Abiogenic hydrocarbons produced under upper mantle conditions

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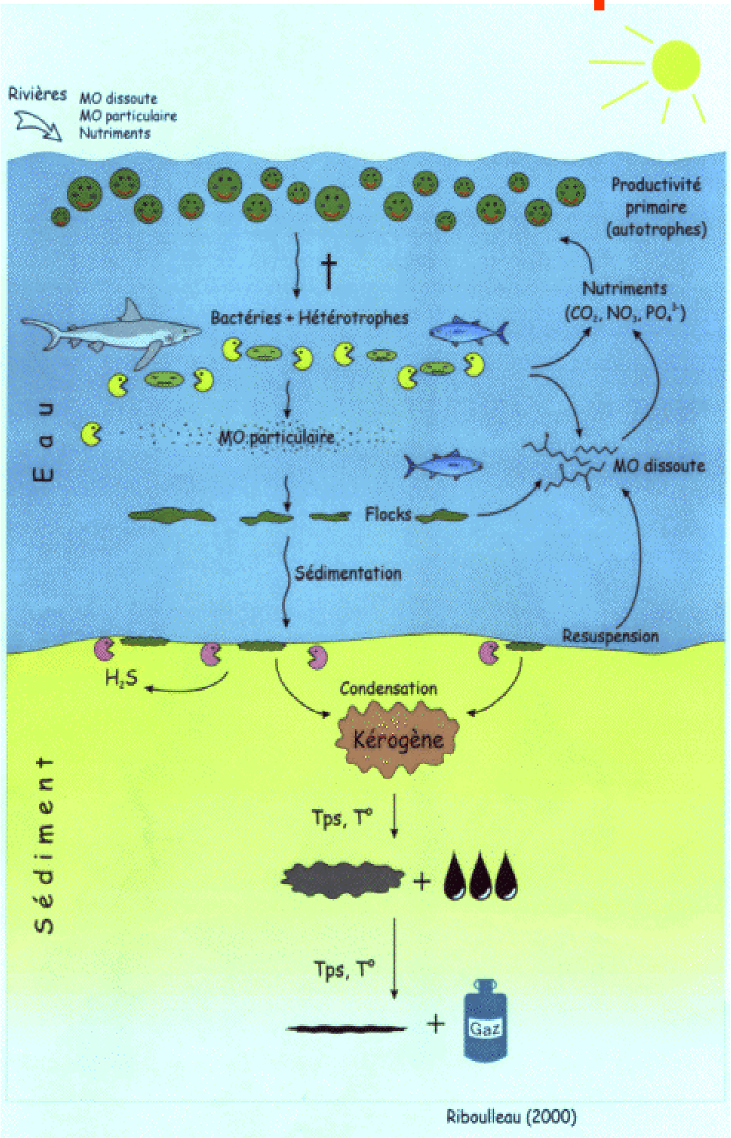
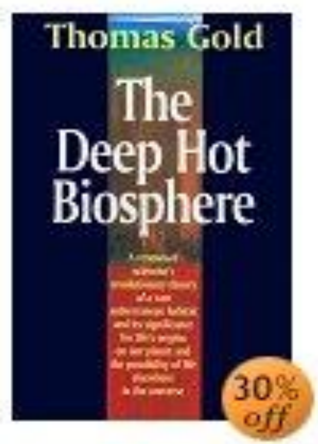
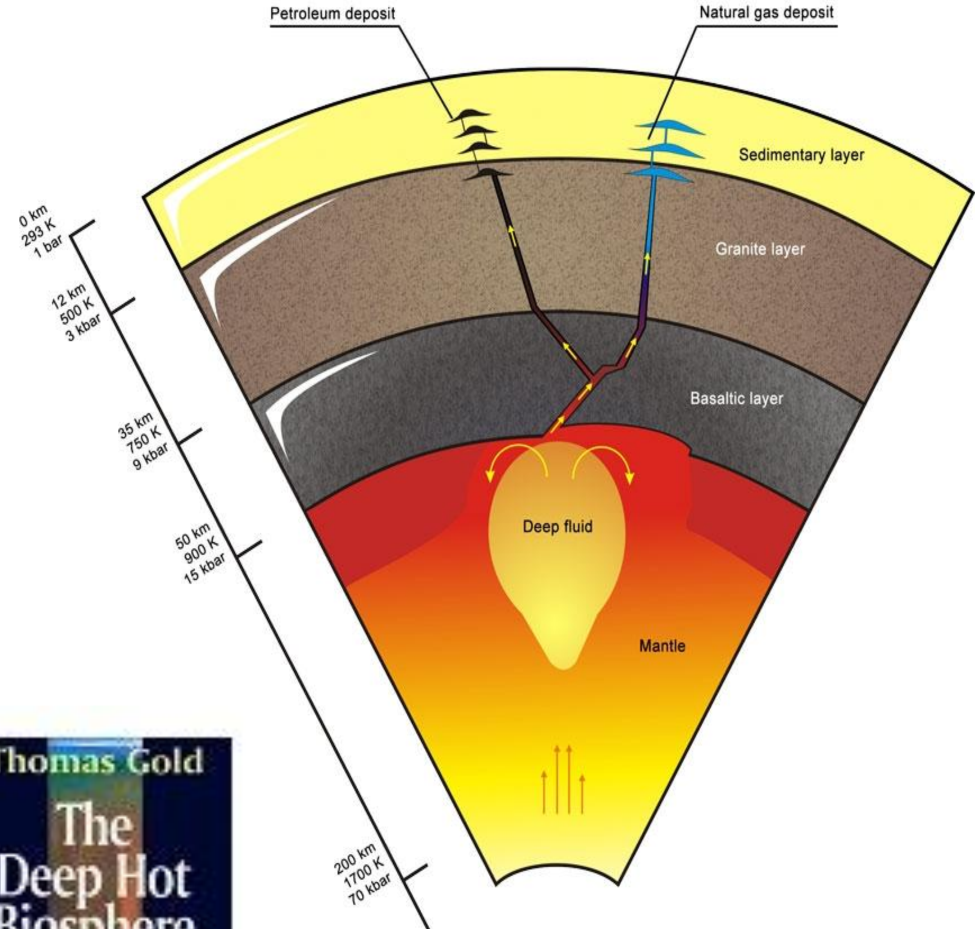
Deep abiotic organics



Oil Company View





Russian-Ukrainian School

Synthesis of hydrocarbons

$$nCaCO_3 + (9n+3)FeO + (2n+1)H_2O \rightarrow nCa(OH)_2 + (3n+1)Fe_3O_4 + C_nH_{2n+2}$$

Kenney, Kutcherov et al. (2002), KONAK chamber
3-5 GPa, 1200-1500K

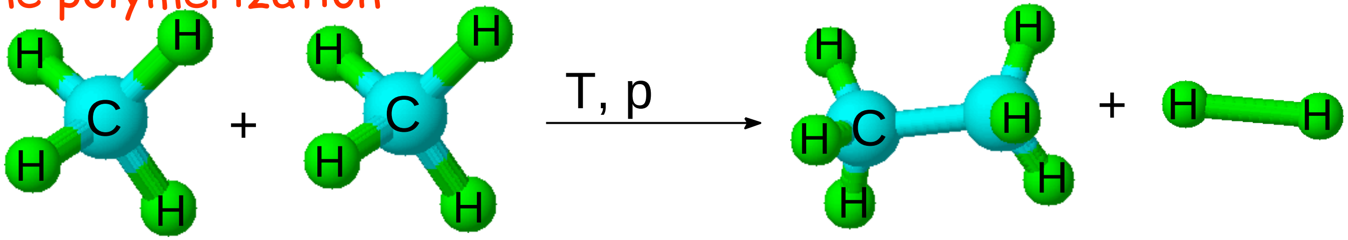
$$CaCO_3 + 12FeO + H_2O \rightarrow CaO + 4Fe_3O_4 + CH_4$$

Scott et al. (2004), DAC, 5-11 GPa, 773-1773K

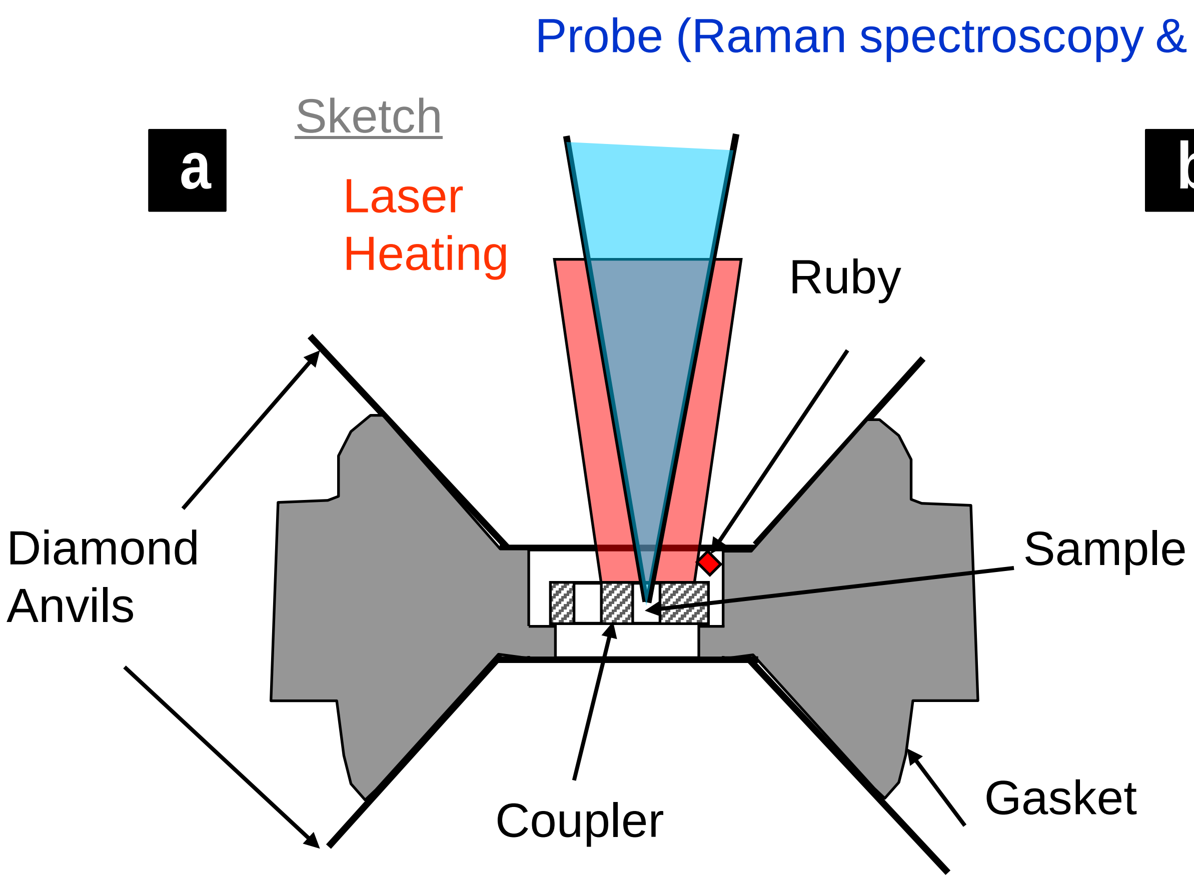
Is this viable for:

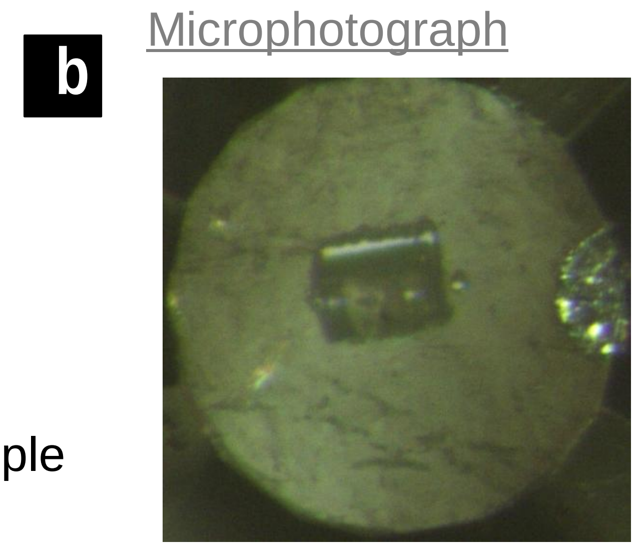
- **Realistic Earth's minerals?**
- **Heavier hydrocarbons synthesis?**
- **Oxidizing conditions?**

Methane polymerization



Laser heating in the diamond anvil cell





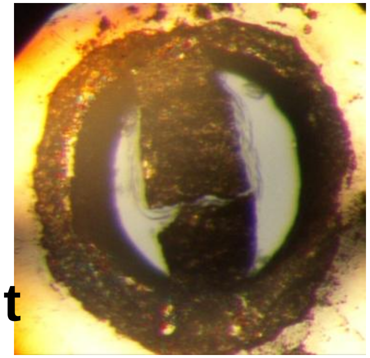
Methane in Re gasket
with Ir coupler

- ✓ *In situ* measurements at high temperature
- ✓ Mapping of quenched samples

Sample preparations: minerals

- Fayalite ($Fe_{1.92}Mn_{0.08}SiO_4$): Rockport
- Olivine ($Mg_{1.8}Fe_{0.2}SiO_4$): San Carlos
- Mineral Assemblages: Peridodite & Basalt

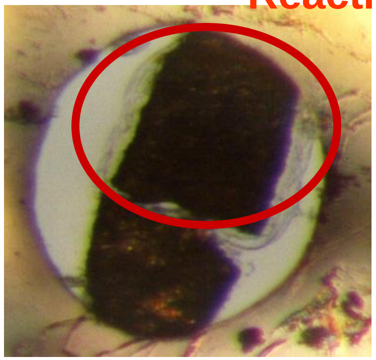
Before:



Carbonate in 1:8 molar ratio ground and mixed in diamonite mortar/pestle

- Ir coupler or compacted powder
- Loaded with H_2O
- Adequate care with all aspects of cleaning

After:



Methanogenesis from minerals

☑ **Fayalite ($Fe_{1.92}Mn_{0.08}SiO_4$): Rockport**

❑ **Olivine ($Mg_{1.8}Fe_{0.2}SiO_4$): San Carlos**

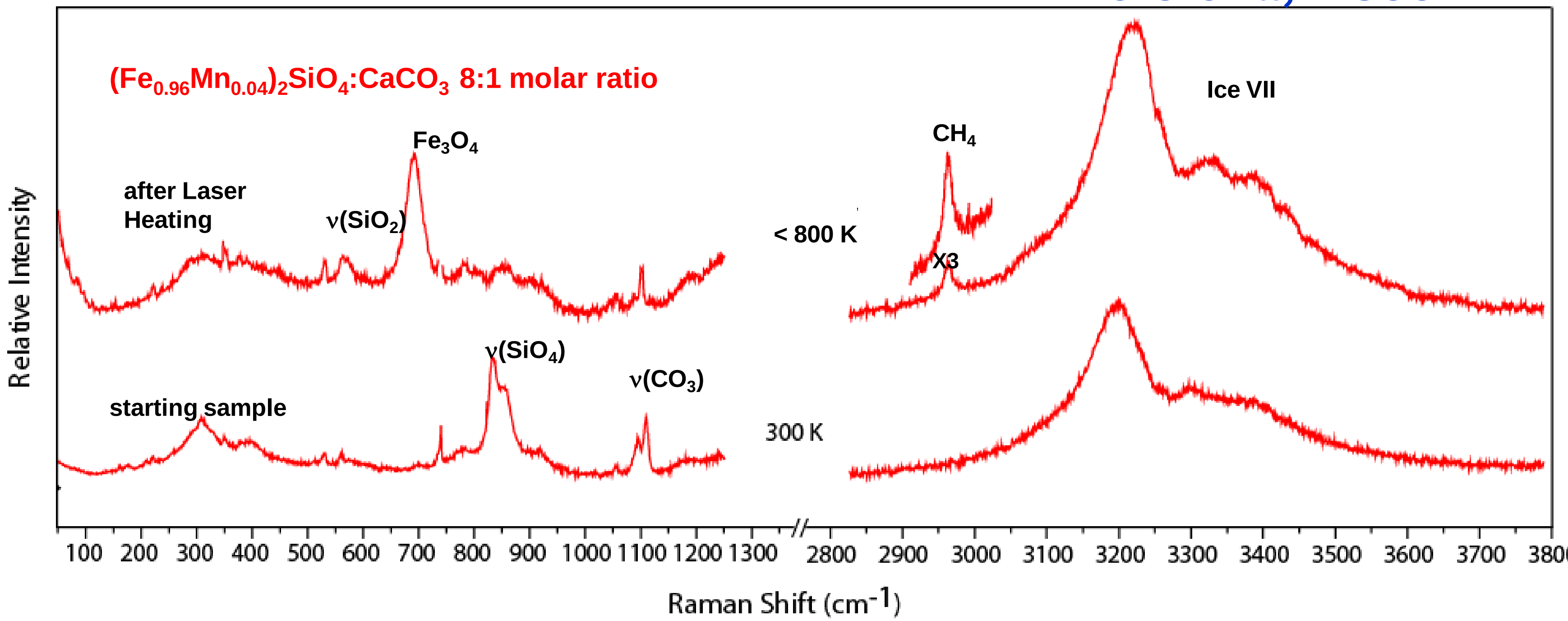
❑ **Mineral Assemblages: Peridodite & Basalt**

- Methane formation at relatively low temperatures; suggested pathway:

  $6\ Fe_2SiO_4 + CaCO_3 + 2\ H_2O = 4\ Fe_3O_4 + CH_4 + 6\ SiO_2 + CaO$

  - Hydrous phases were not observed

5-6 GPa, < 800 K



Methanogenesis from minerals

❑ Fayalite ($Fe_{1.92}Mn_{0.08}SiO_4$): Rockport

☑ **Olivine ($Mg_{1.8}Fe_{0.2}SiO_4$): San Carlos**

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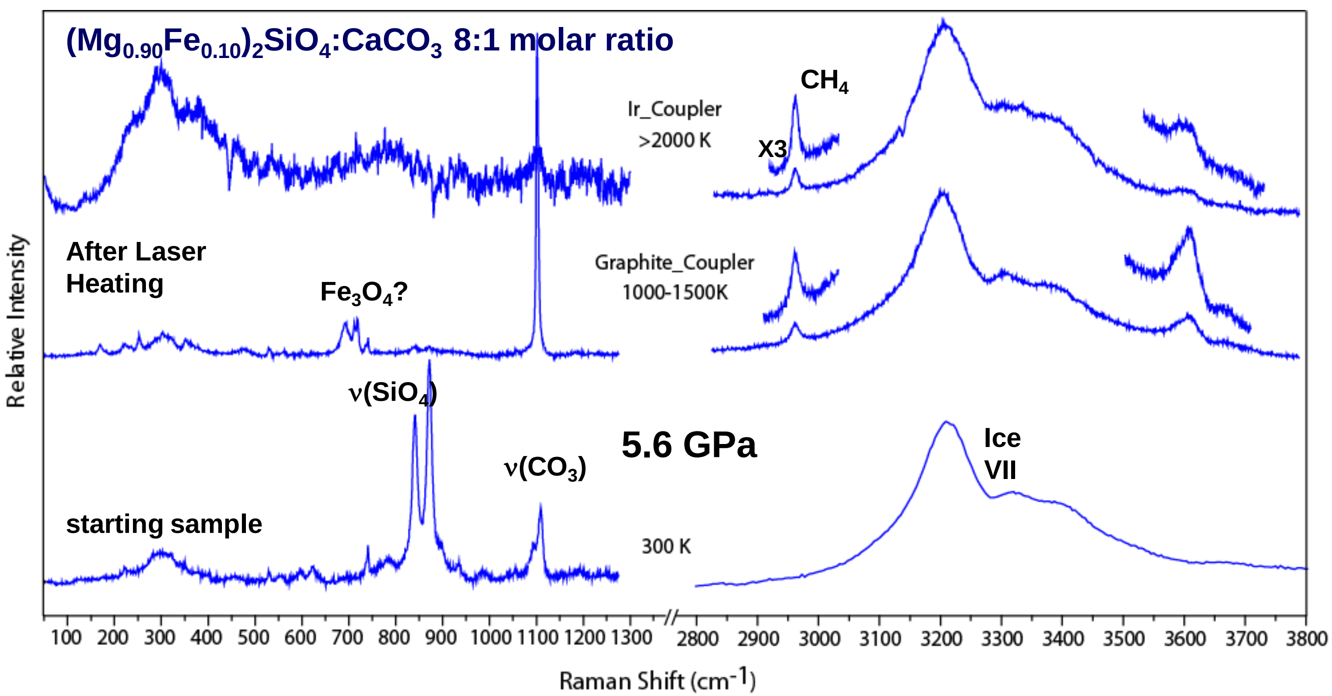
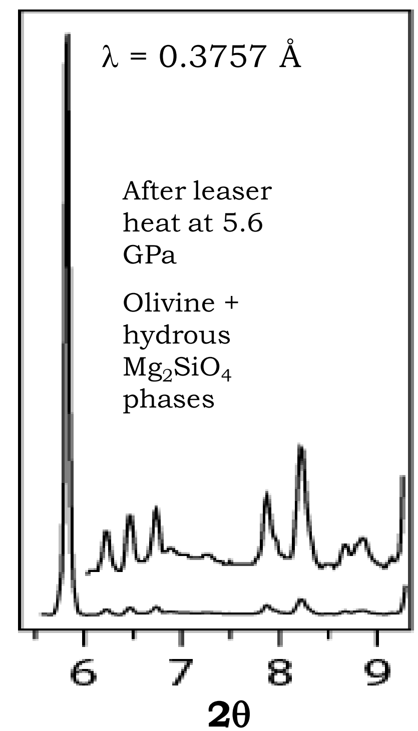
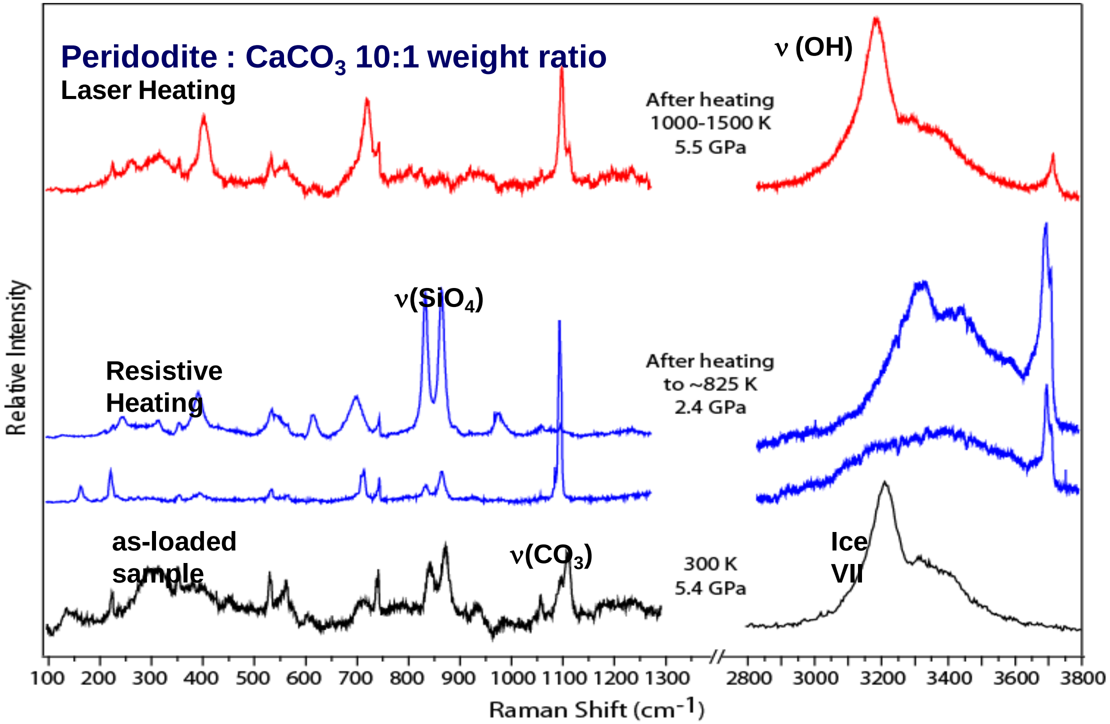
- Methane formation at T > 2000 K, 5-6 GPa
  - Hydrous phase formation





Methanogenesis from minerals

- ❑ Fayalite ($Fe_{1.92}Mn_{0.08}SiO_4$): Rockport
- ❑ Olivine ($Mg_{1.8}Fe_{0.2}SiO_4$): San Carlos
- ☒ **Mineral Assemblages: Peridodite & Basalt**
  - No methane formation at T > 1500 K, 5-6 GPa
    - Hydrous phase formation



Methanogenesis from minerals

- ☑ Fayalite ($Fe_{1.92}Mn_{0.08}SiO_4$): Rockport
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- ☒ Mineral Assemblages: Peridodite & Basalt

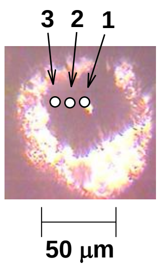
Conclusions

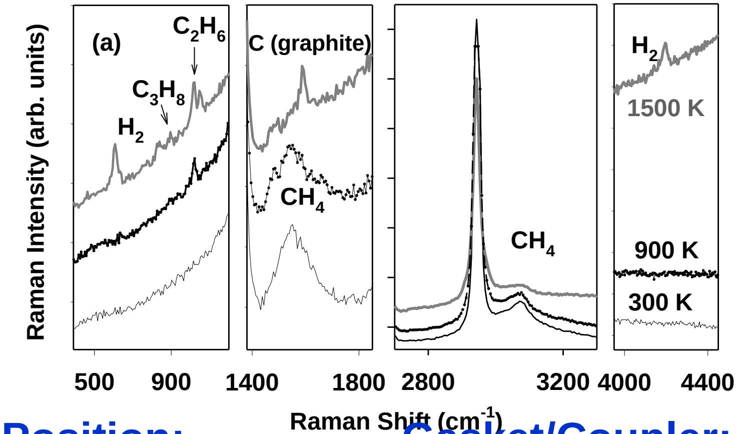
- Carbonate reduction to CH_4 observed even with Mg-rich mantle minerals
- Further XRD characterization of reaction products and thermochemical calculations are needed.
- Diamond reactivity (found in control experiments) need to be better addressed
- Explore polymerization to higher hydrocarbons.

Methane and ethane reactivity: *in situ* Raman diagnostics

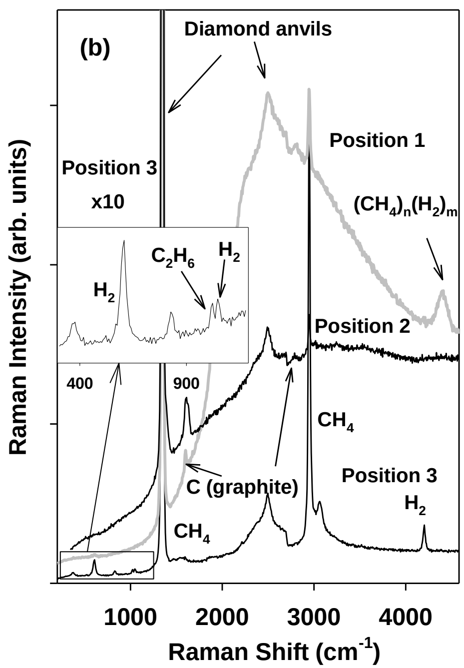
Temperature:

Positions:

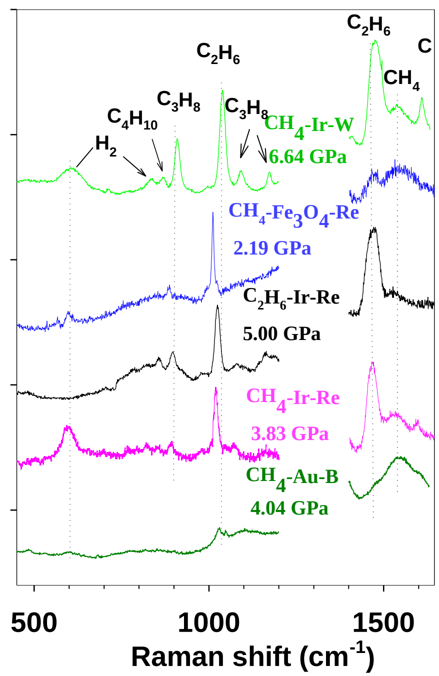




Position:



Gasket/Coupler:



Methane:

$CH_4 \rightarrow C_2\text{-}C_4$ alkanes $+ H_2$

$CH_4 \rightarrow C + H_2$

To check reaction reversibility

Ethane:

$3C_2H_6 \rightarrow 2C_3H_8 + H_2$

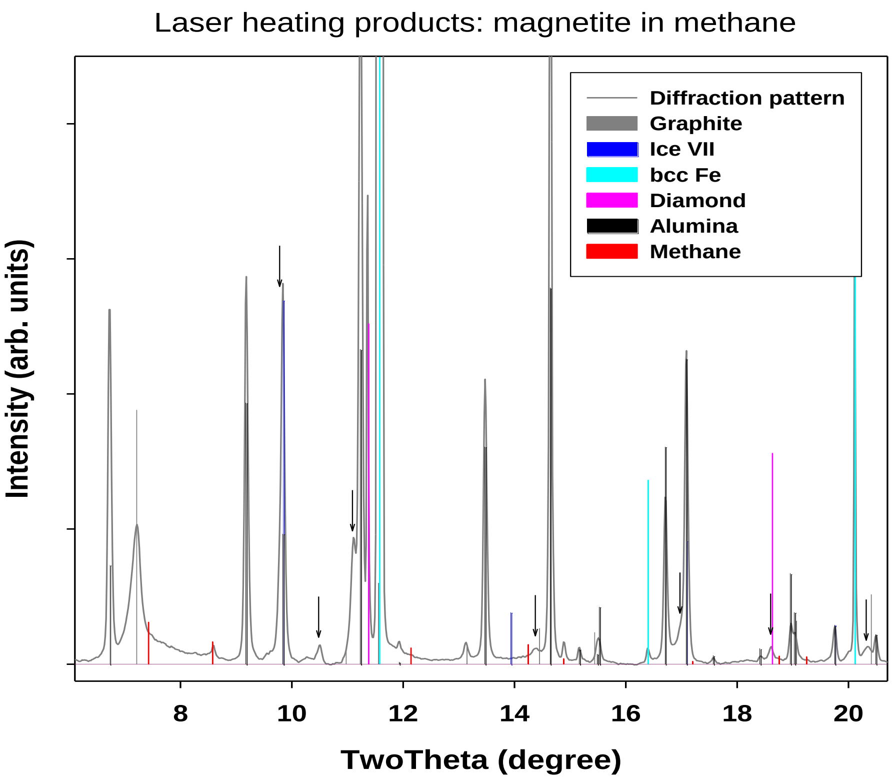
$C_2H_6 + H_2 \rightarrow 2CH_4$

Gasket: Re, W, Au (liner)

Coupler: Ir, B, Fe_3O_4

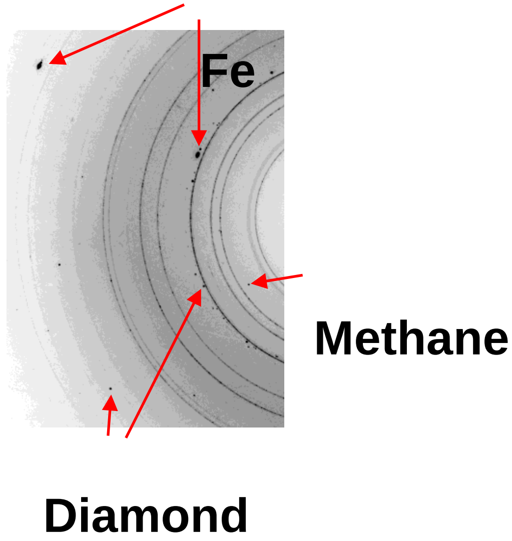
Thermal insulation: Al_2O_3 (in selected exp.)

X-ray diffraction of the quenched products in oxidized conditions with Fe_3O_4 coupler

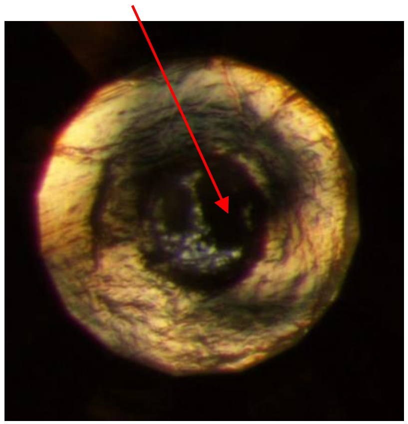


$$Fe_3O_4+2CH_4 \rightarrow 3Fe+2C+4H_2O$$

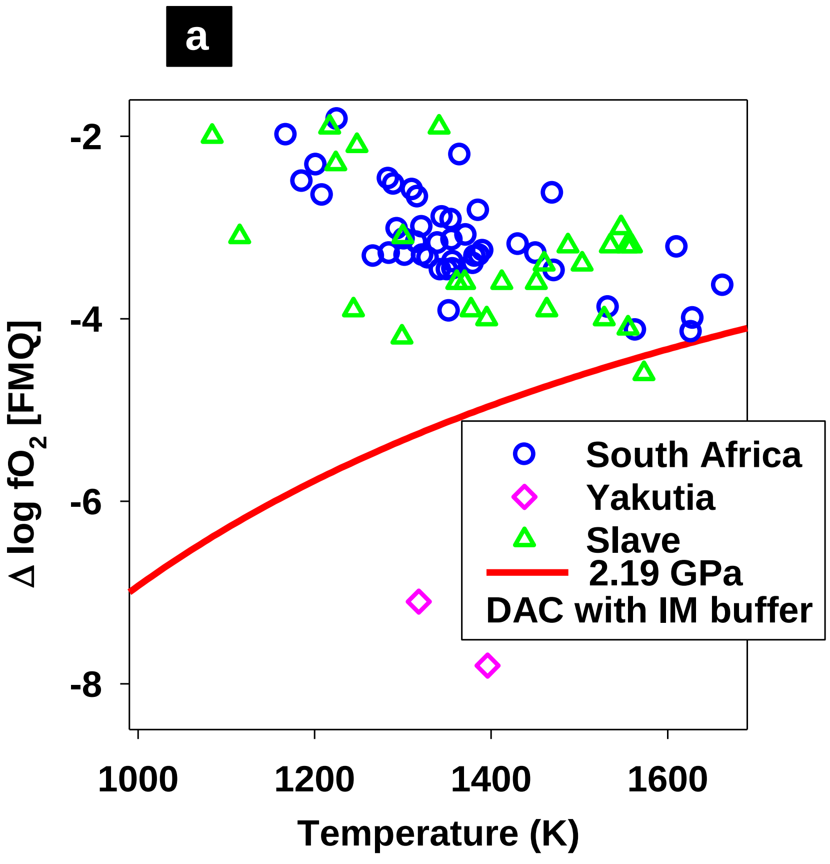
Single-crystal diffraction



Single crystal Fe_3O_4



P-T-fO_2 conditions in the DAC experiments and in the upper mantle



Conclusions

Methane above 2 GPa and 1000-1500 K partially reacts and forms saturated hydrocarbons (C2-C4 alkanes: ethane, propane, butane), molecular hydrogen and graphite.

The reaction does not require catalysts and proceed in oxidized conditions.

Formation of methane in similar experiments on ethane suggests reversibility of hydrocarbon formation.

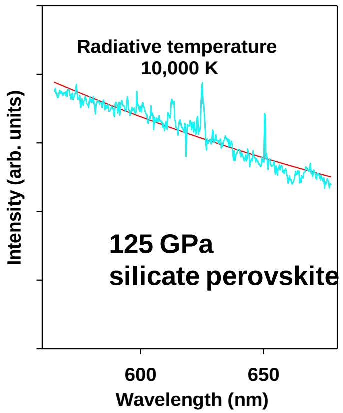
The experimental *P-T-*fO_2 conditions of methane derived hydrocarbon synthesis are appropriate for the Earth's mantle, creating the possibility of the abiogenic synthesis of petroleum components in of the Earth's upper mantle.

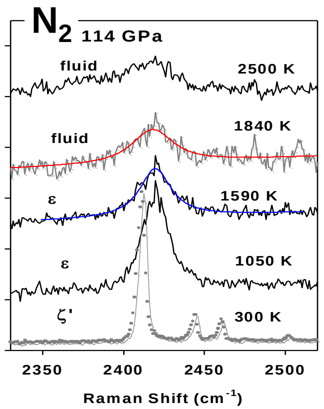
Outlook: Chemical Reactivity of Deep Earth's Carbon Bearing Phases using Optical spectroscopy at high *P-T*

Future scientific directions:

- shorter time-scale to study chemical kinetics & dynamics
- to make data comparable to molecular dynamic simulations

Pulsed laser heating in DAC

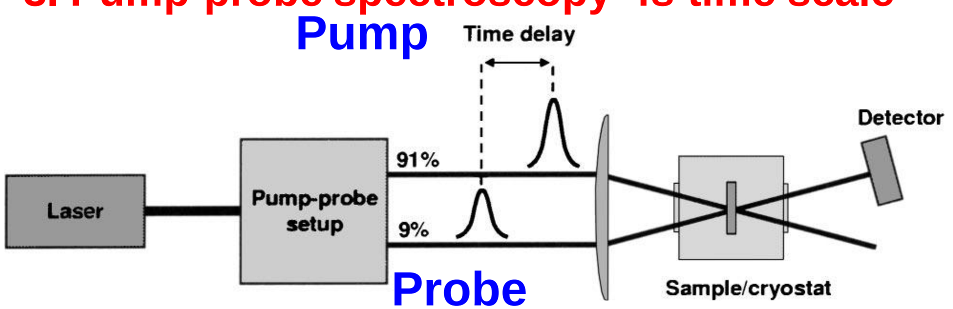




Pulsed Raman probe

Future technical developments of the laser heated DAC:

1. Pulsed laser heating
2. CARS & broadband fs spectroscopy in the DAC
3. Pump-probe spectroscopy- fs time scale



Lupke et al., 2003

Time resolution (determined by the laser pulse width ≃10's fs) is comparable with bond break/creation time.

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