Science Drivers

- *In Situ* Sensors
  - Development of autonomous and remote platforms
    - ROVs, AUVs
    - Cabled observatories
  - Desire to analyze targets with discrete stability regions in the deep ocean
    - Hydrothermal vent fluid
    - Gas hydrates
- Spectroscopic Sensors
  - Desire to analyze multiple species at once
  - Desire to analyze solid, liquid and gaseous targets
  - Desire for non-destructive, non-invasive analyses

Spectroscopic Sensors

- Mass Spectrometry
  - Atomic mass to charge ratio
- Laser Raman Spectroscopy
  - Molecular vibrational modes
- Laser Induced Breakdown Spectroscopy
  - Atomic emission
- Visible Reflectance Spectroscopy
  - Reflected color

Mass Spectrometry

- Analytes (molecules, atoms) are differentiated based on their charge to mass ratio
  - Analytes are ionized
  - Ions are accelerated through a magnetic or electric field which alters the trajectory of the ion beam
  - The differentiated beams are focused onto a detector

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Please see: http://www.atmosphere.mpg.de/enid/0,55a304092d09/Nr_ss_May_2__5_vegetation/CO2/R__Monitoring_carbon_dioxide_4ni.html

In Situ Mass Spectrometer

- Gemini In Situ Mass Spec
  - Quadrupole mass spectrometer
  - Built by Rich Camilli, WHOI/DSL
  - 10 kg in air, 50 cm long, 5000 m depth rating
  - Measures molecules from 2 to 300 AMU
  - parts-per-billion detection limit

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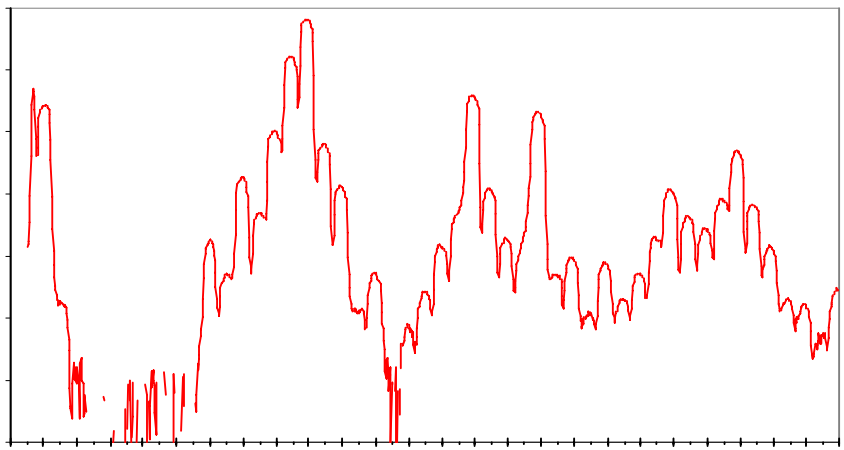


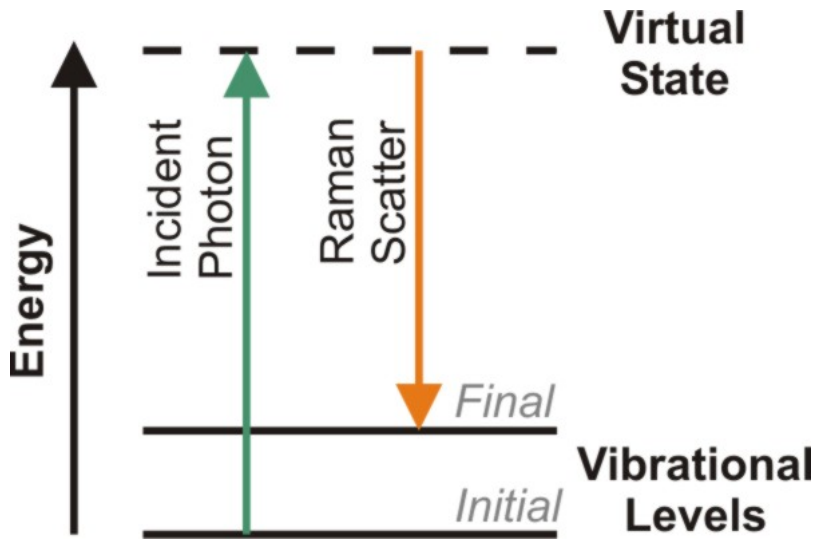
In Situ Mass Spectrometry

- Advantages
  - Can analyze liquids and gases
  - Detects multiple species in a single measurement
  - Non-destructive
  - Requires no consumables
- Disadvantages
  - Cannot analyze solids
  - Is invasive
    - Sample must be drawn into the instrument
  - Must maintain an ultra high vacuum (10^{-5} Torr)

Laser Raman Spectroscopy

- Raman scattering
  - Discovered by C. V. Raman
    - 1930 Nobel Prize

- Inelastic scattering of monochromatic radiation
  - Sample is interrogated by a laser
  - Some of the backscattered radiation is frequency shifted
  - Shift in energy is equal to the vibrational energy of the molecule



Laser Raman Spectroscopy

- Solids State laser for excitation
  - 532 nm, 785 nm
  - ~1-30 mW power
- Notch filters for Rayleigh line rejection
- Holographic grating
  - Duplex grating splits the spectrum into two strips
- Charge-coupled device (CCD) detector
  - Images full spectrum

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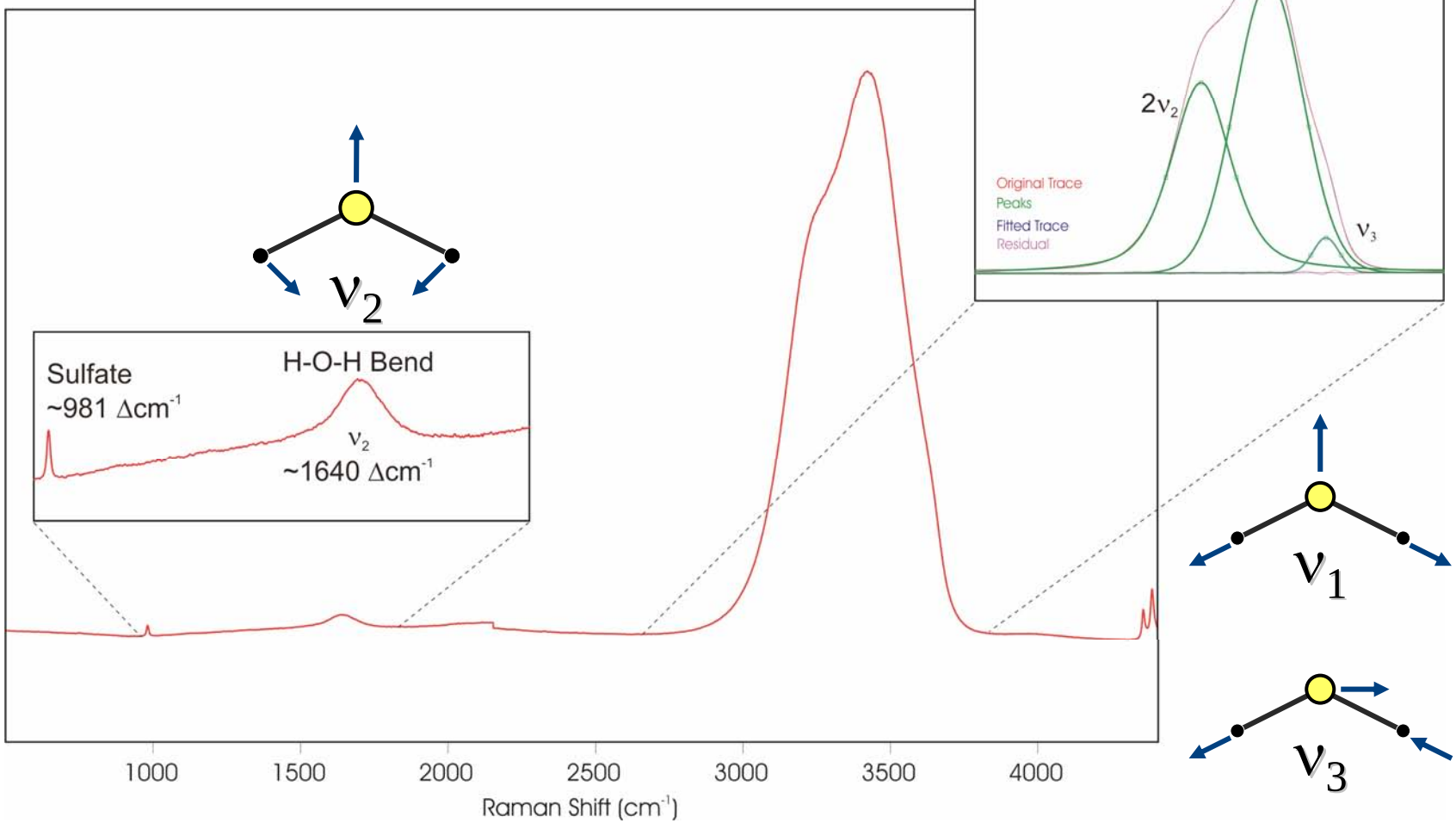
Please see: http://www.kosi.com/

Laser Raman Spectroscopy

- Raman spectrum provides a “fingerprint” of a substance based on chemical composition and crystal structure
  - Peak positions change with phase changes, pressure and temperature changes
  - Note that not all vibrational modes are Raman active
    - Depends on the polarizability of the molecule
    - Often complementary to IR spectroscopy

Seawater ➔ water + sulfate

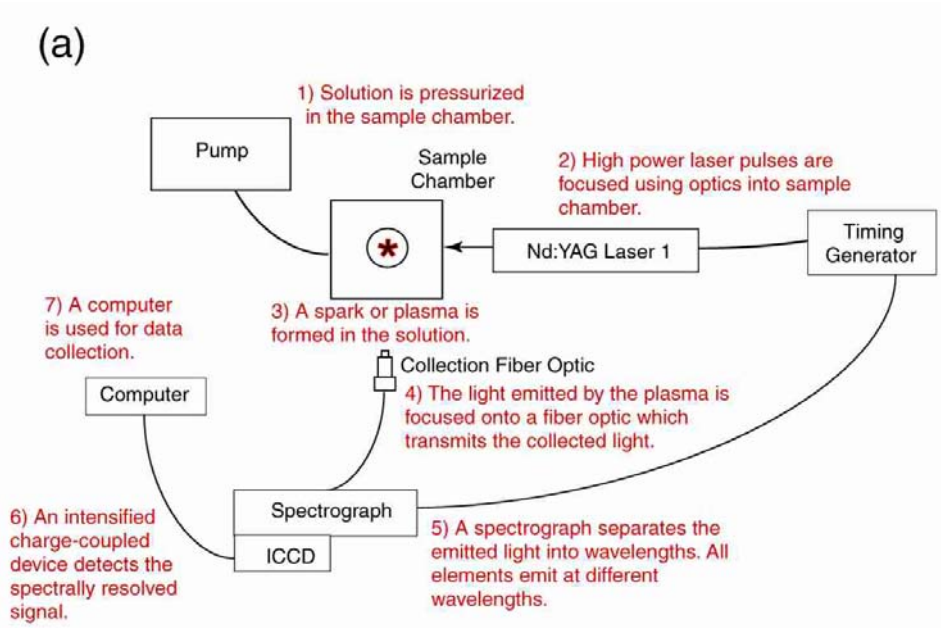


Laser Raman Spectroscopy

- Advantages
  - Can analyze solids, liquids and gases
  - Detects multiple species in a single measurement
  - Non-destructive
  - Non-invasive
  - Requires no consumables
- Disadvantages
  - Requires precise positioning to analyze opaque targets
  - Fluorescence can overwhelm Raman signal
  - Not all species are Raman active

Laser Induced Breakdown Spectroscopy (LIBS)

- High power laser is used to “plasmize” a sample
  - Only picograms to nanograms are used
- The spectral lines emitted from the plasma indicate the constituent elements
- Work done by Anna Michel, WHOI/DSL



Courtesy of Anna Michel. Used with permission.

LIBS

- Advantages
  - Can analyze solids, liquids and gases
  - Detects multiple species in a single measurement
  - Non-destructive
  - Non-invasive
  - Requires no consumables
- Disadvantages
  - Requires precise positioning to analyze opaque targets
  - Quenching of plasma by liquids

Visual Reflectance Spectroscopy

- A target is illuminated with white light
- The spectrum of the reflected light is analzed

- Color can be used as a proxy for some mineral species (e.g., iron species tend to be red)

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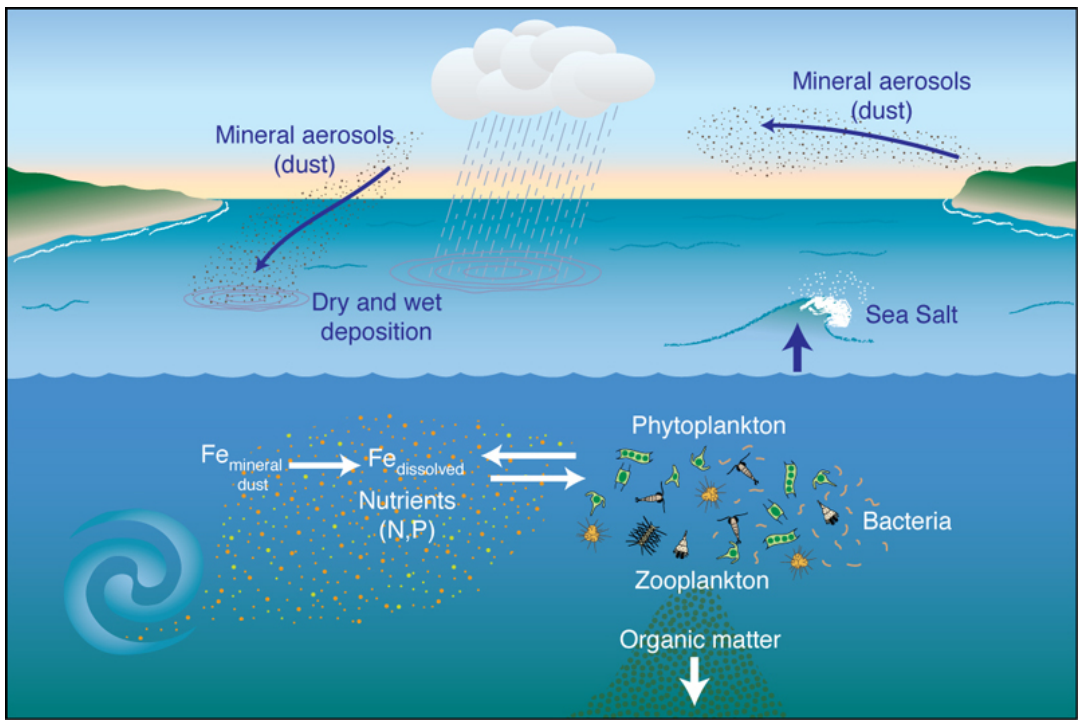
Please see: http://imagers.gsfc.nasa.gov/ems/visible.gif

Visual Reflectance Spectroscopy

- Aerosol Dust Application
  - Iron is deposited in the ocean by aerosol dust
  - Iron may be a limiting nutrient for phytoplankton
  - Buoy sampler can collect and analyze samples *in situ*



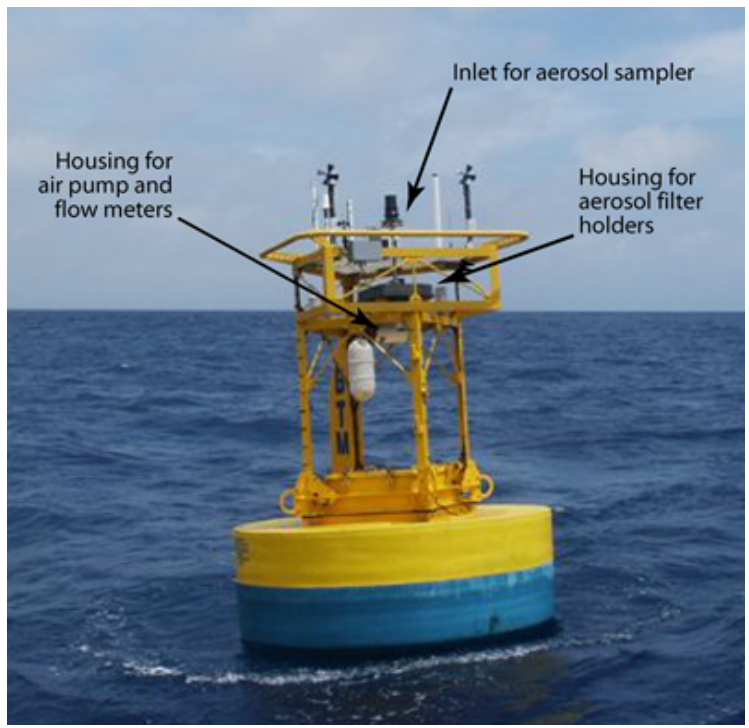
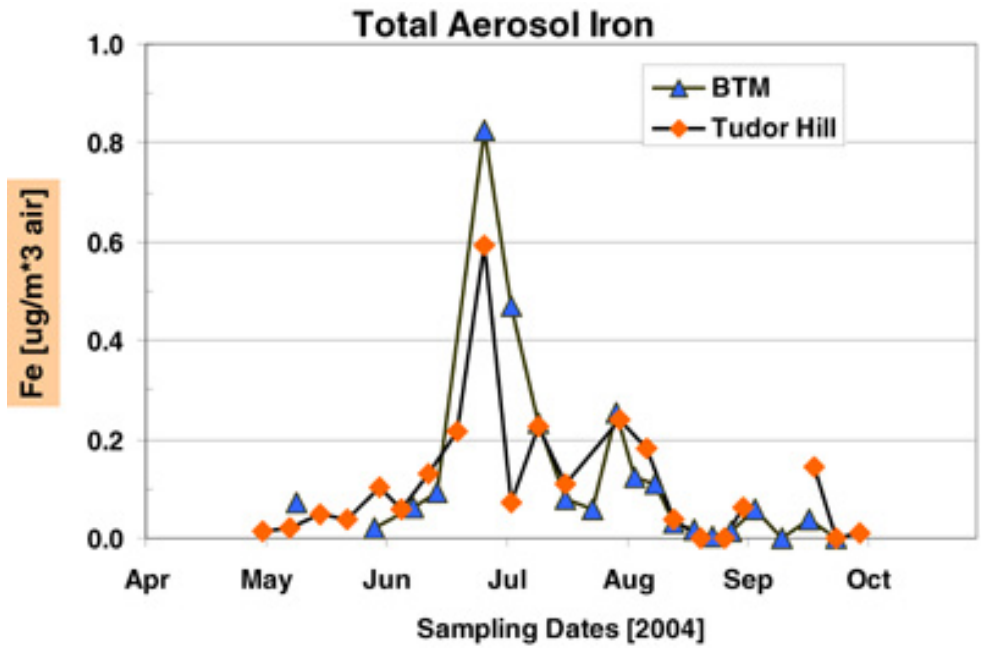


image credit: WHOI

Visual Reflectance Spectroscopy

- Aerosols collected on filters show dust events
- Color of the filter corresponds to iron content



Courtesy of Ed Sholkovitz. Used with permission.

Visual Reflectance Spectroscopy

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Arimoto R., W. Balsam, and C. Schloesslin. "Visible spectroscopy of aerosol particles collected on filters: iron-oxide minerals." *Atmospheric Environment* 36, no. 1 (January 2002): pp. 89-96(8). (Elsevier Science)

Visual Reflectance Spectroscopy

- Advantages
  - Simplicity
    - No high vacuum
    - Not a weak signal
    - No high power laser
  - Non-destructive
  - Non-invasive
  - Requires no consumables
- Disadvantages
  - Not necessarily species specific
  - Cannot necessarily differentiate between multiple species in a sample