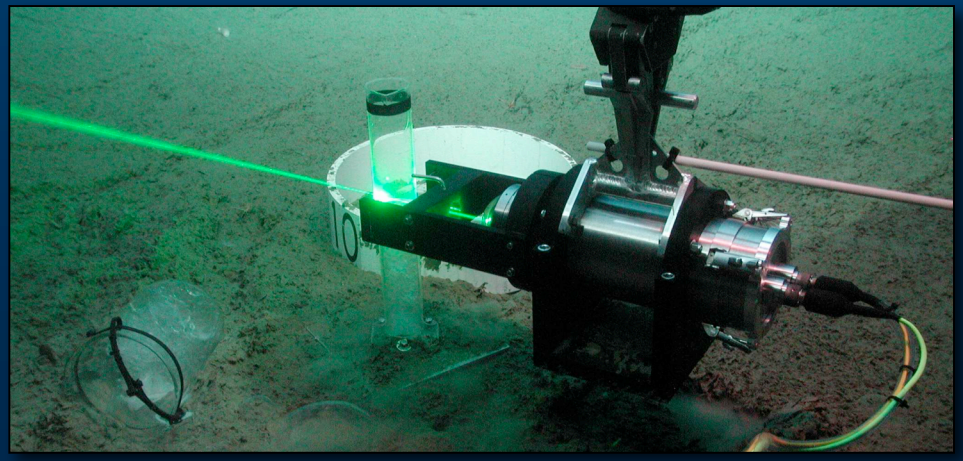
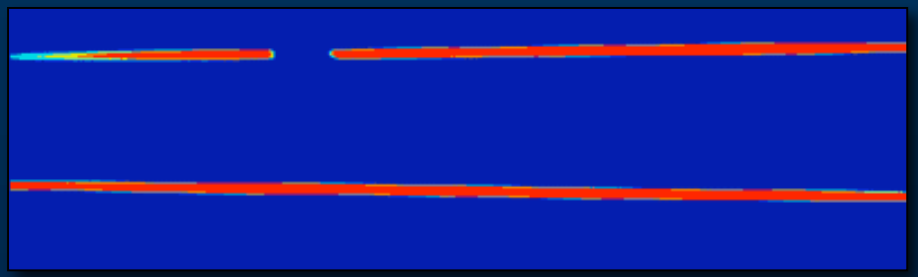
Laser Raman Spectroscopy

- Type of vibrational spectroscopy
  - Capable of analyzing solids, liquids, gases
  - Capable of *in situ* analysis
- Target is interrogated with a laser
  - Backscattered, inelastic radiation provides a fingerprint of chemical composition and structure



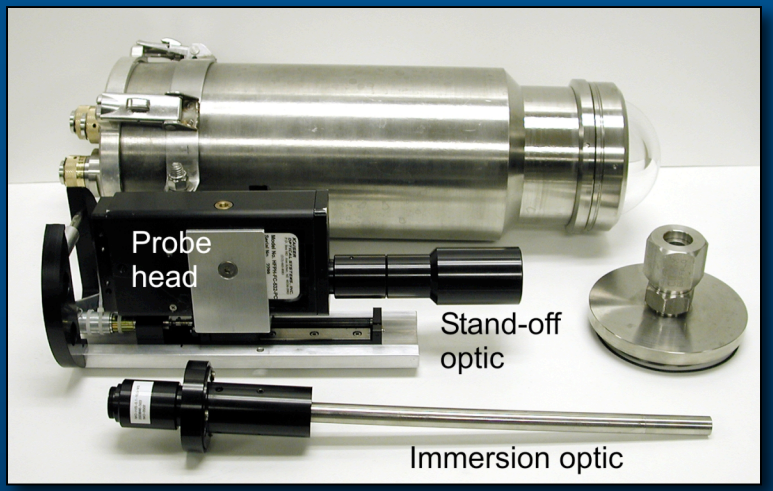
Laser Raman Spectroscopy

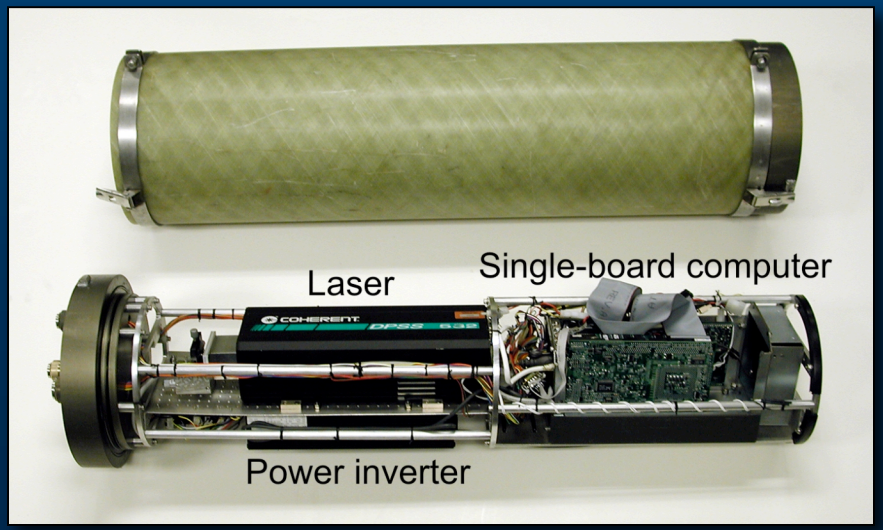
- DORISS (Deep Ocean Raman *In Situ* Spectrometer)
  - Modified laboratory model Kaiser Optical Systems, Inc. HoloSpec
    - 532 nm Nd:YAG laser
    - Holographic filtered probe
    - HoloPlex – duplex holographic grating
      - (100-4400 Δcm^{-1} range)
    - 512 x 2048 CCD

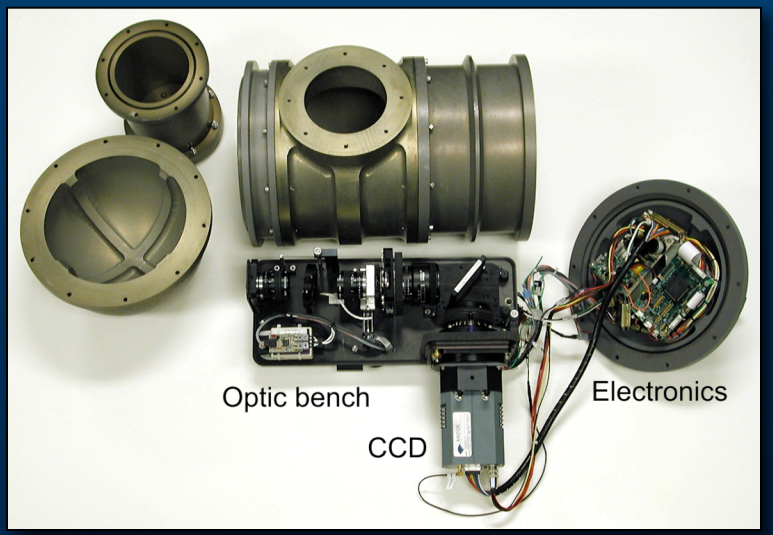


DORISS

- Probe head housing
- Electronics housing
- Spectrometer housing

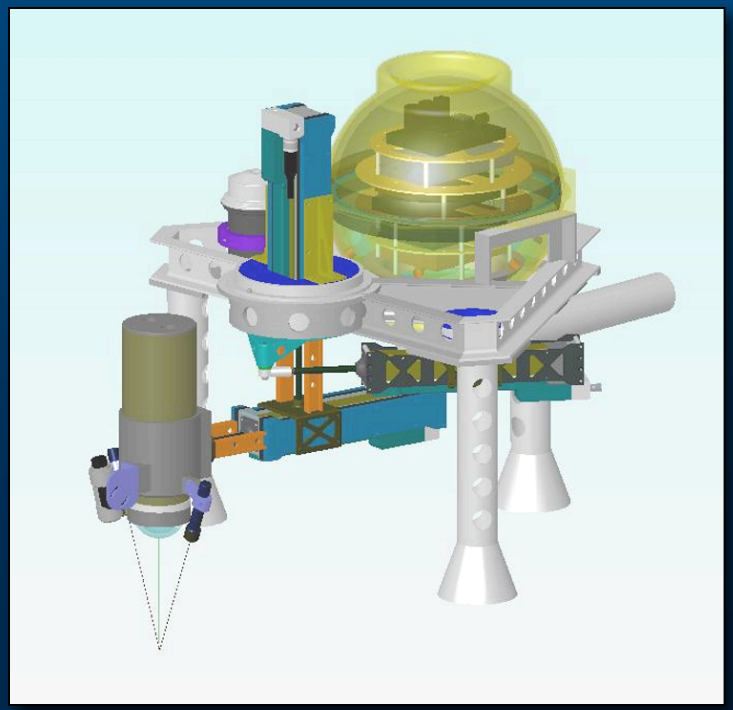




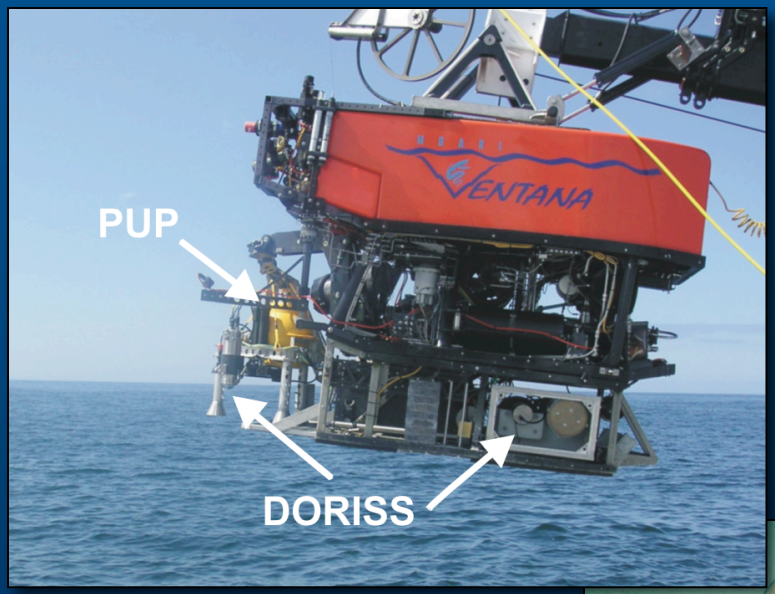


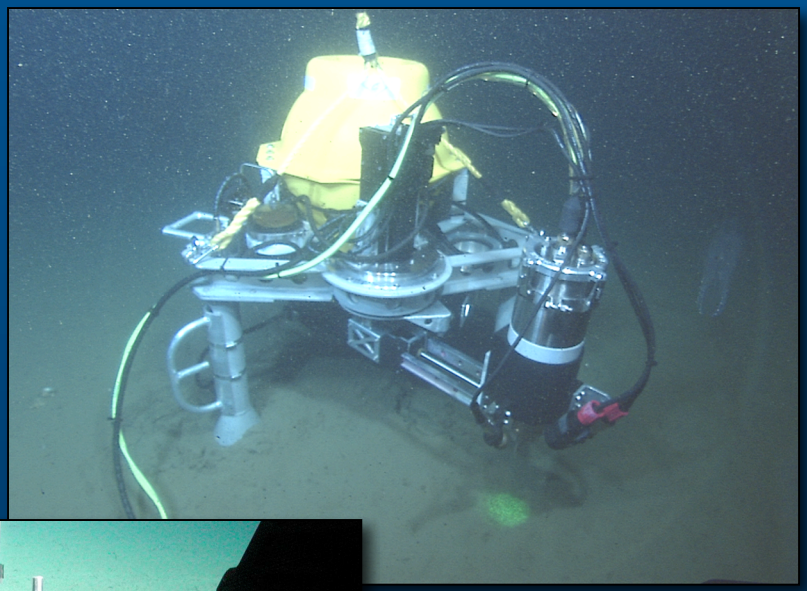
Laser Raman Spectroscopy

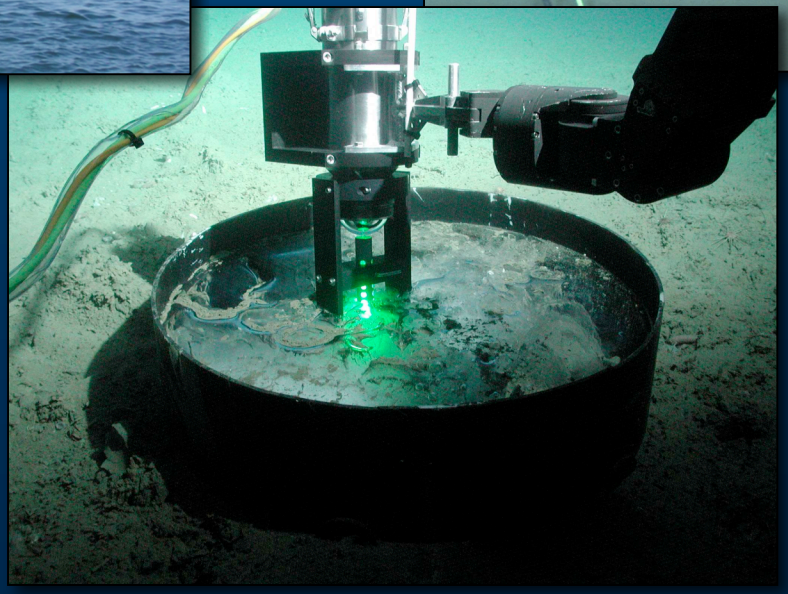
- PUP (Precision Underwater Positioner)
  - Provides the stability and precision movement necessary to analyze opaque targets on the seafloor
    - 0.1 mm precision
    - 15 cm up-down (Z)
    - 15 cm in-out (R)
    - 58 deg sweep (theta)



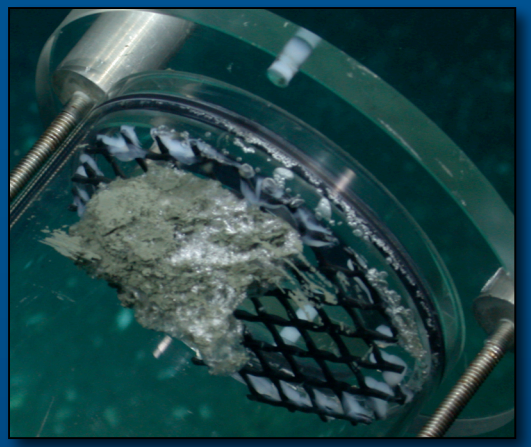
DORISS & PUP





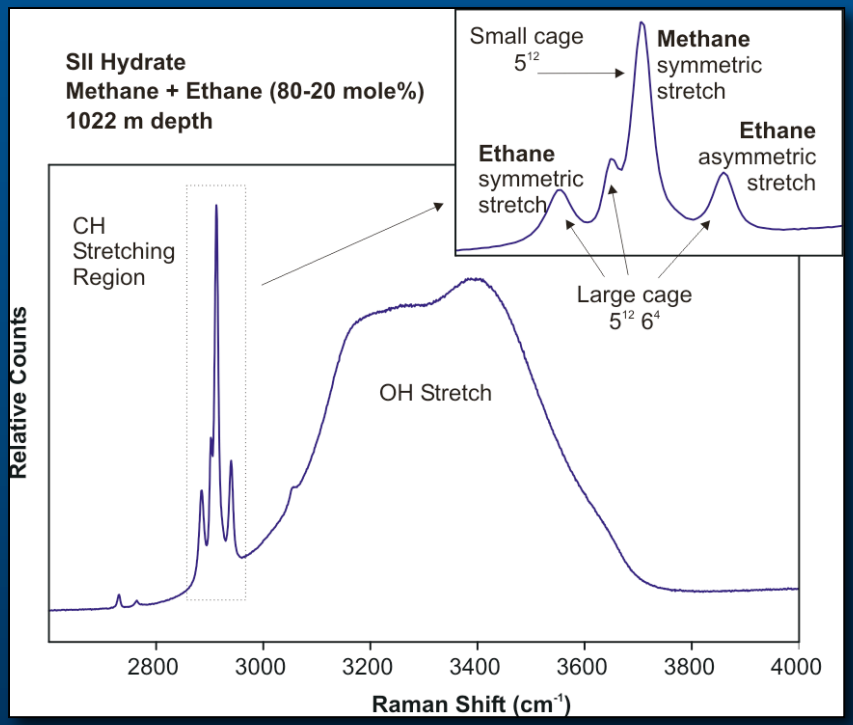


Gas Hydrates



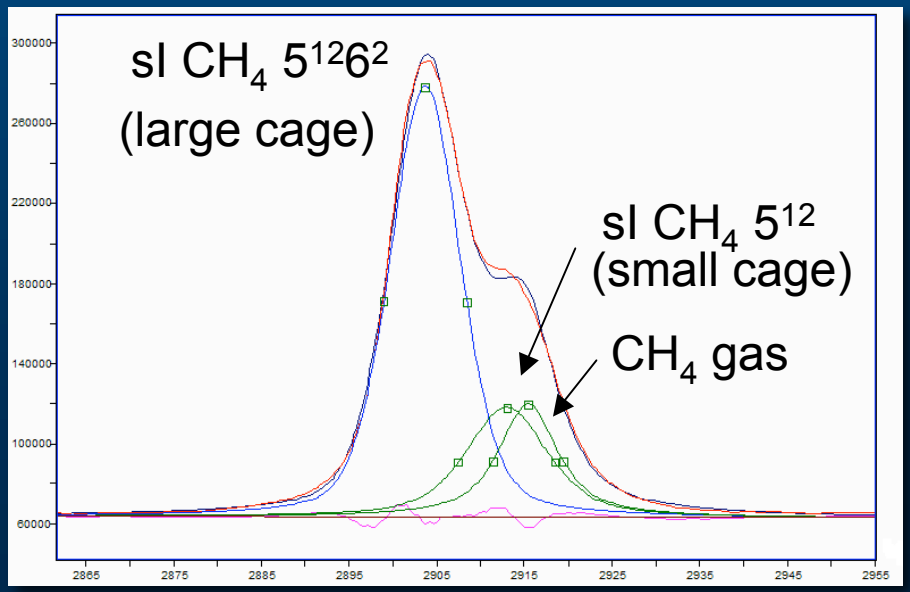
- Questions…
  - What is the structure of seafloor hydrates?
  - What gases are confined in seafloor hydrates?
  - How much gas is confined in seafloor hydrates?
- Raman spectroscopy can…
  - Identify sI, sII and sH hydrates
  - Identify constituent gases
  - Determine where the gases are

Gas Hydrates



Synthetic Hydrate
(Methane & Ethane)

Natural Hydrate
(Hydrate Ridge)
Excess hydrate is present
outside of lattice cages



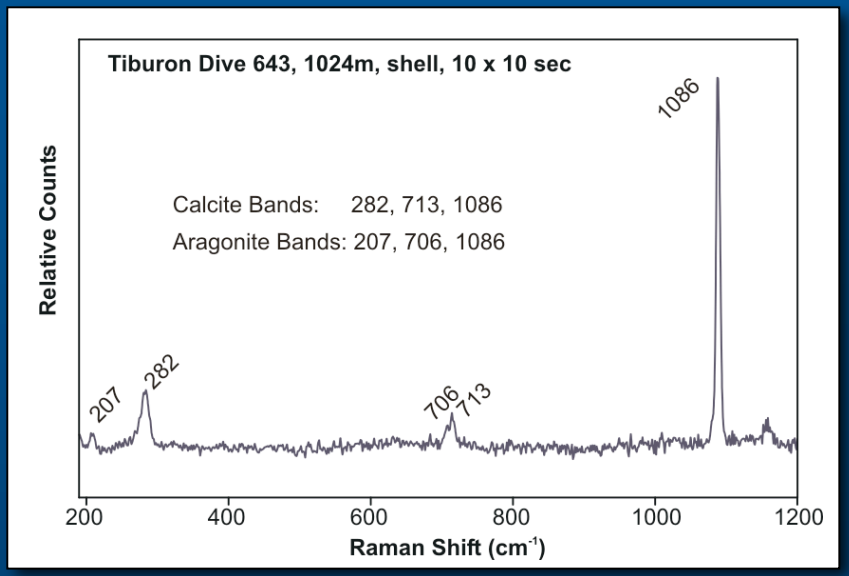
Raman Shift (Δcm^{-1})

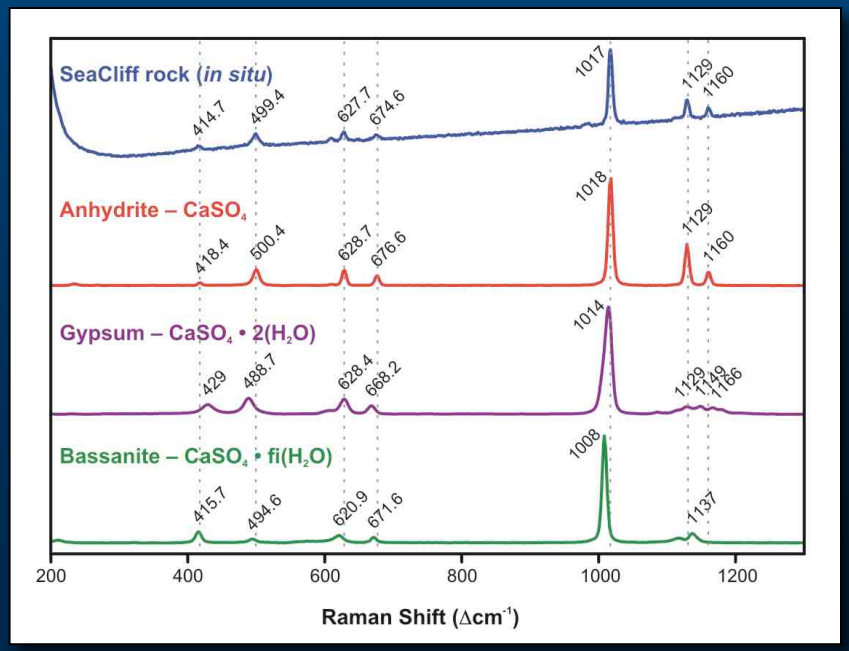
Mineralogy

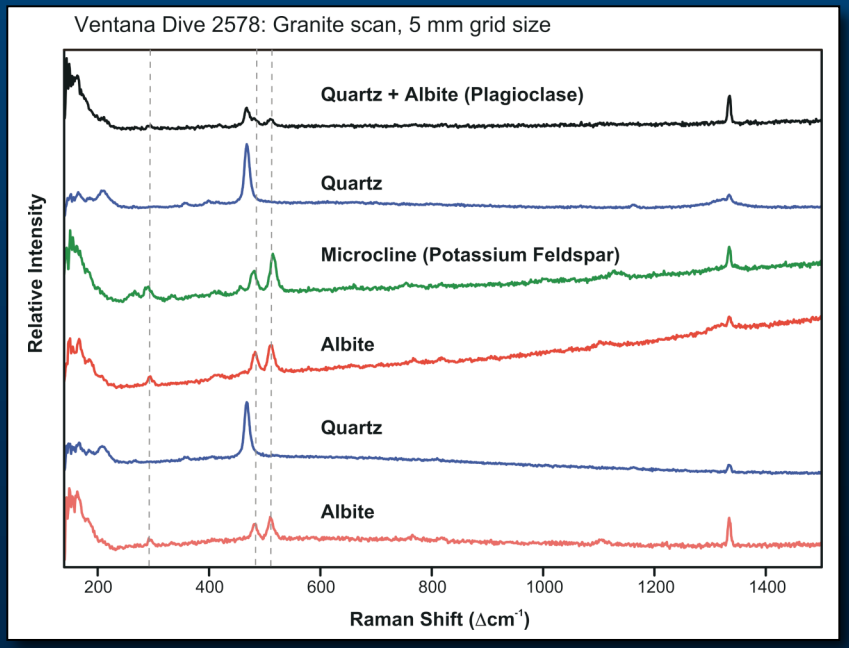
- Questions…
  - What minerals are precipitated in hydrothermal plumes?
  - What minerals are precipitated in chimneys?
  - What is the distribution of those minerals?
- Raman spectroscopy can…
  - Identify minerals
  - Distinguish between polymorphs
  - Determine bulk composition and/or distribution through point counting

Mineralogy

- Raman active…
  - Pyrite, chalcopyrite, sphalerite, barite, anhydrite, etc.

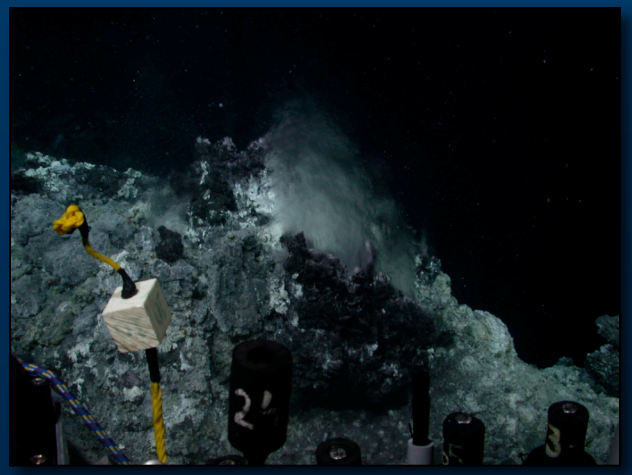




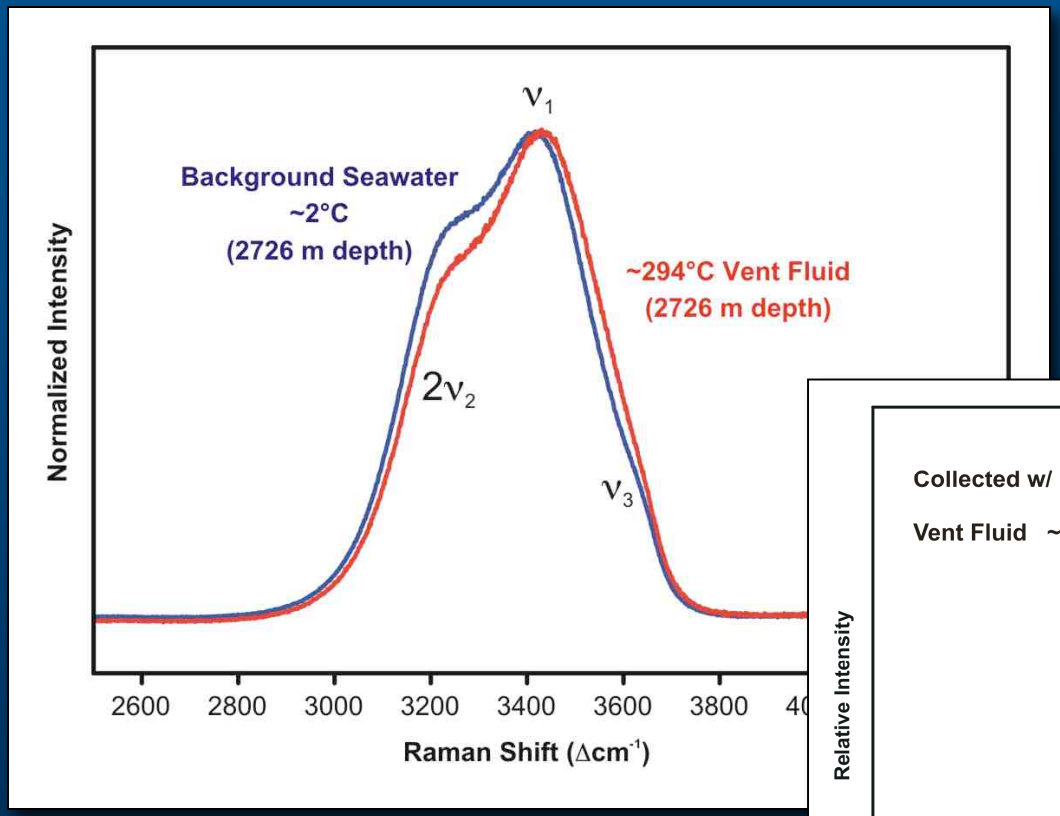


Hydrothermal Fluids

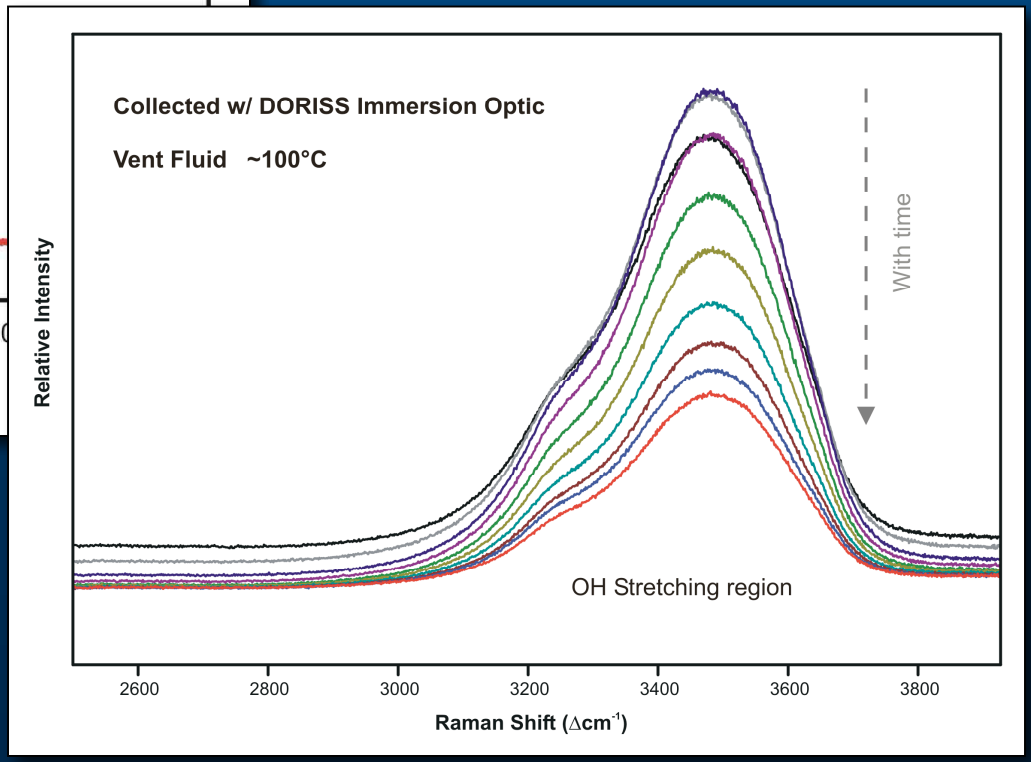
- Questions…
  - What is the composition of vent fluid?
    - What are the gas concentrations?
    - How does composition vary over time?
  - Can fluid temp be mapped non-invasively?
- Raman spectroscopy can…
  - Identify some components (including gases H_2S, CO_2, N_2, CH_4)
  - Determine water temp



Hydrothermal Fluids

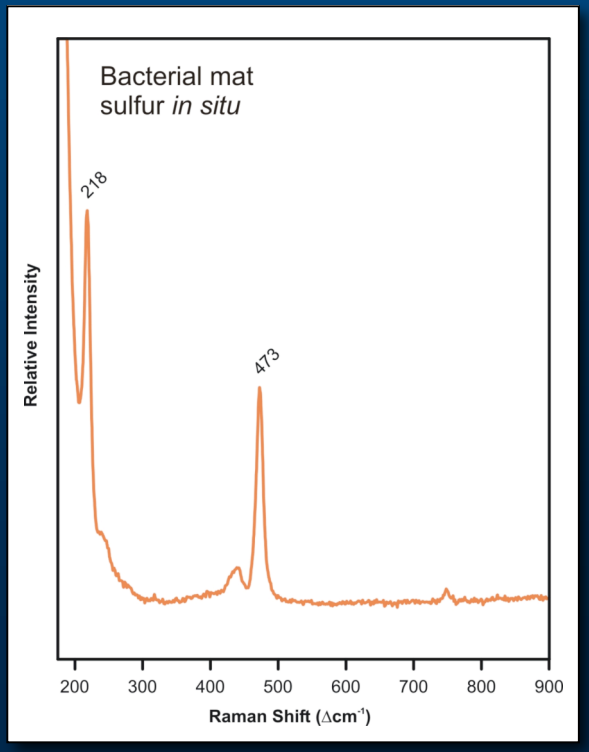


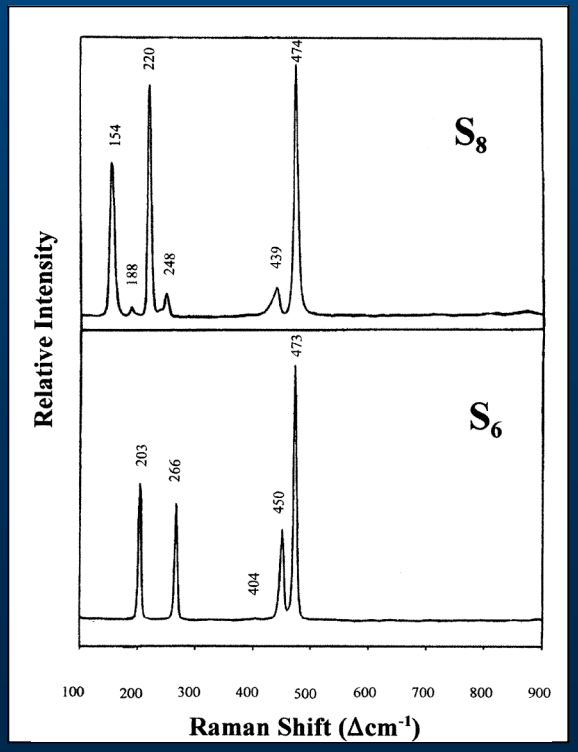
Sea Cliff Hydrothermal Field, Gorda Ridge



Bacterial Mats

- Questions…
  - What materials are produced by bacterial mats?
- Raman spectroscopy can…
  - Identify sulfur species

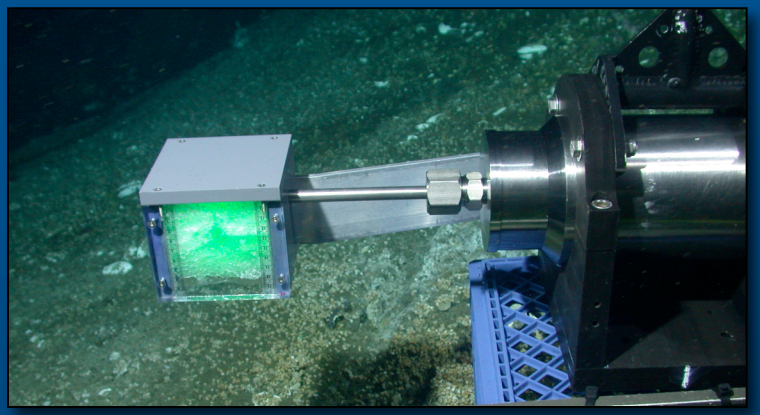


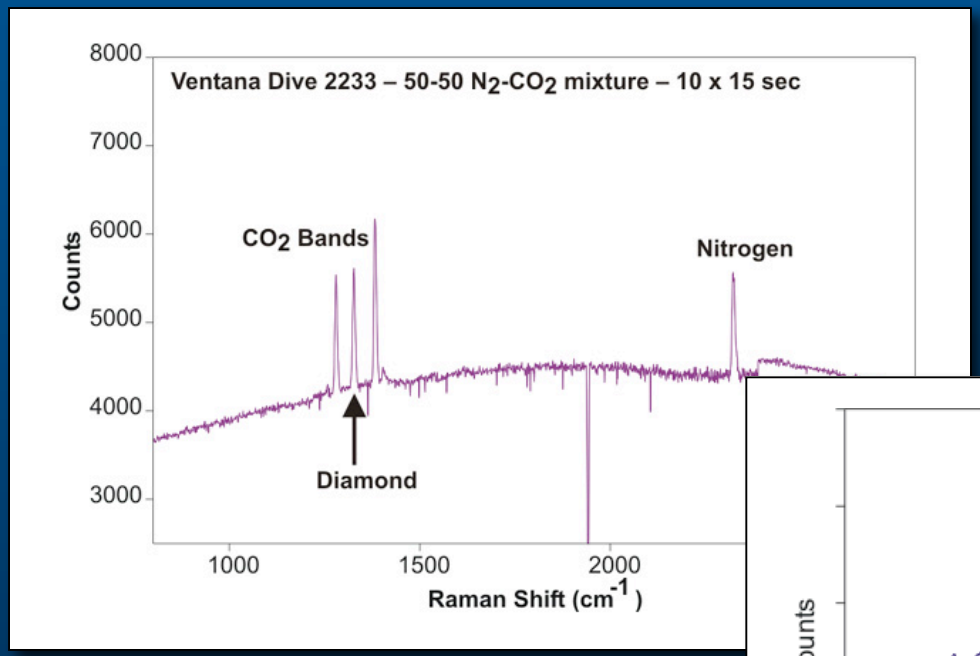


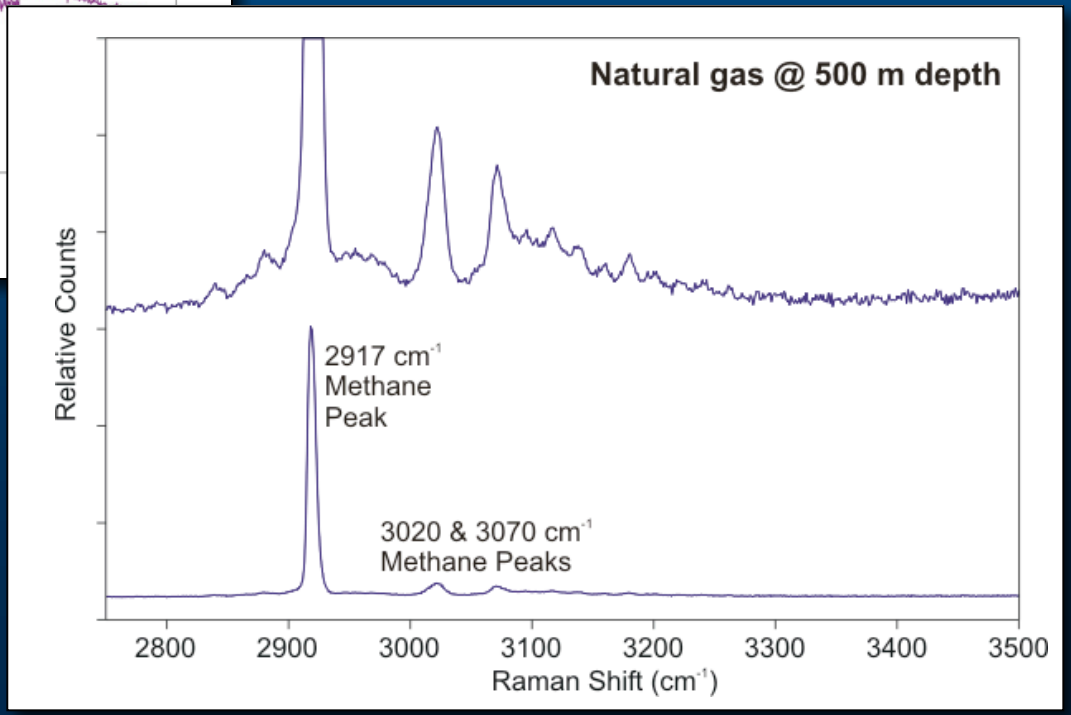
Gases

- Questions…
  - What are the constituents of natural gas venting from the seafloor?
  - Can the CO_2 system be studied *in situ?*
  - What happens to CO_2 when it is introduced into the ocean?
- Raman Spectroscopy can…
  - Determine the components of gas mixtures
  - Observe changes in gas concentration
  - Detect various phases of gases

Gases







CO_2-N_2 dissolution experiment

Natural gas from the Gulf of California analyzed *in situ*

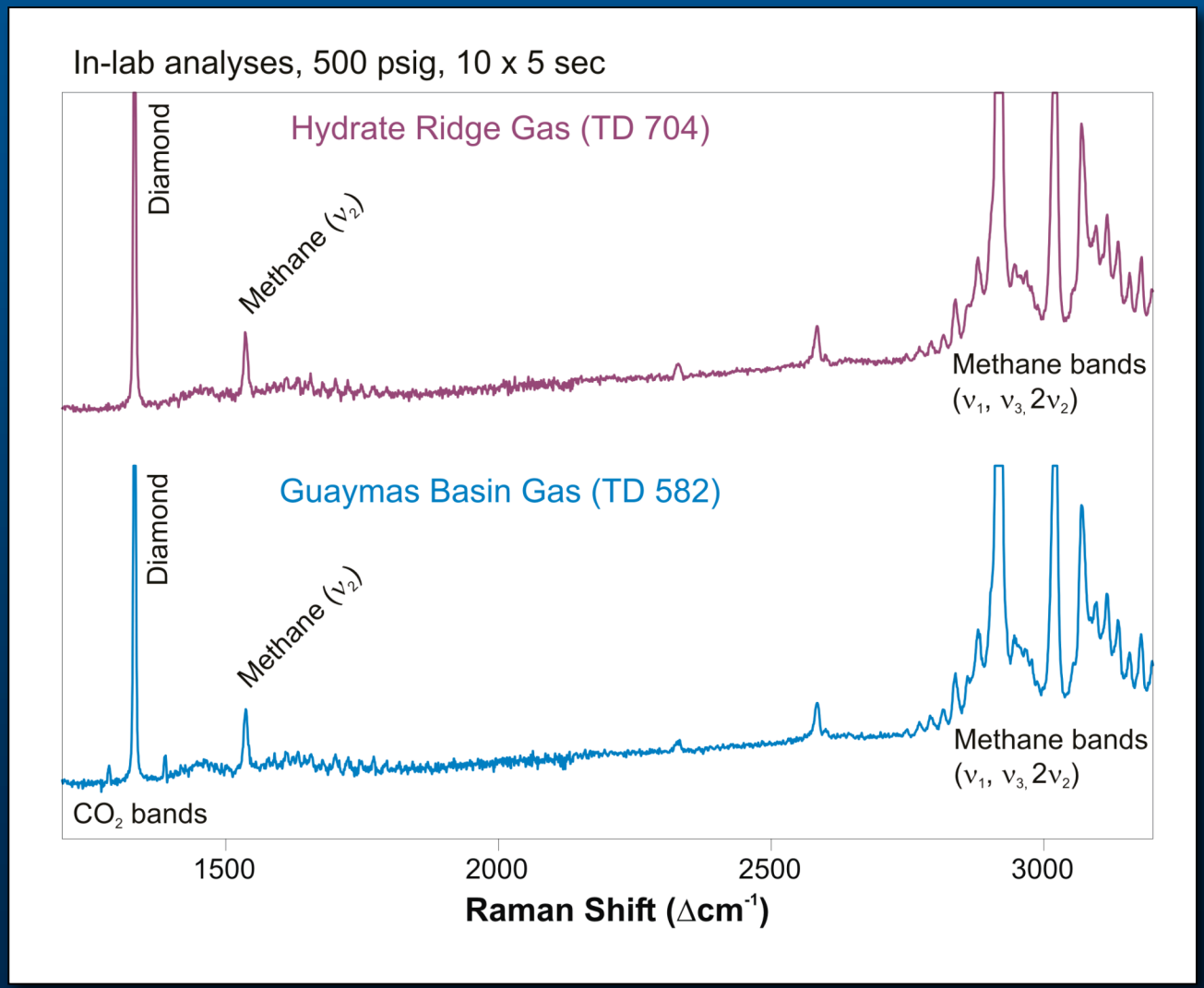
Gases

Hydrate Ridge

~0.16 mole% CO_2

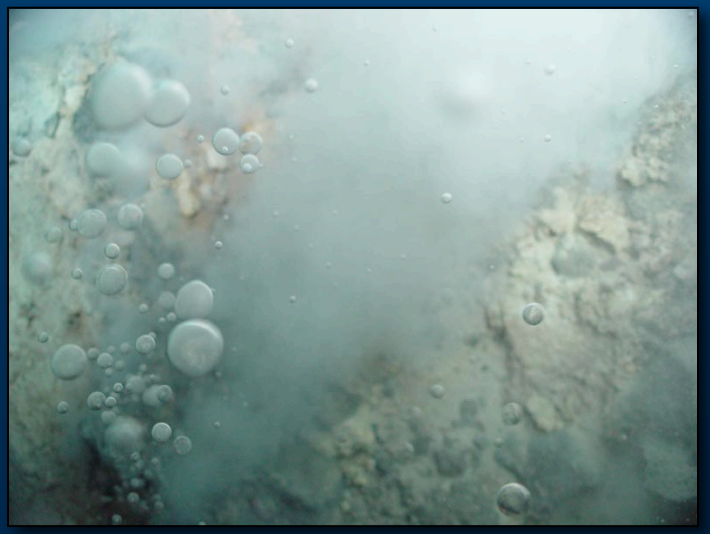
Guaymas Basin

~3.0 mole% CO_2



Future Advancements

- Smaller instrument
  - DORISS II (mid-2005)
- Improved sensitivity
- Deployment at more seafloor sites
  - Rainbow Hydrothermal Field (2006?)
- Smaller, more specific “sensor” instruments
  - Designed to analyze certain species
- Raman imaging
  - For mapping mineral species, etc.



Champagne Vent