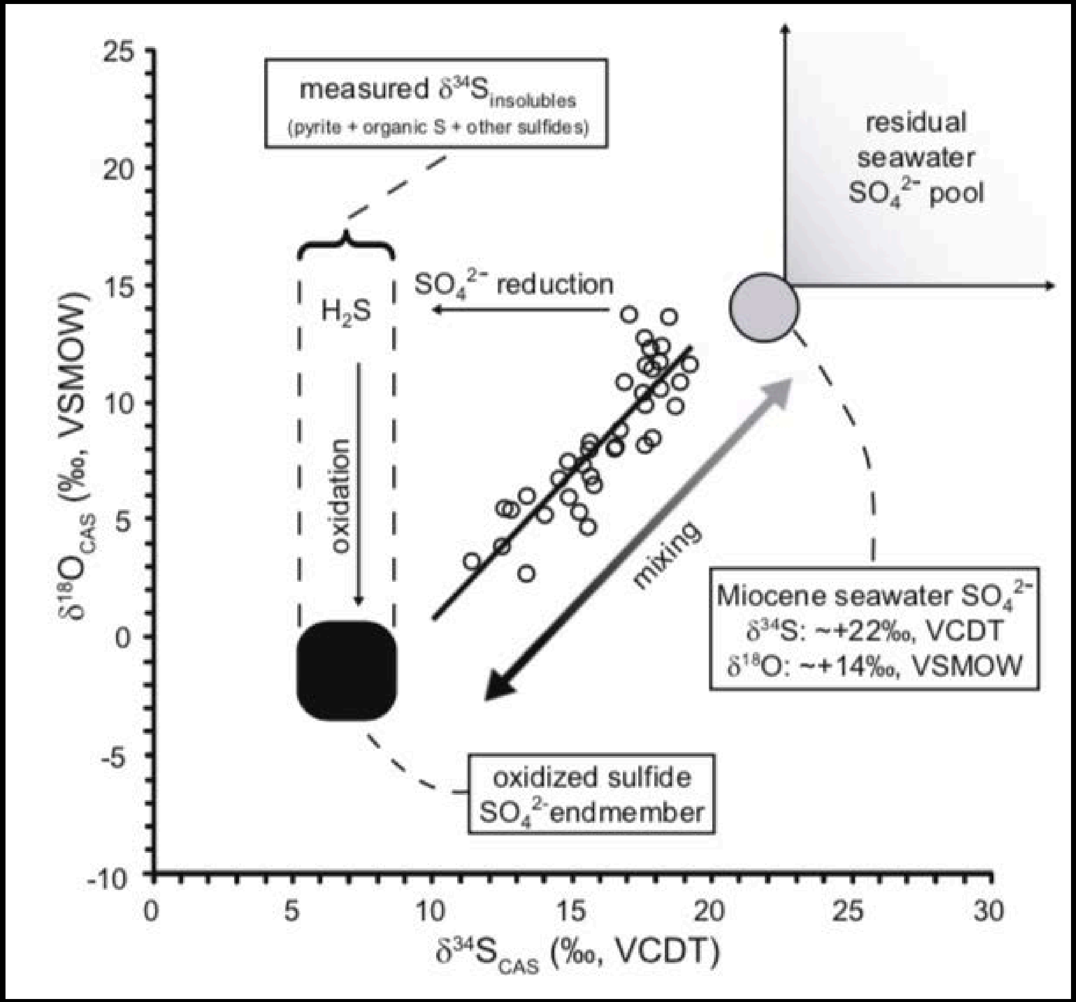


Image: adapted from Neveu+, 2020

Isotopic records of a microbial ecosystem

- Theiling+Coleman, 2019
- Sulfate reducing microbes preferentially consume $^{32}SO_4^{2-}$, yielding enriched $\delta^{34}S_{sulfate}$ and depleted $\delta^{34}S_{H2S}$
- Sulfide oxidizing bacteria preferentially produce $^{32}S[^{16}O]_4^{2-}$
- Data points reflect mixing between different redox environments



See also: Reeves+Fiebig, 2020

Evolution in Identification of Terrestrial Abiotic Hydrocarbons

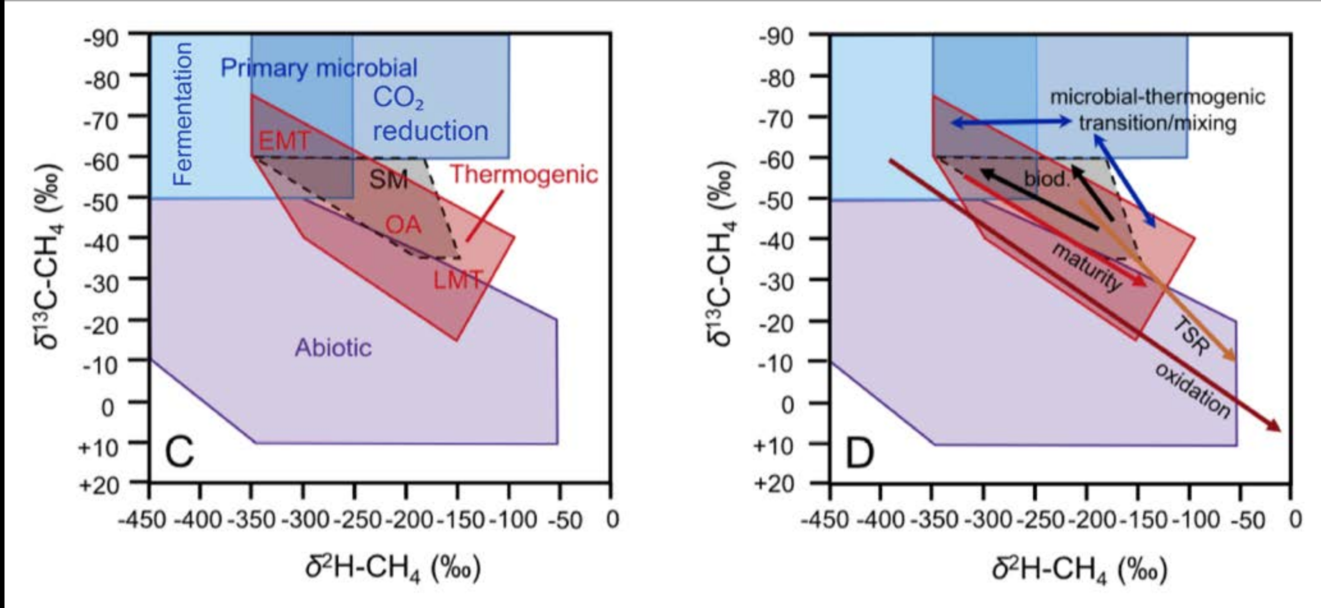
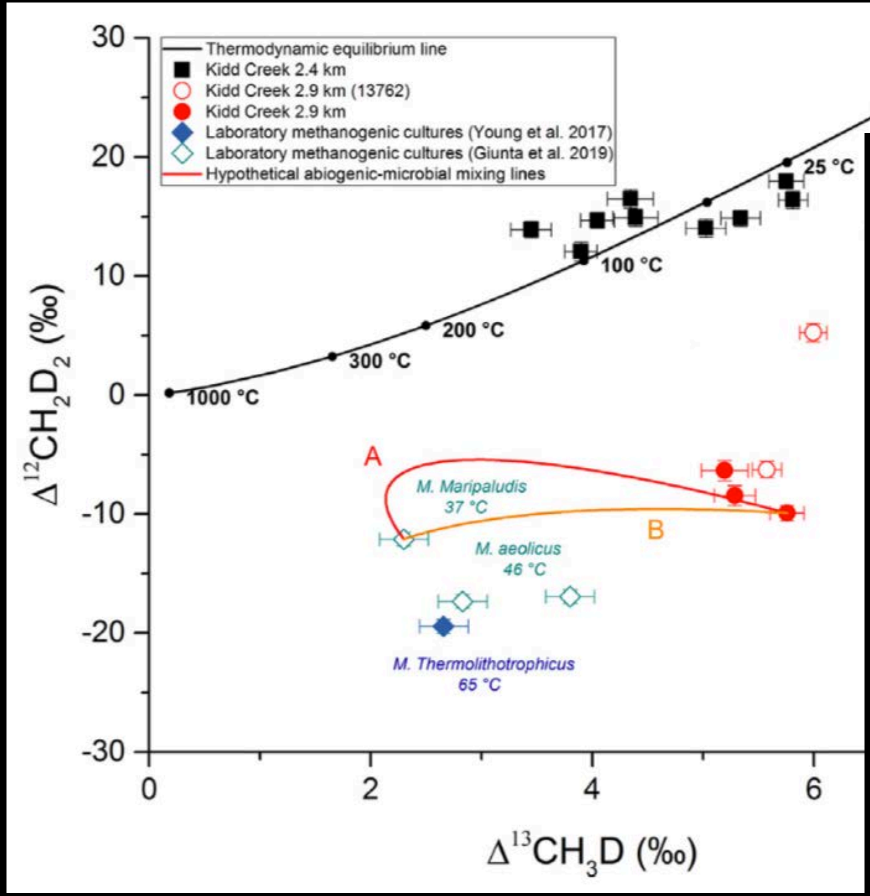


Image: Milkov+Etiope, 2018

Image: Warr+, 2021



- Empirical definition of abiotic δ^{13}C and δD isotopic fields for terrestrial methane (Milkov+Etiope, 2018)
- Isotopic trends in carbon chain length match between abiotic Murchison meteorite and Kidd Creek – a terrestrial abiotic reservoir? (Sherwood Lollar+, 2002)
- "Clumped isotopes" have more than one rare isotope (e.g. $^{13}CH_3D$ and CH_2D_2) and are commonly used for thermometry (e.g. Guo+Eiler, 2007). Clumped methane at Kidd Creek suggests mixing of biotic and abiotic sources (Warr+, 2021).

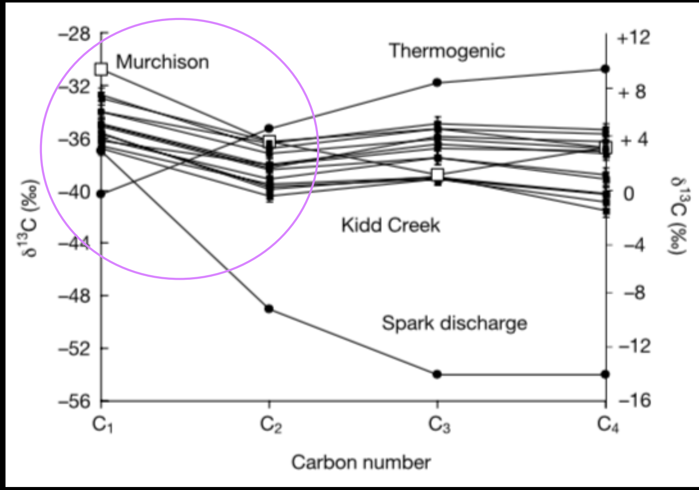


Image: Sherwood Lollar+, 2002

Position-Specific Isotopic Ratios

^{12}C-^{12}C-^{13}C
Vs.
^{12}C-^{13}C-^{12}C

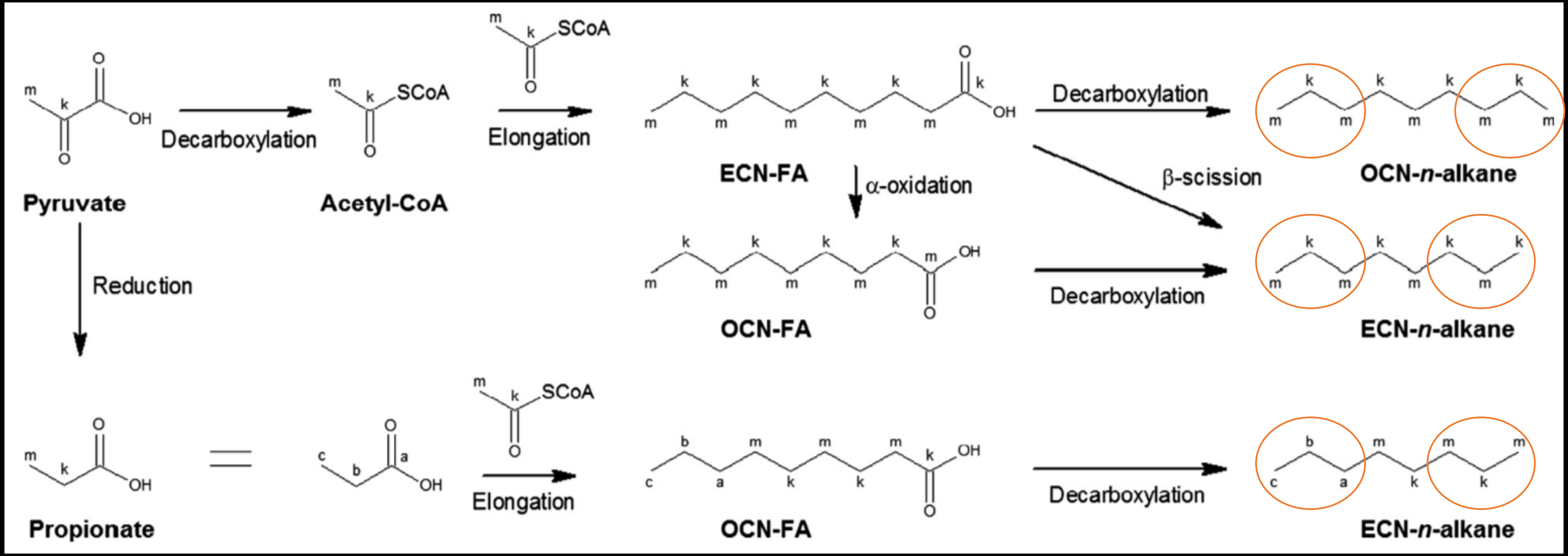


Image: Gilbert+, 2013

Analytical Tools and Techniques

Direct Sampling

- **Requires ingestion of sample - destructive, places limitation on location**
- **Tend to have higher specificity, lower uncertainties**
- **Examples of applications: isotopic ratios of carbonates or organics from Martian sediments**

- Mass spectrometry
- Tunable laser spectroscopy
- Millimeter spectroscopy

Spatial Heterodyne Spectrometer

- Example of application: measurement of Martian atmospheric constituents from lander

Remote Sensing

- **Greater flexibility in spatial relationship to target**
- **Non-destructive**
- **Typically greater uncertainties**
- **Examples of applications: isotopic ratios of Martian atmospheric constituents from orbiter**

- Millimeter/submillimeter limb sounding
- UV spectroscopy

Earth based observatories

- Example of application: Time-sensitive campaigns for observation of Martian atmospheric constituents

Ground Based

Laboratory analytical techniques:

- **Requires sample return**
- **Easier to implement sample work up and analysis**
- **Greater precision and accuracy**

Summary

- CHONS isotopic analyses are key tools for biogeochemistry and the search for biosignatures
  - Demonstrated value in terrestrial applications
  - Geochemical context is critical to interpretation
- Up and coming techniques like clumped isotopes and position-specific isotopic analyses will continue to advance the gold standard
- Several strong analytical techniques mature and/or developing; best technique depends on the specific problem being solved

Recommendations for Investment

- Sample preparation, separation, and introduction technologies for direct sampling and returned sample analyses
- Mitigation and reduction of contamination, including low-outgassing materials, maintaining spacecraft cleanliness through launch, and lessons learned from current and past missions;
- Curational and calibration facilities
- Laboratory and modeling studies to develop frameworks for the interpretation of mission data

Thanks to the CHONS Isotopes White Paper Team!

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