The application of micro-Raman spectroscopy (and micro-LIBS) to the characterization of crystal structure variability in biogenic calcite

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Introduction

- **Rapid evaluation of intra-individual variability in Benthic Foraminifera**
- **Raman Spectroscopy**
  - ? **Sensitive to Mg/Ca variation in calcite**

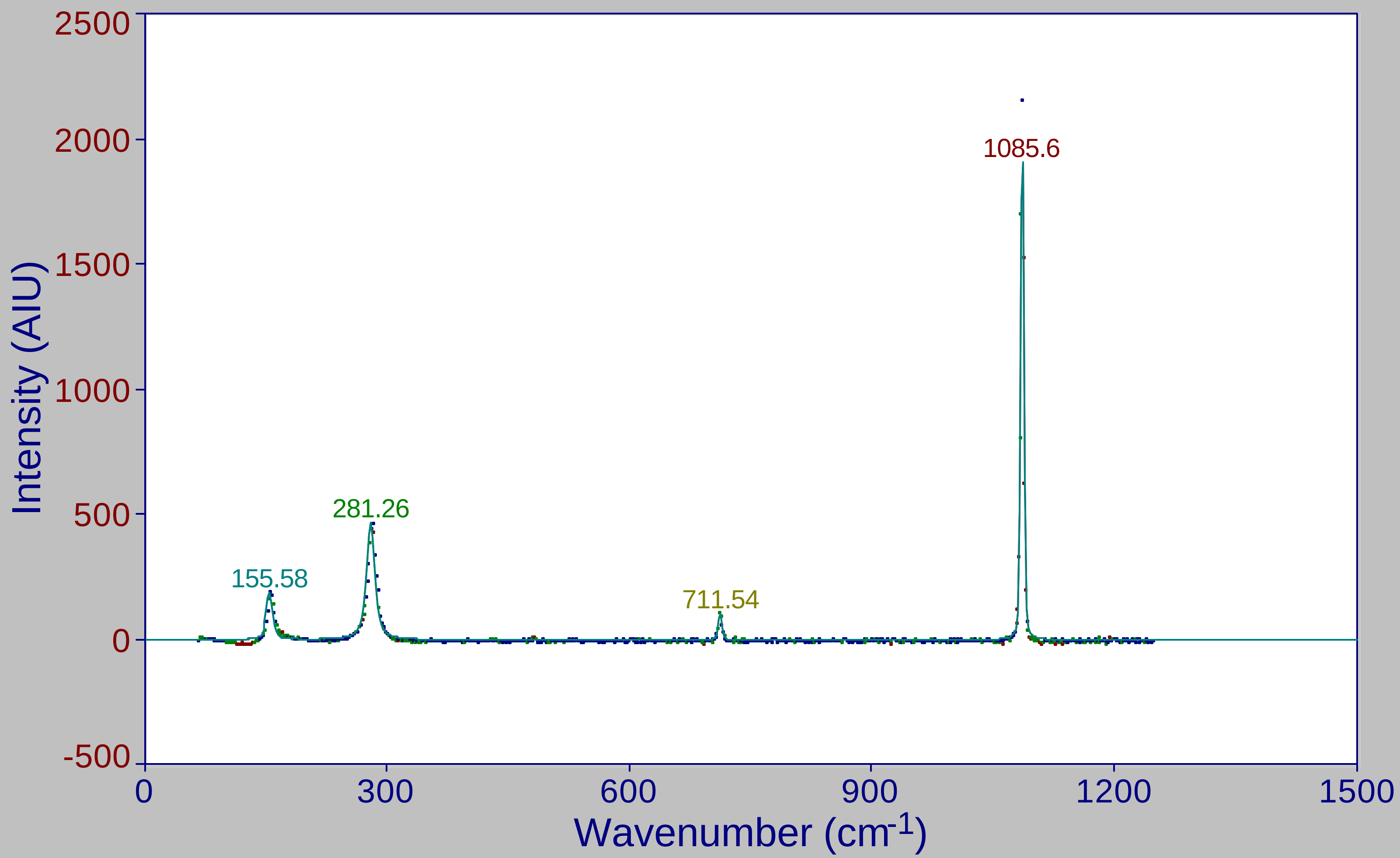
    Tlili et al. 2003

  - ? **Identify Structural Variation in Biogenic Carbonates**

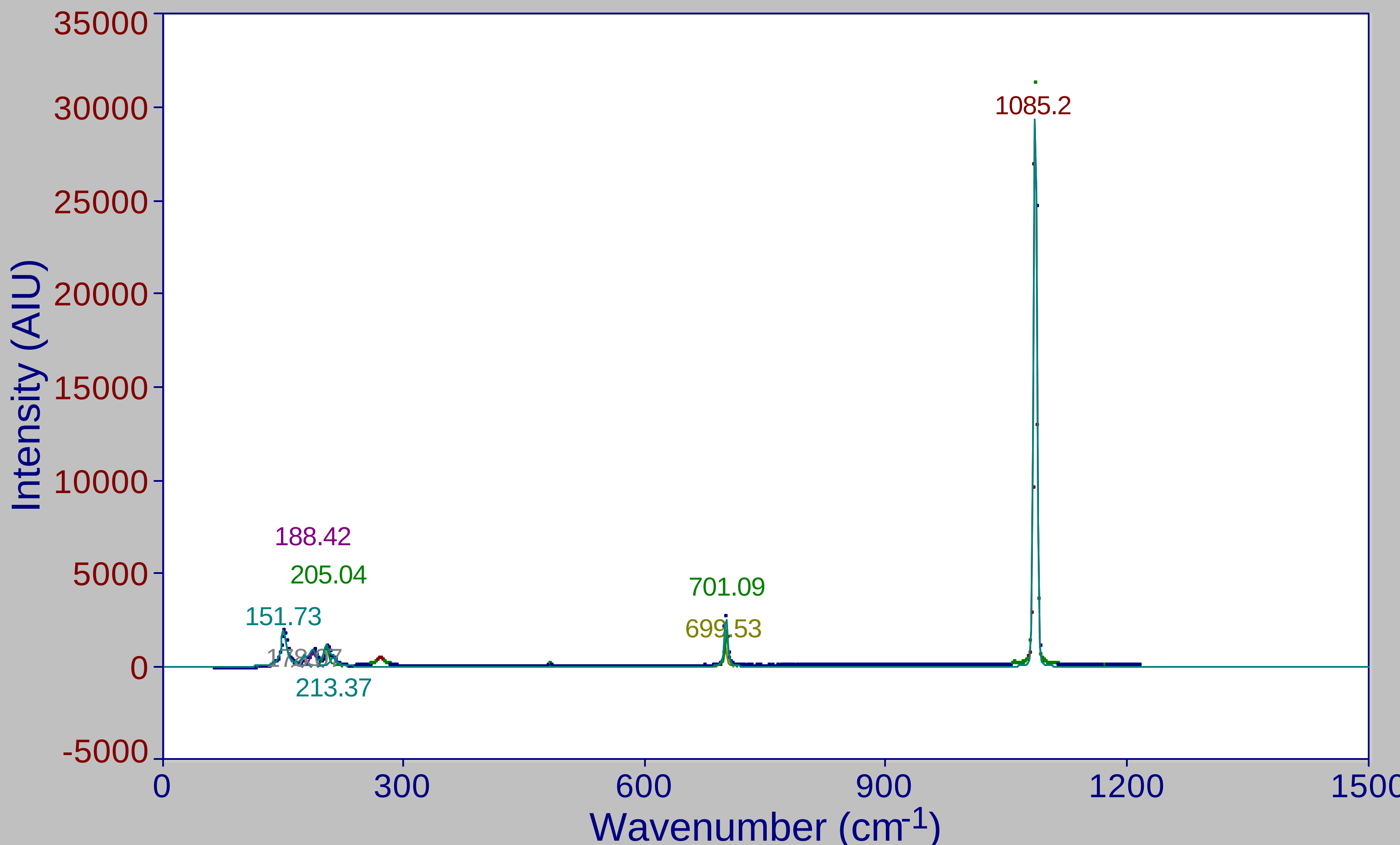
    Urmos et al., 1991

- **Microscopic optics provides for micrometer resolution**

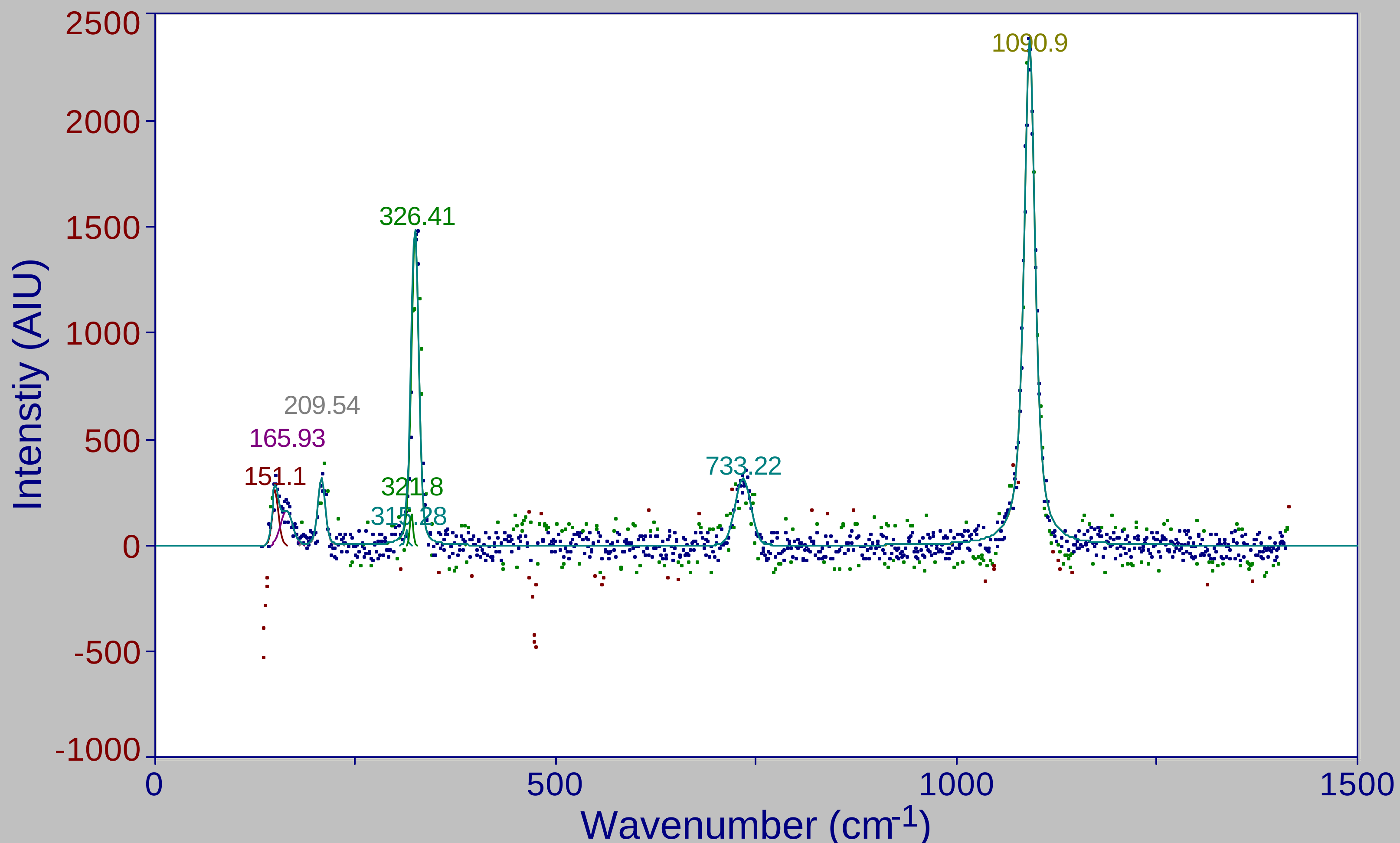
Calcite Reference Material



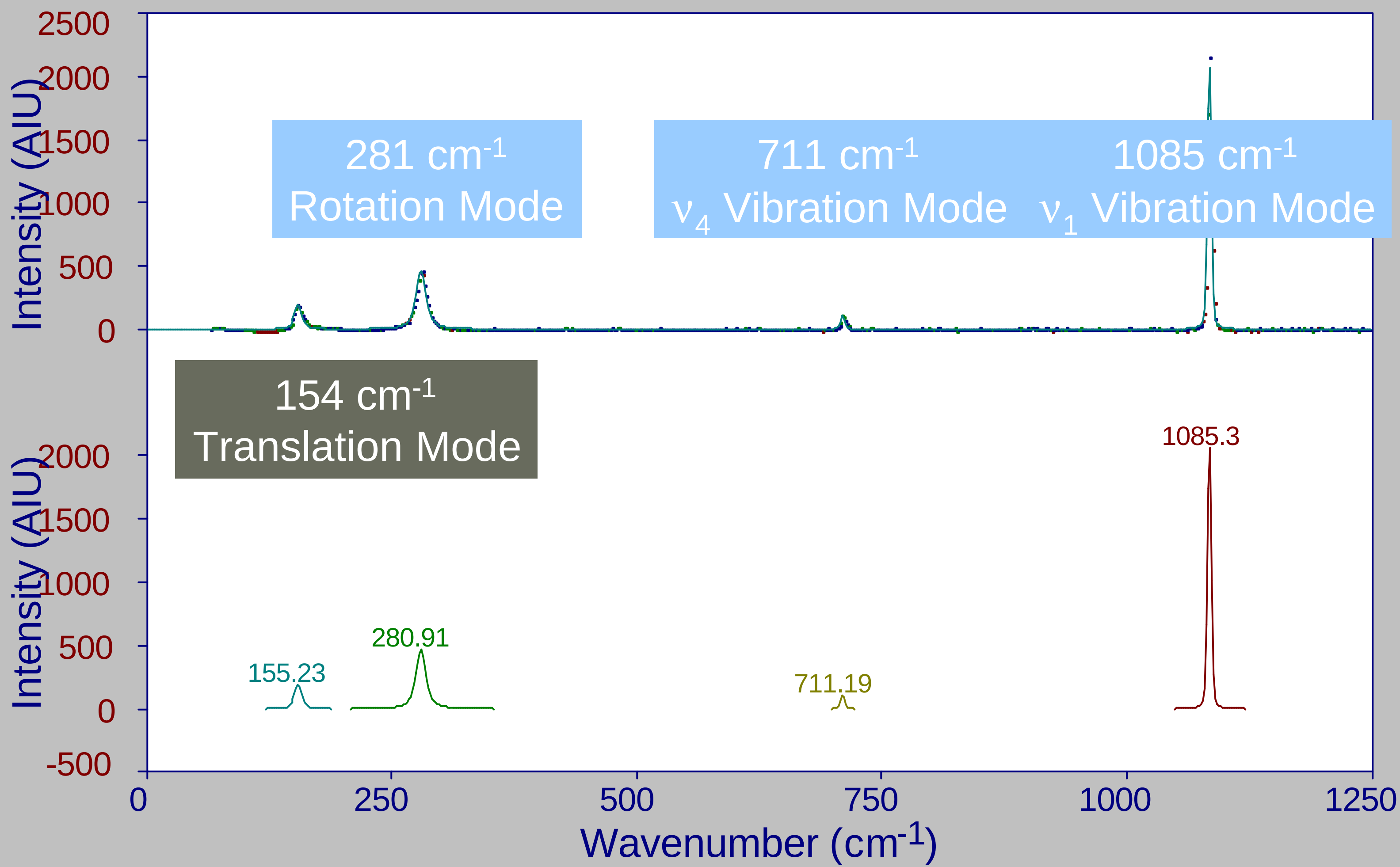
Aragonite Reference Material



NIAIST - Magnesite($MgCO_3$) China

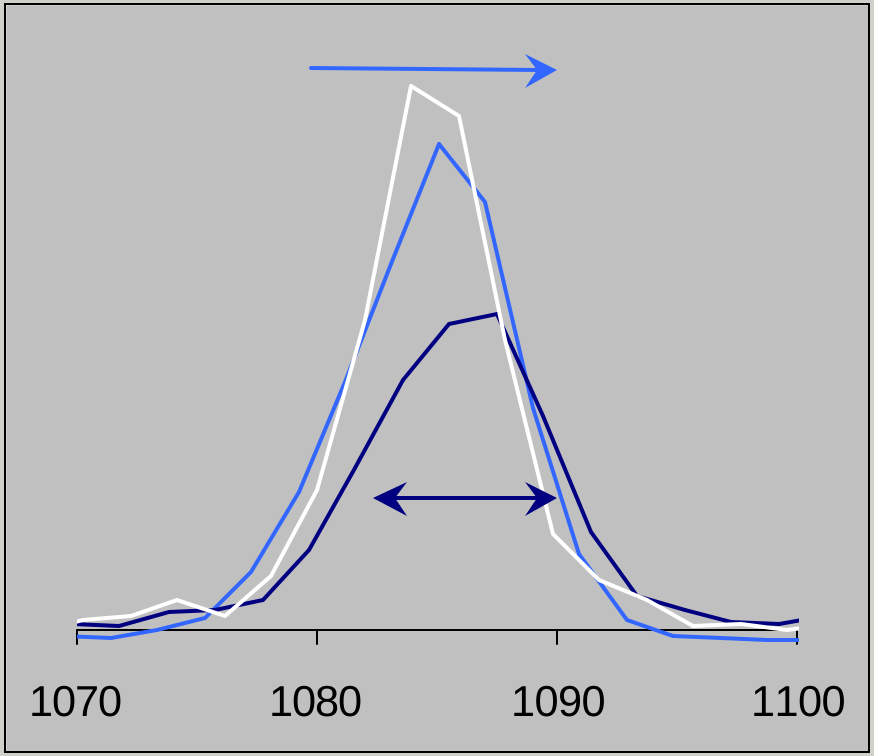


Calcite Reference Material



Raman Spectroscopy Cont.

- **Unique Raman Spectra for each Substance**
  - ? **Wavenumber Shift**
  - ? **Peak Width and Area**



Instrumentation

- **Jobin-Yvon Horiba LabRam Infinity micro-Raman Spectrometer**
  - ? **10´ objective (20-mm spatial resolution)**
  - ? **Continuous Wave Laser Excitation**
    - ? **532 nm frequency-doubled Nd:YAG**
    - ? **785 nm diode laser**
  - ? **Programmable X-Y Stage**
  - ? **Four 15-30 s Exposures; 70 cm^{-1} - 1250 cm^{-1}**

Sample Preparation

- **Cultured Benthic Foraminifera**

Havach et al., 2001
Hintz et al., 2004

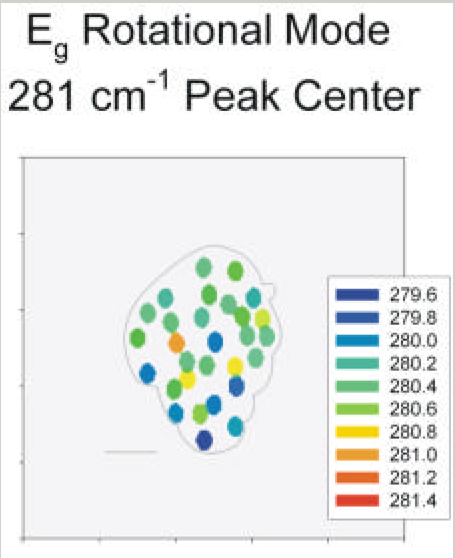
- **Foraminiferal Cleaning**
  - ? **5% NaOCl for 24 h**
  - ? **4´ Methanol Rinses (2´ 25 ºC; 2´ 60ºC)**
  - ? **1:1 30% H_2O_2 : 0.1 M KOH (60ºC) for 10 m**
  - ? **0.25 M Citric Acid in 16 M NH_4OH made up to 1 M in Hydrazine (60ºC) for 2 m**

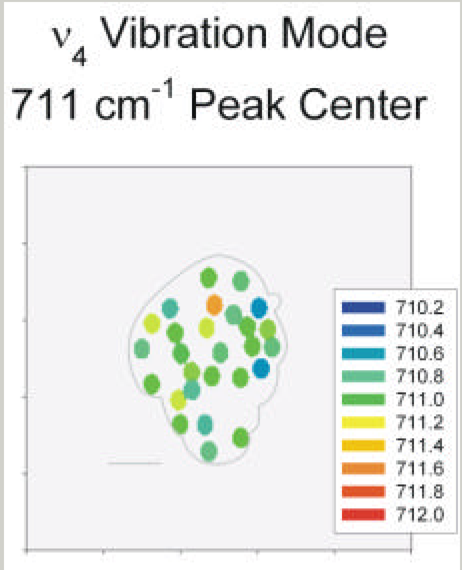
Boyle and Keigwin, 1985/86
Lea and Spero 1992; 1994
Havach et al., 2001
Stoll et al., 2001

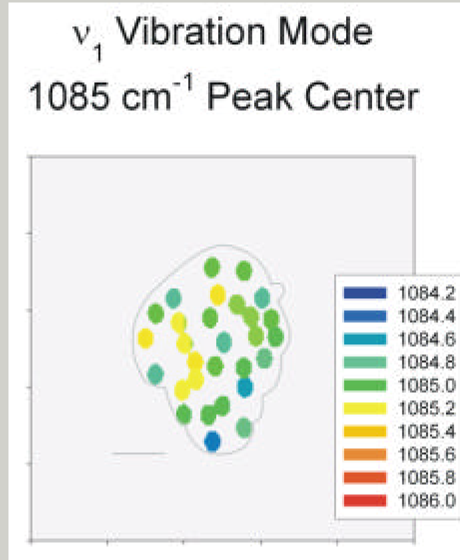
- **Photobleach 48-72 hours with 532 nm laser**

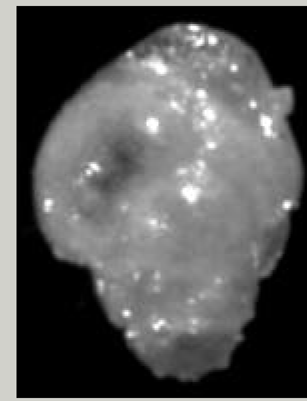
Shea and Morris, 2001

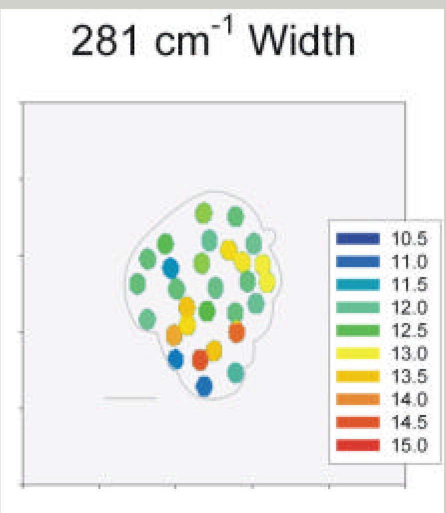
Intra-Individual Variability

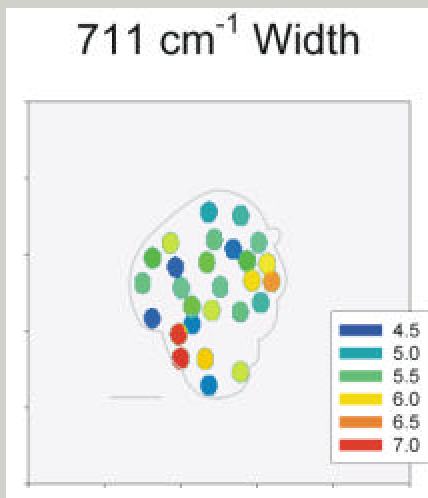


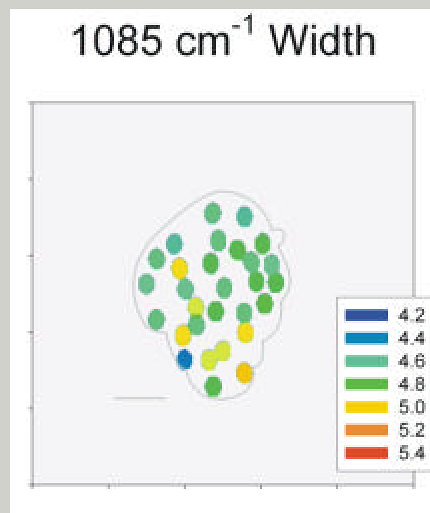




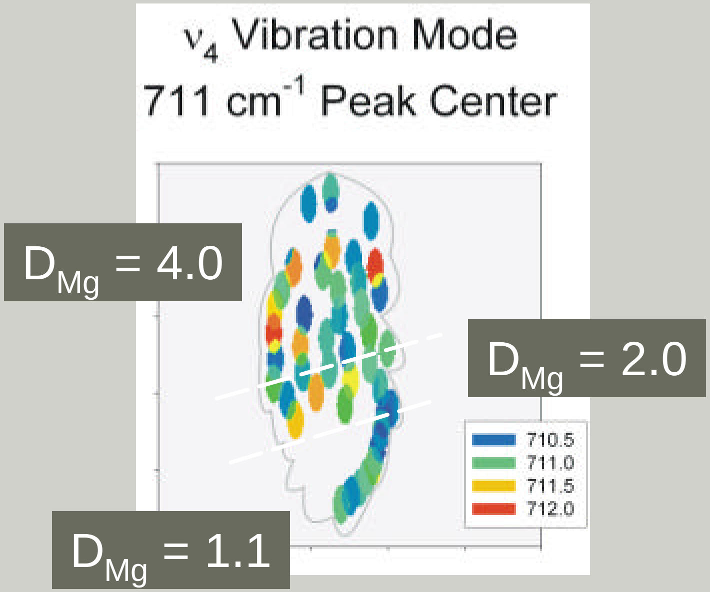


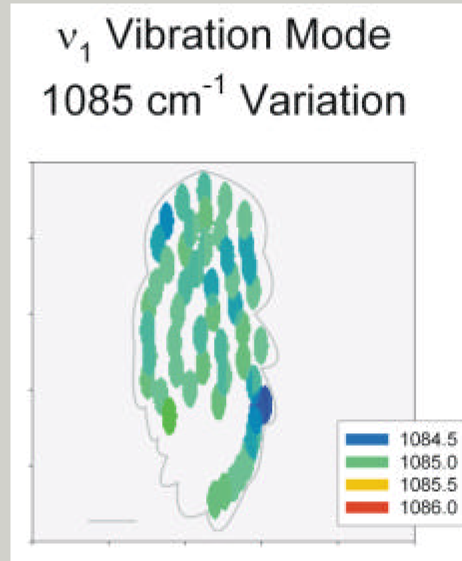


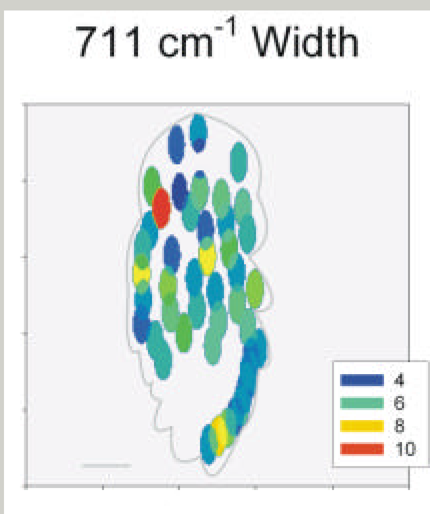


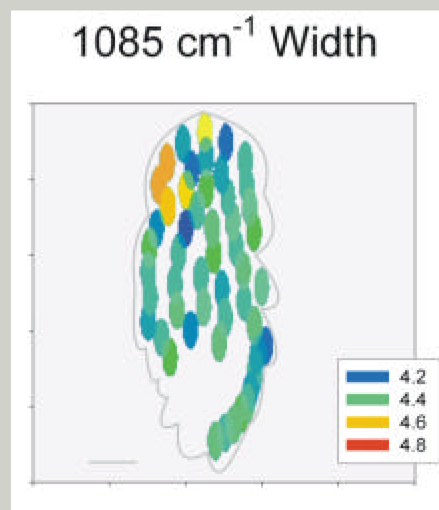


Intra-individual Variability

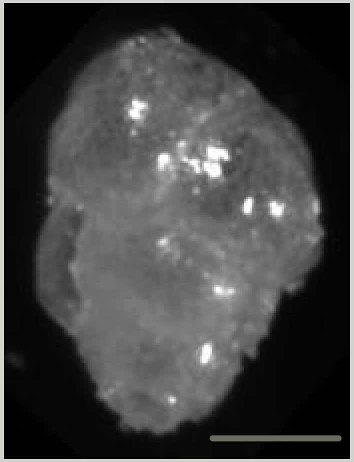


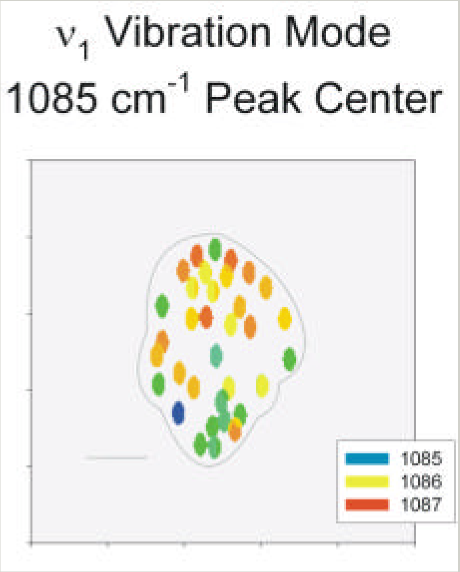


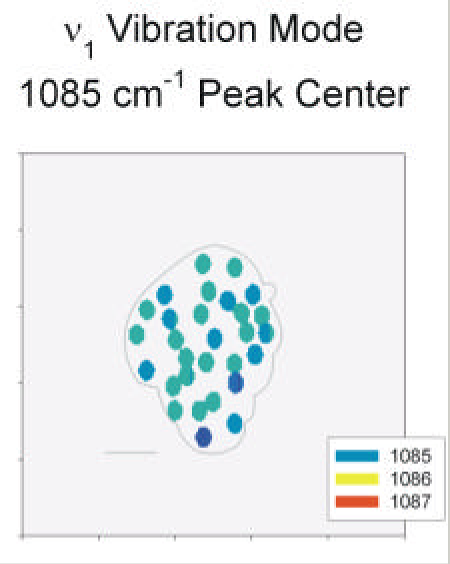


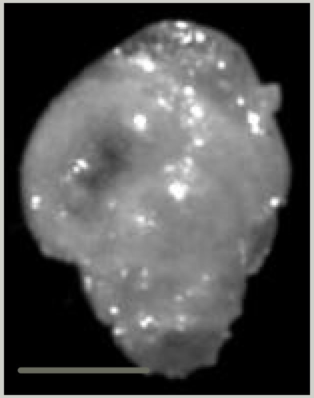


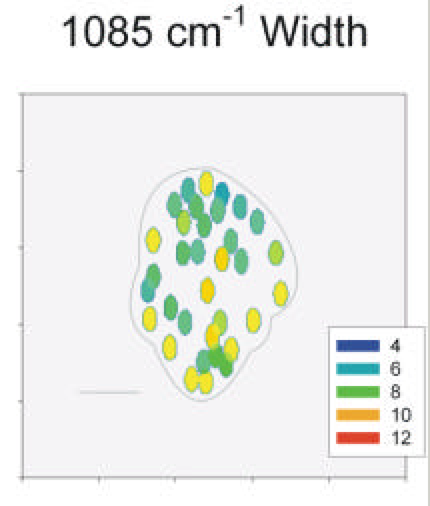
Inter-individual Variability

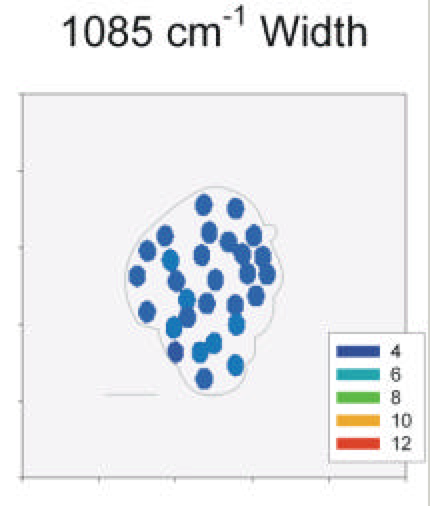




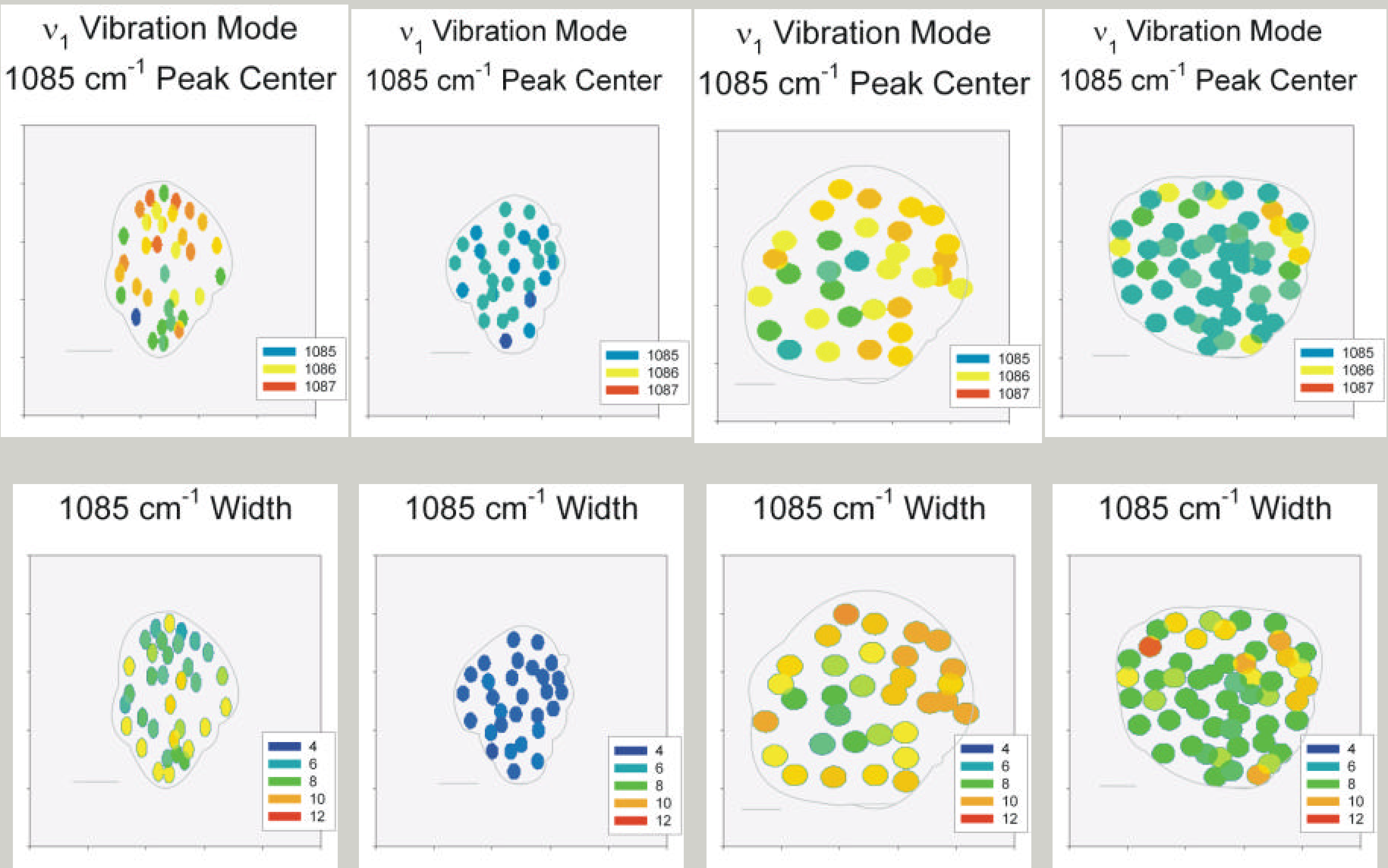






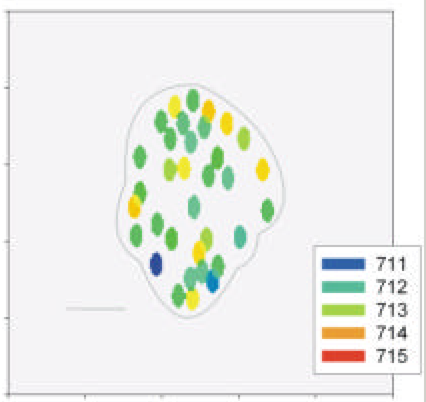


Inter-species Variability

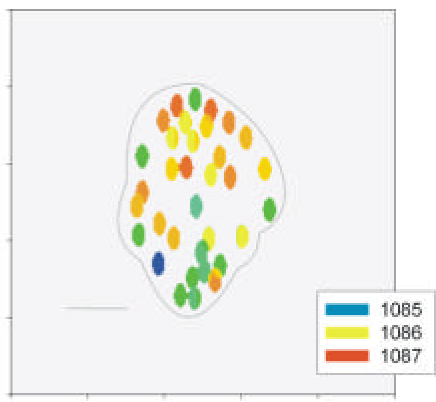


Bulimina aculeata Cleaning

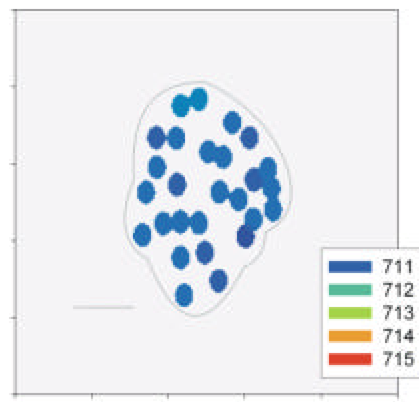
ν_4 Vibration Mode
711 cm^{-1} Peak Center



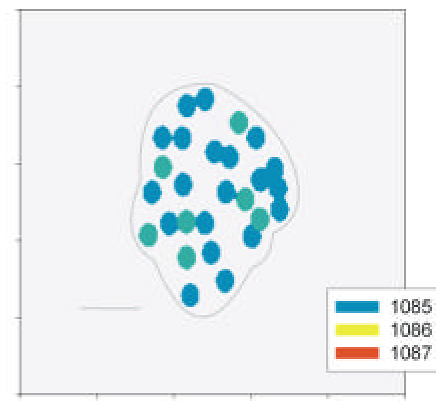
ν_1 Vibration Mode
1085 cm^{-1} Peak Center



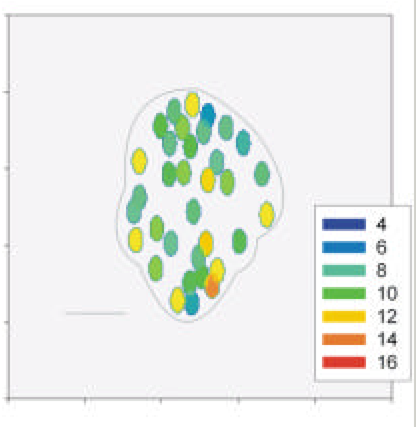
ν_4 Vibration Mode
711 cm^{-1} Peak Center



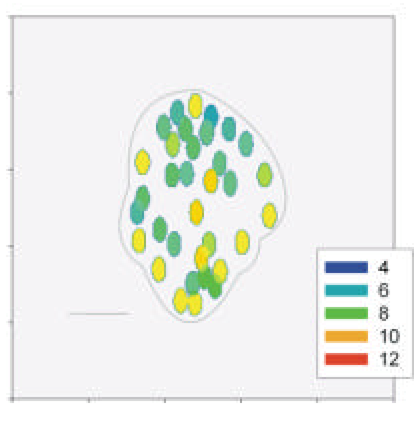
ν_1 Vibration Mode
1085 cm^{-1} Peak Center



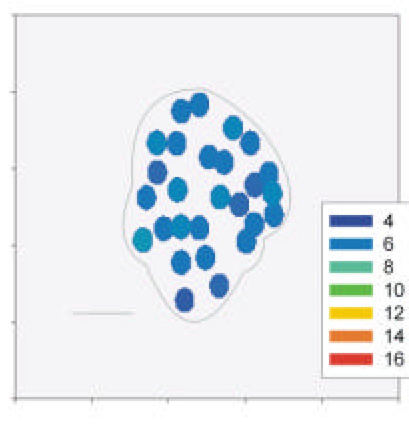
711 cm^{-1} Width



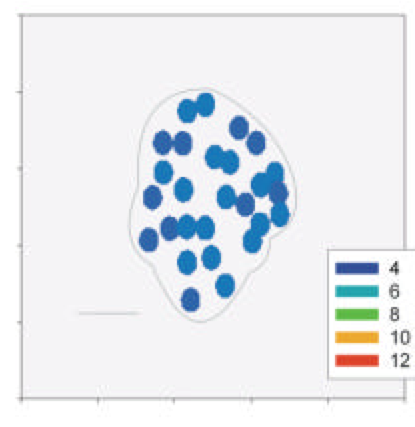
1085 cm^{-1} Width



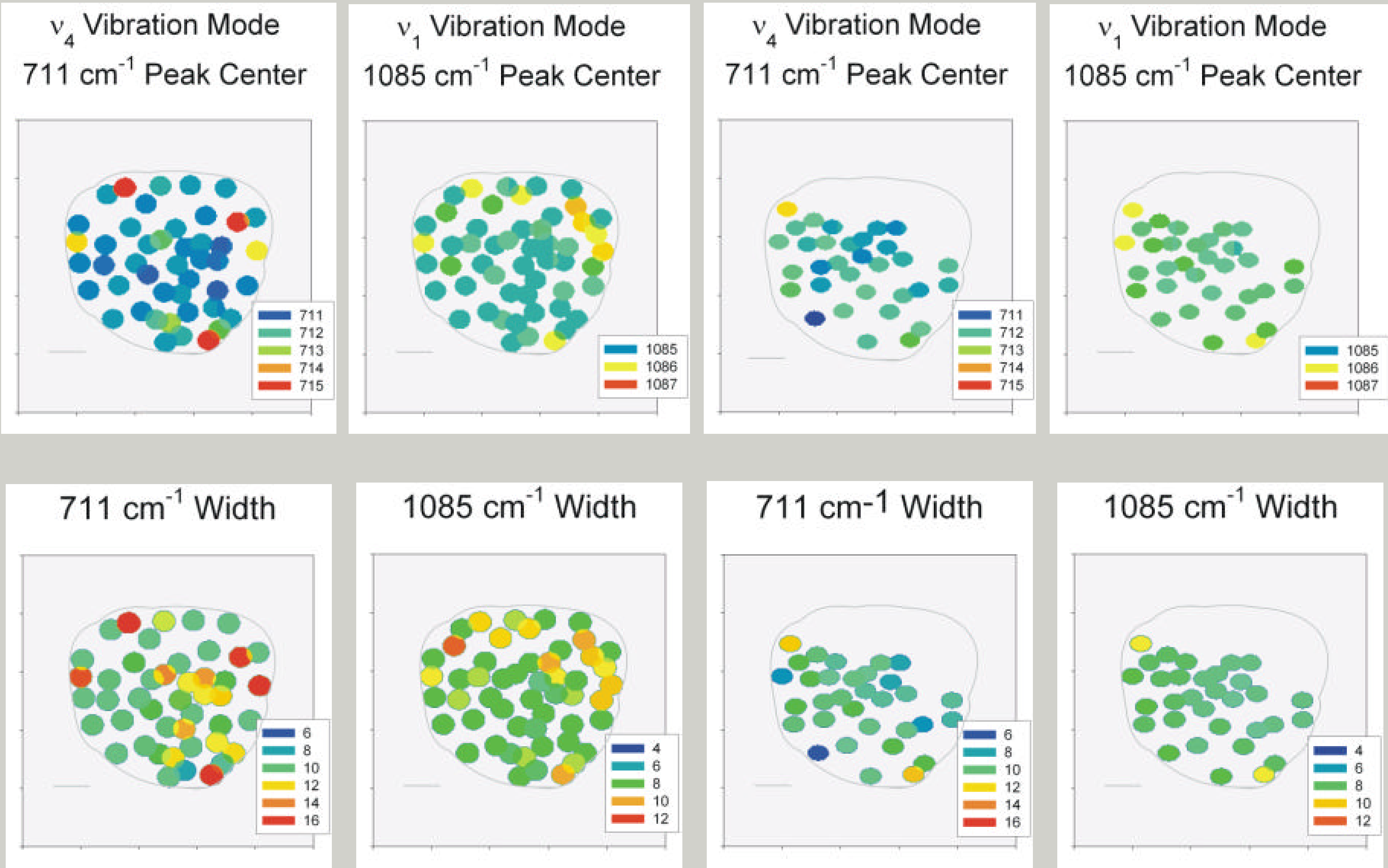
711 cm^{-1} Width



1085 cm^{-1} Width



Rosalina vilardeboana Cleaning

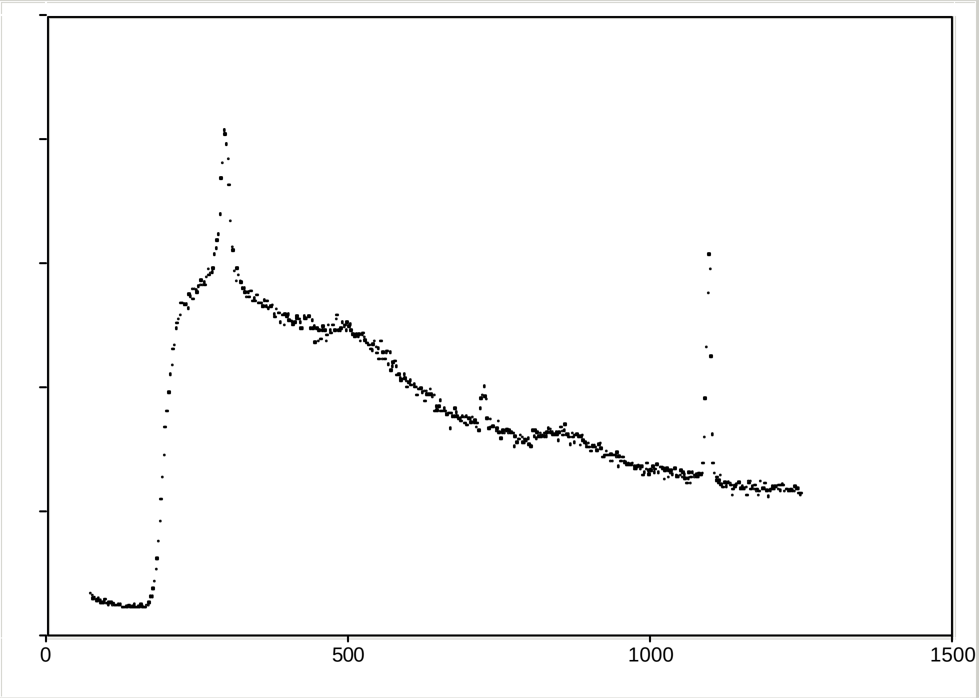


Weaknesses of ns SP LIBS

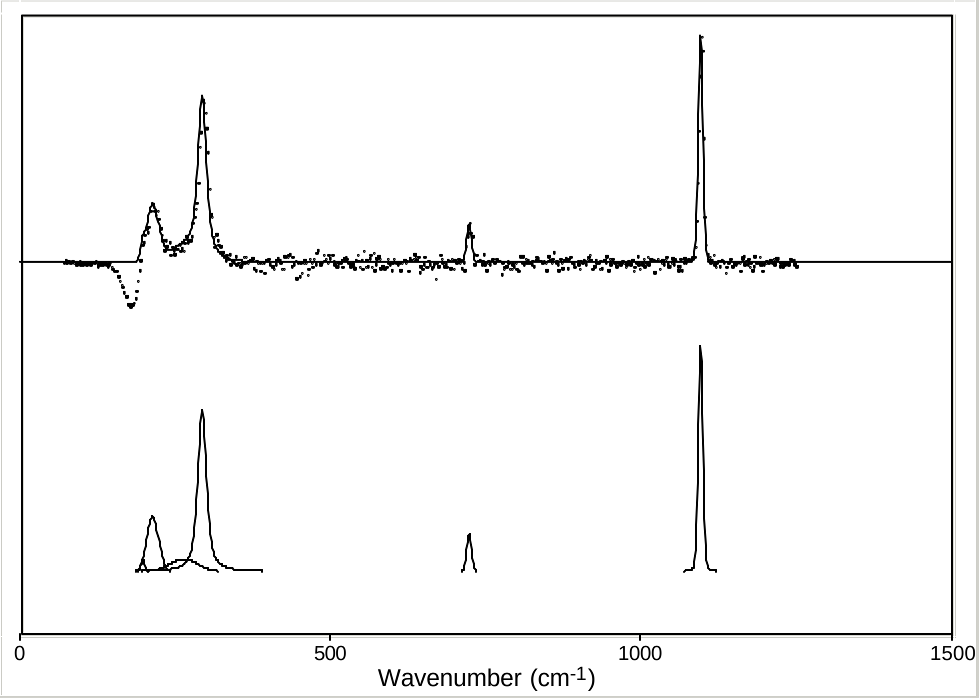
- **Matrix effects**
- **Poor shot-to-shot reproducibility**
- **Poor ablative reproducibility**
- **Part-per-million limits of detection**

Some of the weaknesses of single-pulse LIBS are improved using Dual-Pulse, and ultra-short (fs) pulse excitation.

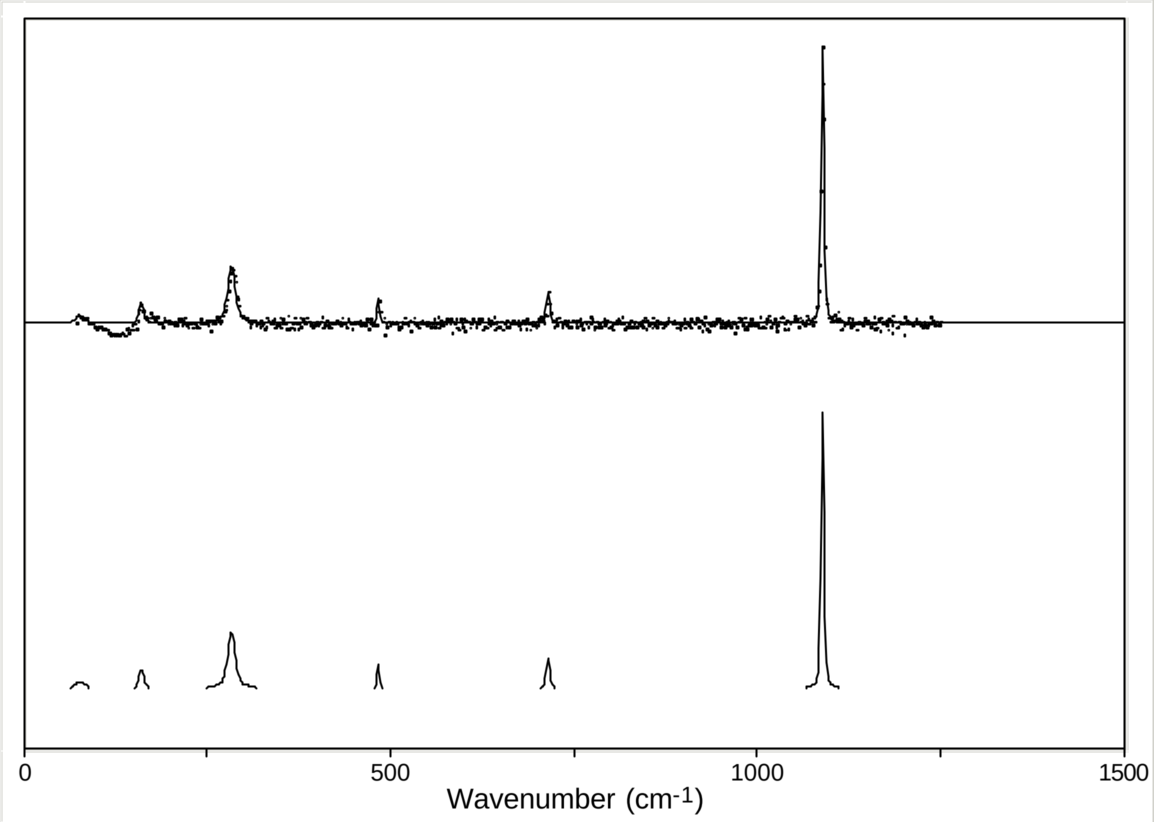
Bulimina aculeata test calcite 785 nm HeNe Laser excitation.



B. *aculeata* Raman spectrum (from Figure 1.) which has been background corrected and fit with Gaussian-Lorentzian distributions.

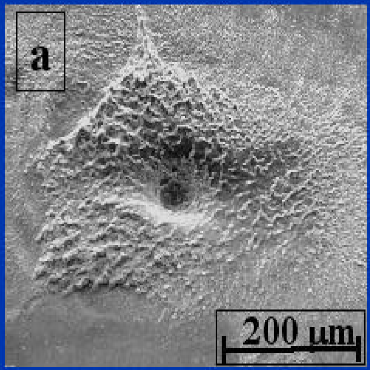


B. aculeata Raman Spectrum after photobleaching using a 532nm frequency doubled Nd:YAG excitation.

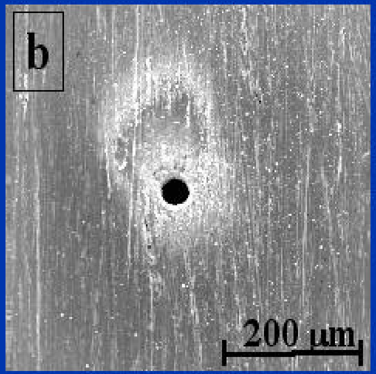


Ultra-short laser ablation improves the precision of material removal

The difference between long and short pulses

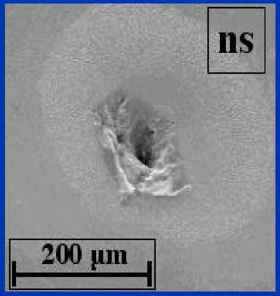


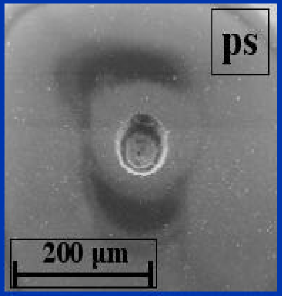
nsec



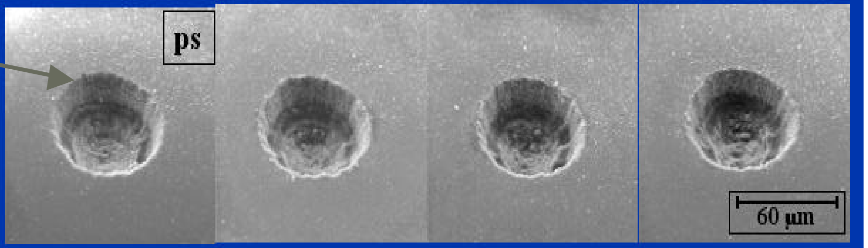
psec

Comparison of 7 ns and 1.3 ps excitation of glass craters





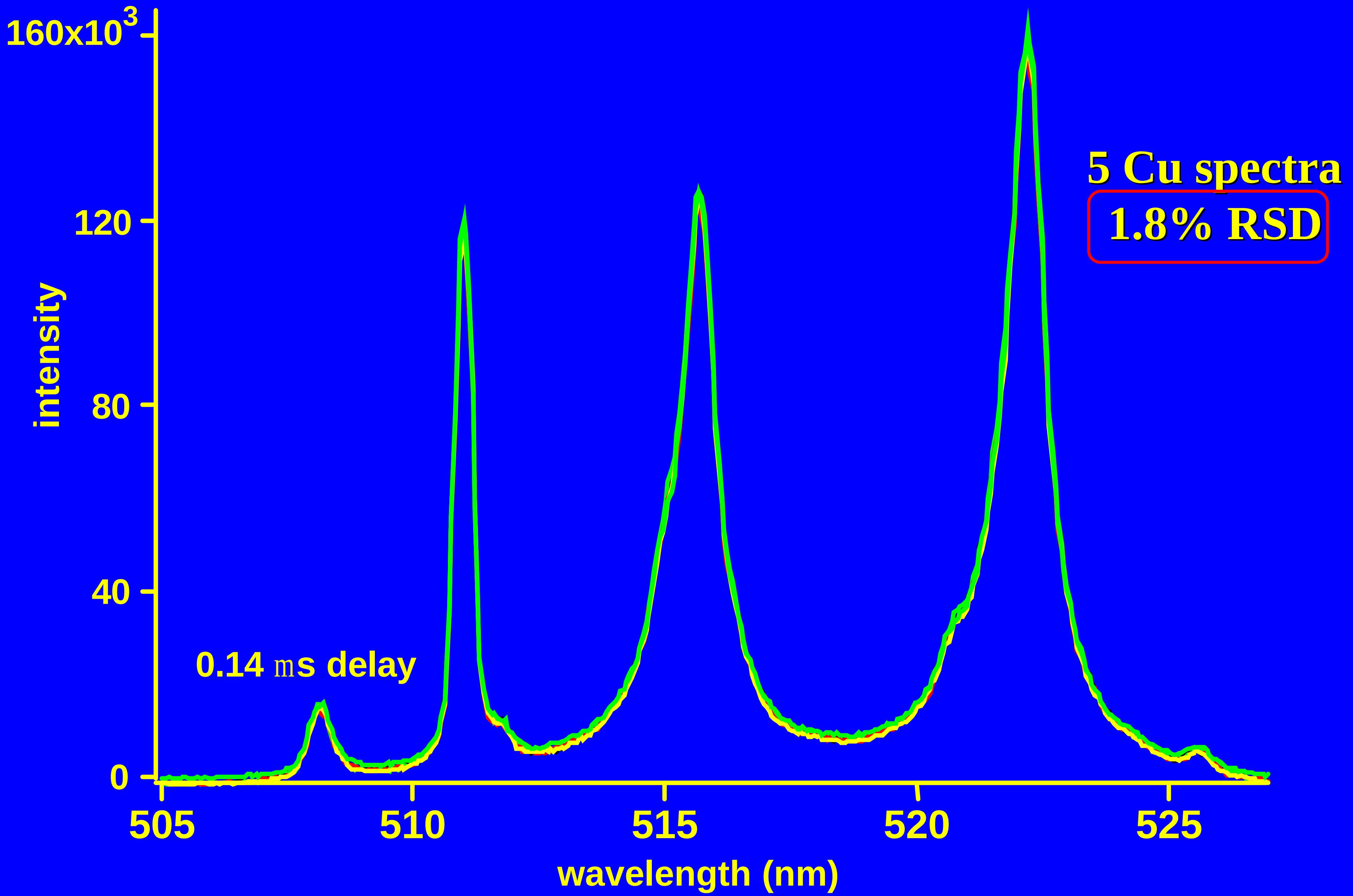
High precision material ablation using ps pulses



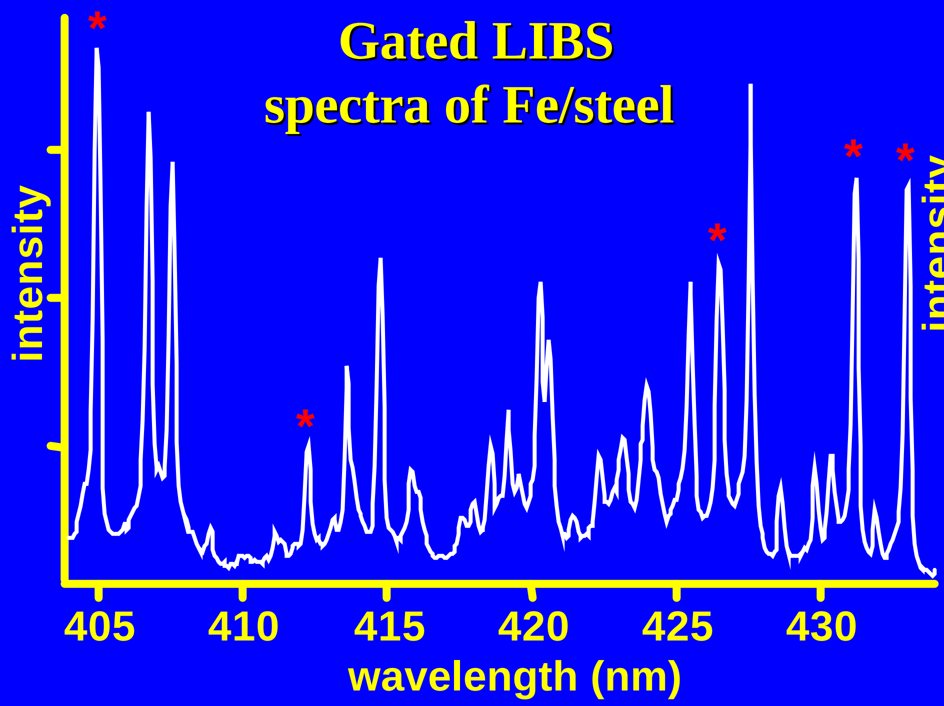
Craters appear very similar with ps excitation

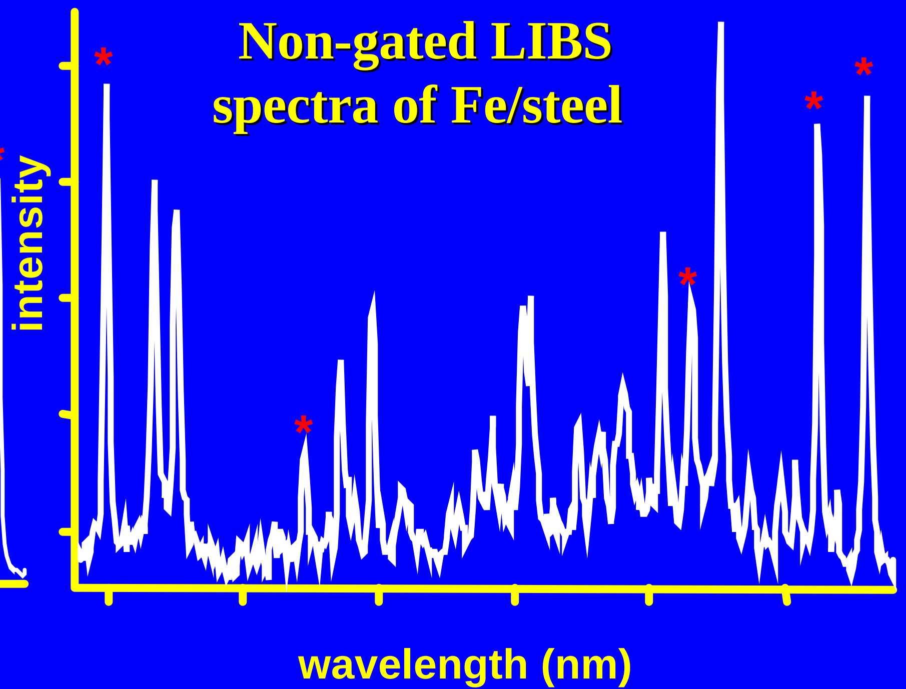
Picosecond ablation for copper and glass samples.

Reproducibility is *very good* using 140 fs excitation



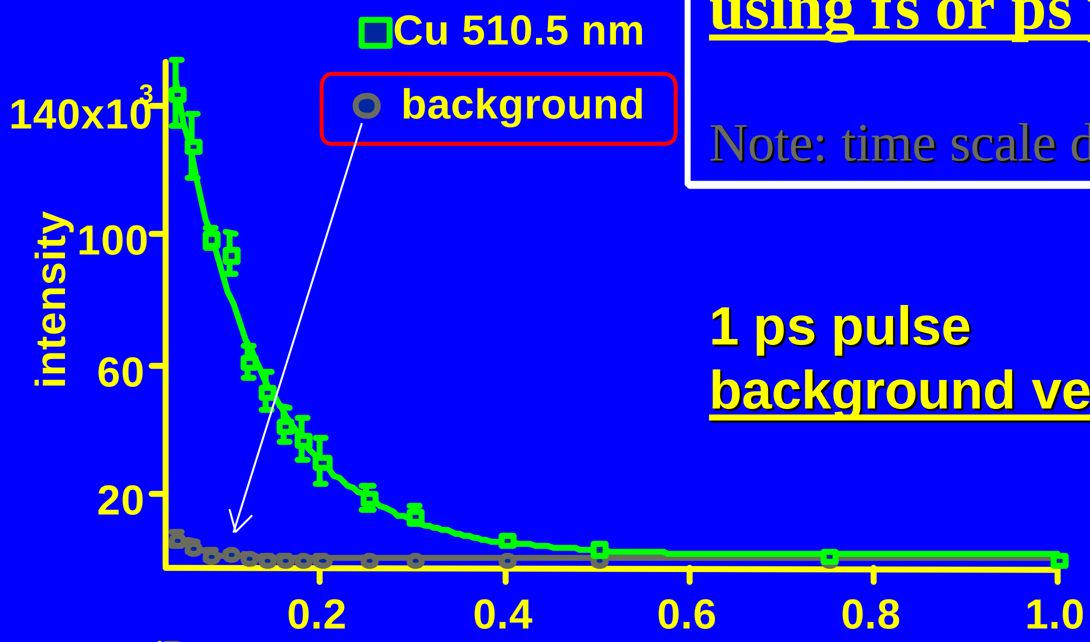
When using 140 fs excitation, the background is low enough to measure high-quality LIBS spectra without gating?





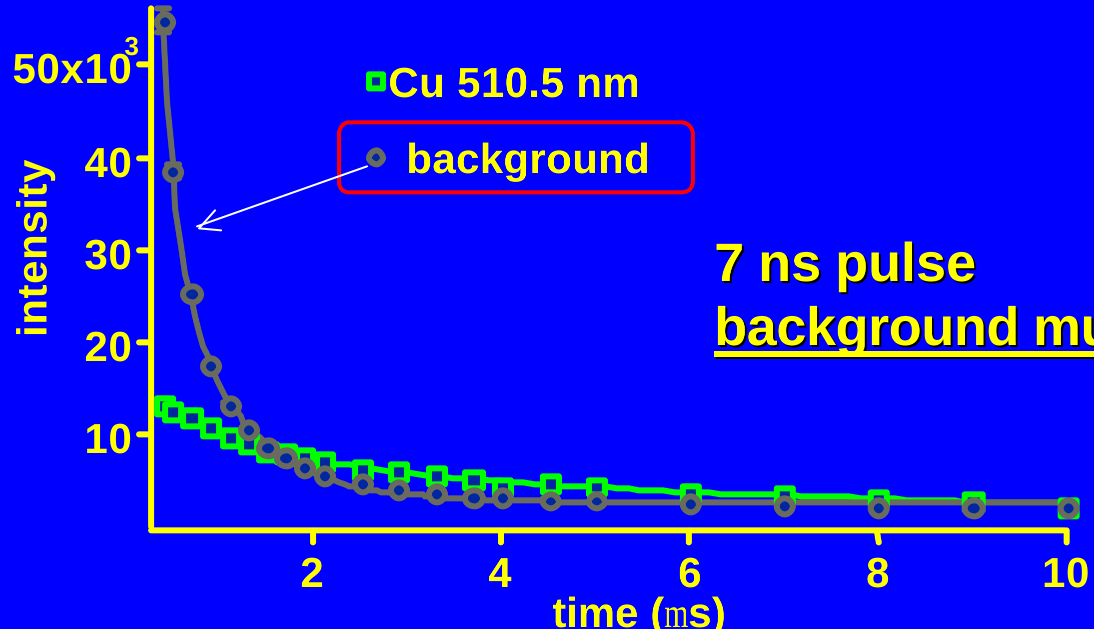
<u>Background emission is very low using fs or ps pulse</u>: no gating!

Note: time scale difference



1 ps pulse

<u>background very low</u>

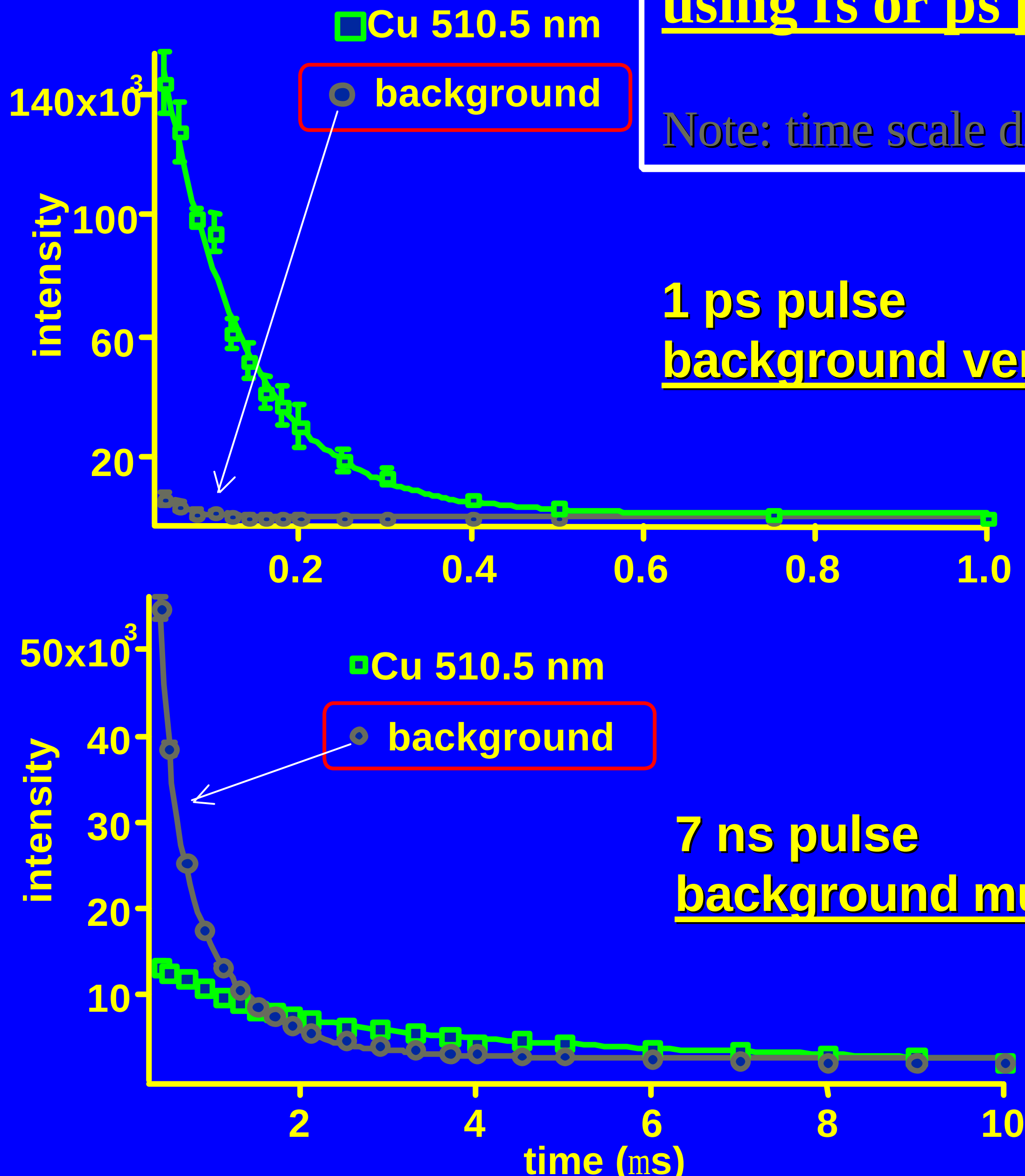


7 ns pulse

<u>background much higher</u>

<u>Background emission is very low using fs or ps pulse</u>: no gating!

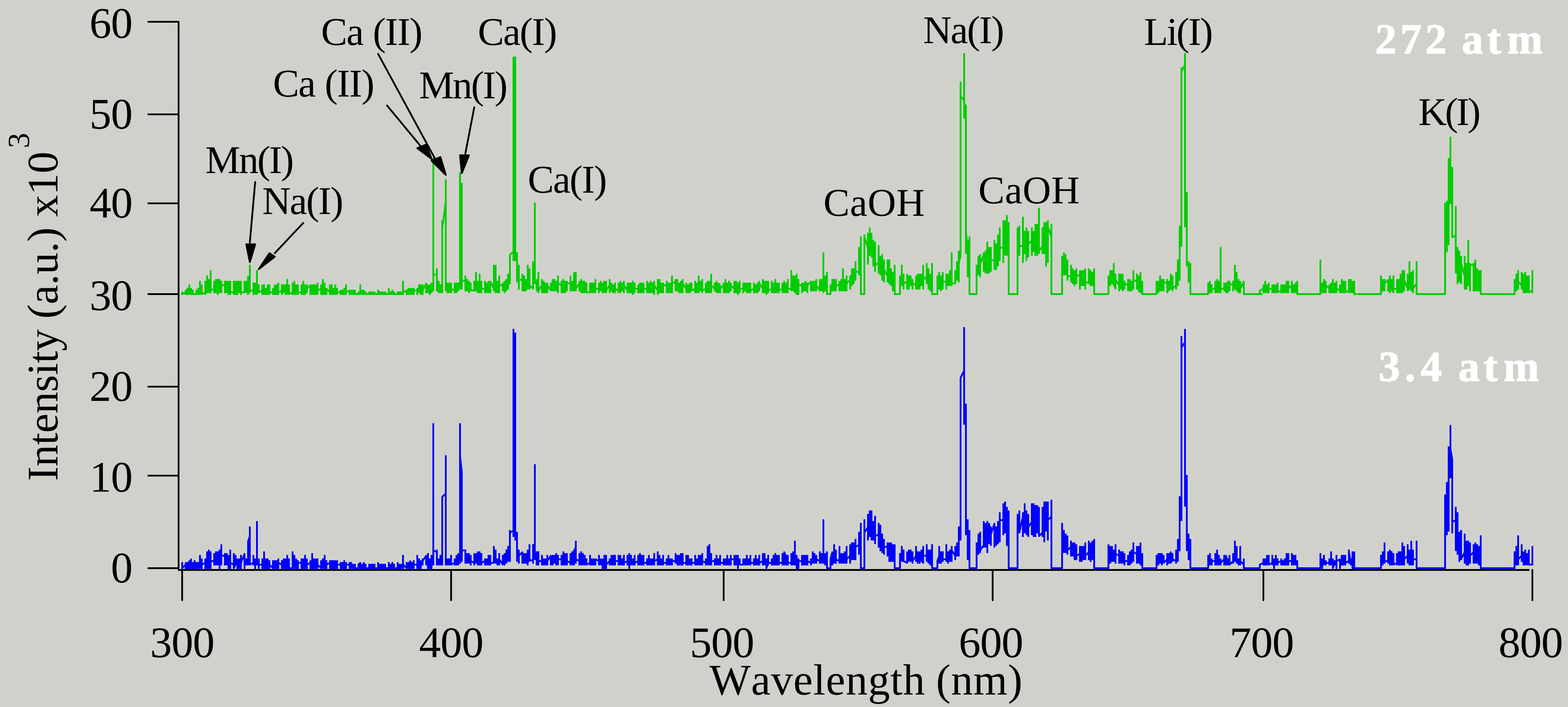
Note: time scale difference



1 ps pulse
<u>background very low</u>

7 ns pulse
<u>background much higher</u>

High Pressure SP-LIBS Spectra



Pressure appears to have little effect on SP-LIBS emission

Several analytes are observed at elevated pressures!

Single-Pulse LIBS Summary

1. Our SP high pressure measurements show we are currently able to detect Li, Ca, Na, K, Mn, Ba, Sr at pressures exceeding 272 atm (corresponding to an ocean depth of approximately 3000 meters).

2. Pressure appears to have little effect on SP-LIBS measurements.

3. Emission decay rates are unaffected by pressure.

4. There are optimal ranges of laser pulse energies that provide the most intense analyte emission. The optimal ranges of laser pulse energies are element dependent but are not affected by pressure.

We previously combined LIBS with Raman (Angel & Cremers). Here, LIBS gives the element (Ca, Mg), Raman gives the anion (CO_3^{2-}, SO_4^{2-})

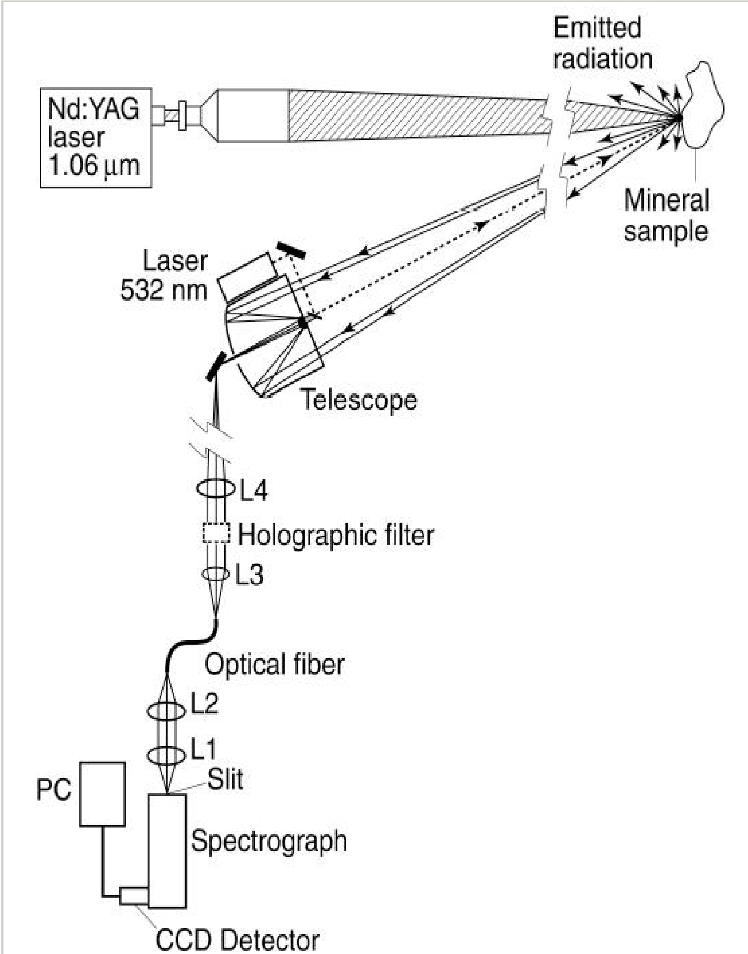
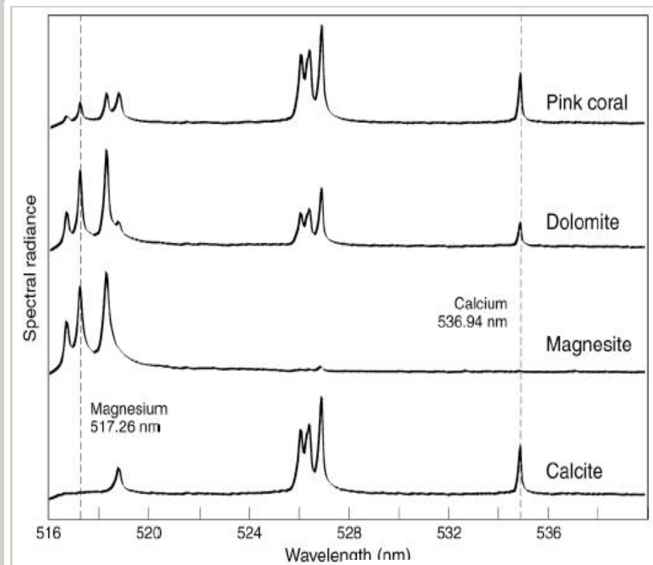
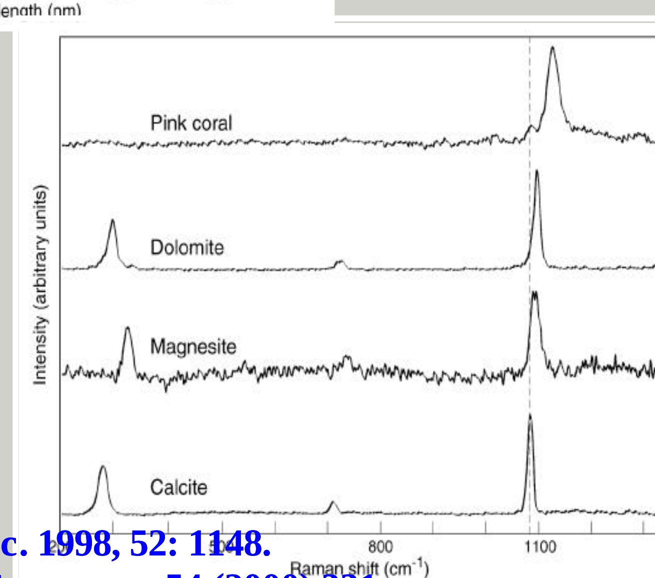


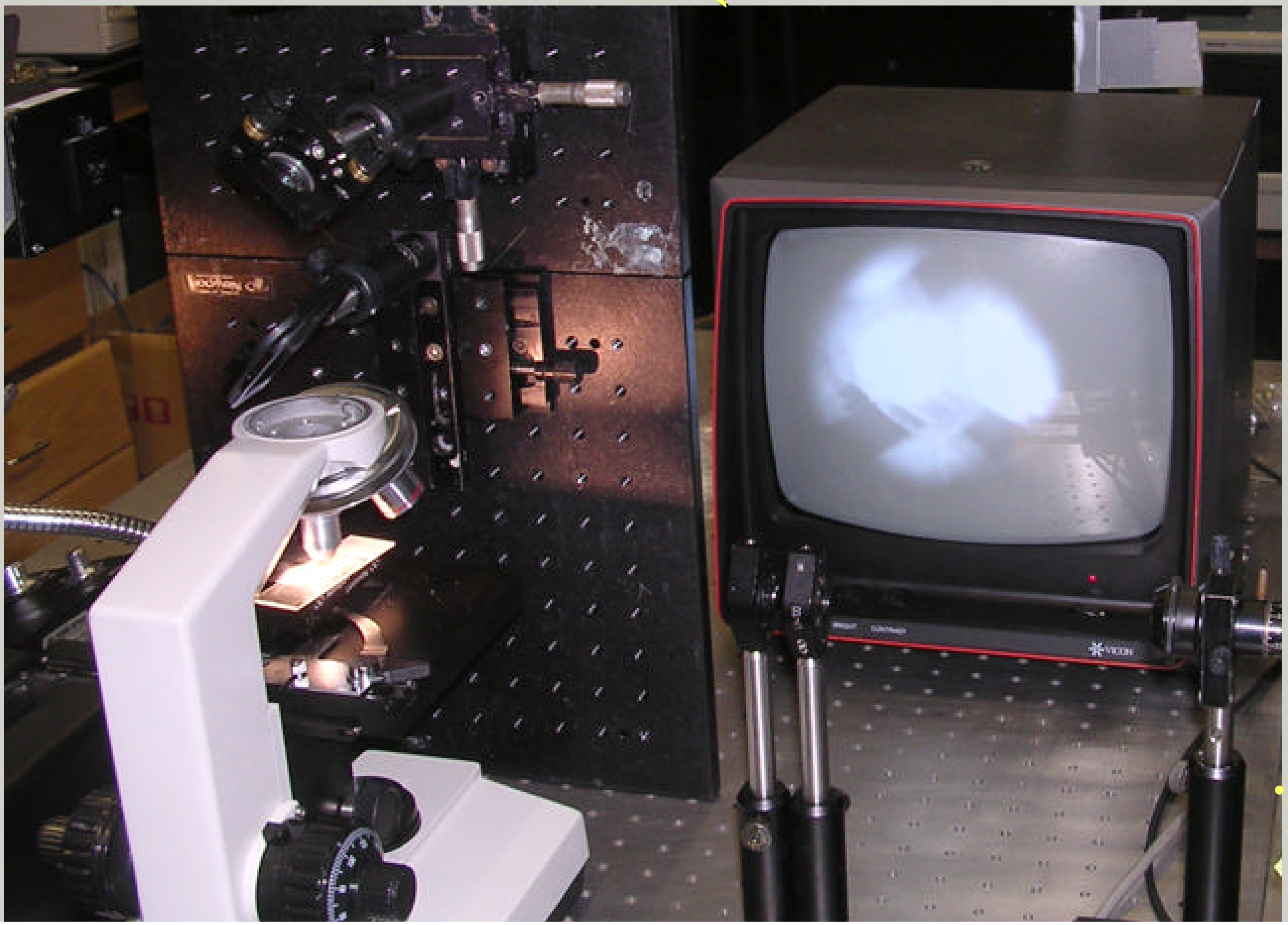
Figure 1. Schematic representation of the remote LIBS and Raman system.

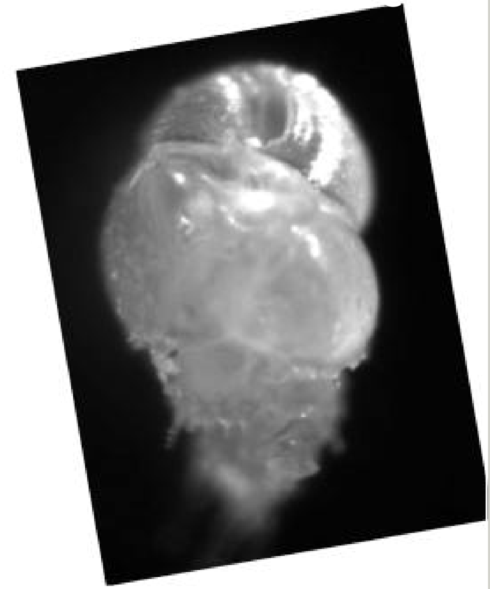




B.J. Marquardt, D.N. Stratis, D.A. Cremers and S.M. Angel, Appl. Spectrosc. 1998, 52: 1148.
S.K. Sharma, S.M. Angel, M. Gosh, H.W/ Hubble, and P.G. Lucey, "Appl. Spectrosc., 54 (2000) 331.
H.W. Hubble, M. Ghosh, S.K. Sharma, K.A. Horton, P.G. Lucey, S.M. Angel and R.C. Wiens, Lunar Planet. Sci., 33 (2002) 1935.

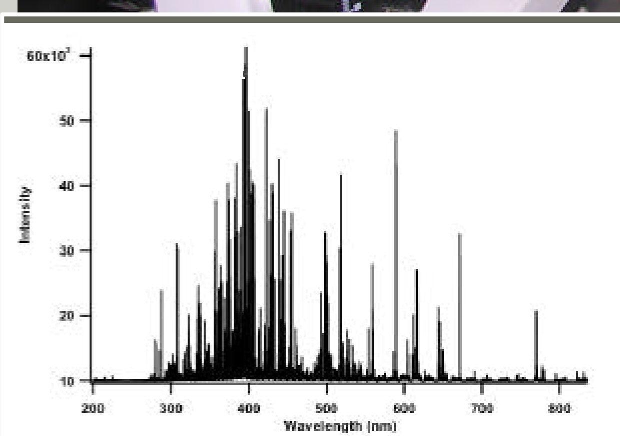
Our first microLIBS: (will combine mLIBS and mRaman)

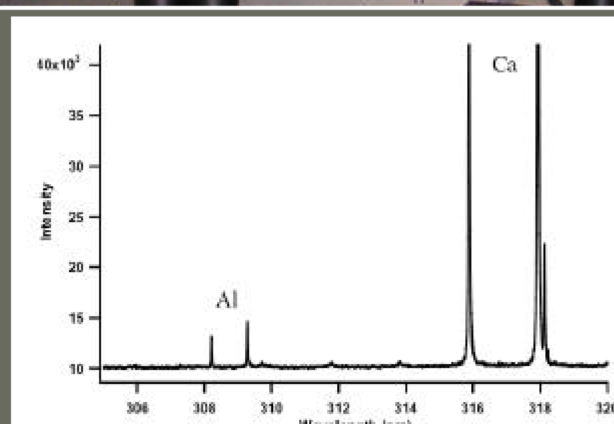


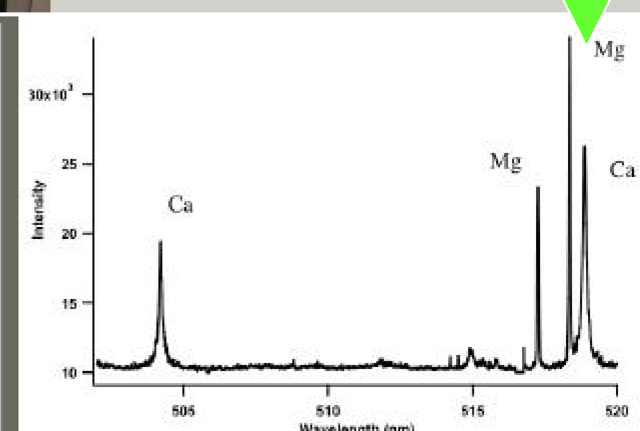


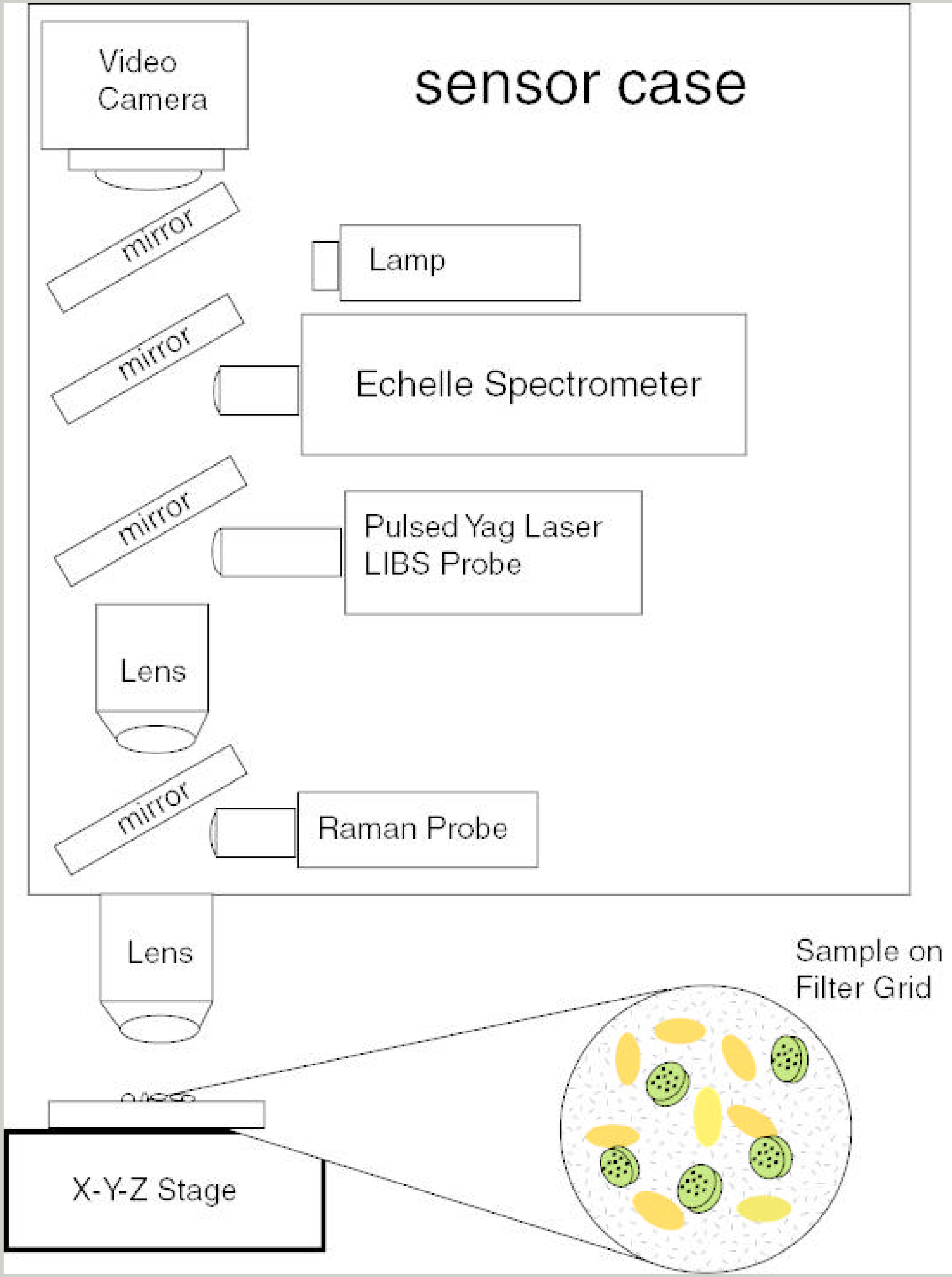
B. aculeata

- LIBS gives minor element ratios: Mg/Ca, Sr/Ca, Ba/Ca

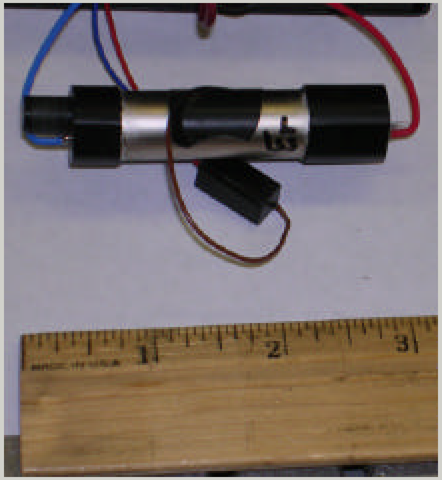








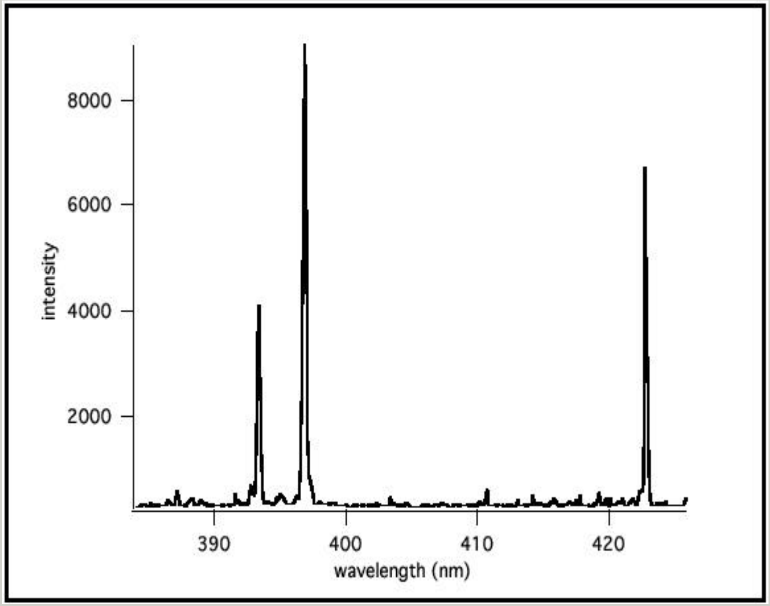
Potential platforms: ships, moorings, sediment traps



Miniature 0.3 J battery powered Nd:YAG laser.

Other uses for microRaman/LIBS

- **Measure dust/pollen particles in ice cores. (Global, paleo-climate research)**
- **Characterization of oceanic particulate phases**
- **Forensic residue/particle analysis**



LIBS spectrum of $CaCO_3$ particles (0.1 mg/mL) in ice taken using a *single* 20 mJ laser pulse. Atomic and ion lines are shown.

photo by Mark Tw Taken from: Chronicles of the Arctic System Science Research Program Spring 1997, Volume 5 Number 1

Conclusions

- **Micro-Raman Spectroscopy**
  - ? **Rapid, non-destructive, high-spatial resolution**
  - ? **Intra-individual variability, inter-species comparisons**
  - ? **Cleaning procedure effects**
- **Mg/Ca incorporation alters Foraminiferal Calcite Crystal Structure**
  - ? **Single Carbonate Signature**
- **Calcite strucutre and composition can be monitored in-situ**

Future Development

- **Mg/Ca Quantification using micro-Raman**
- **Dual micro-Raman / Laser induced Breakdown Spectroscopy (mR-LIBS)**
  - ? **Single instrument**
    - ? **Crystal structure**
    - ? **Minor-element ratios**
  - ? **Minimal sample preparation/cleaning**
    - ? **Limits procedural contamination and artifacts**
  - ? **Rapid analysis of Single Foraminifers**

Acknowledgements

Shana Burnett, Jon Scaffidi, Chris Dockery

Funding for Research

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