Ice-Core Analysis in a Polar Environment using Laser-Induced Breakdown Spectroscopy (LIBS)

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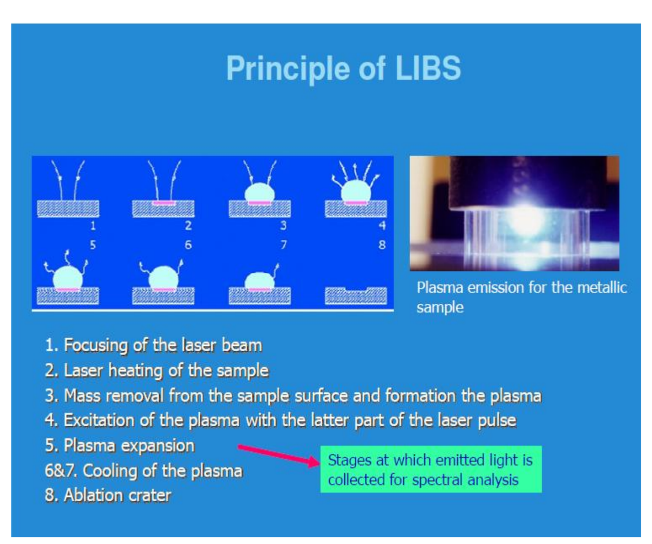
ABTRACT

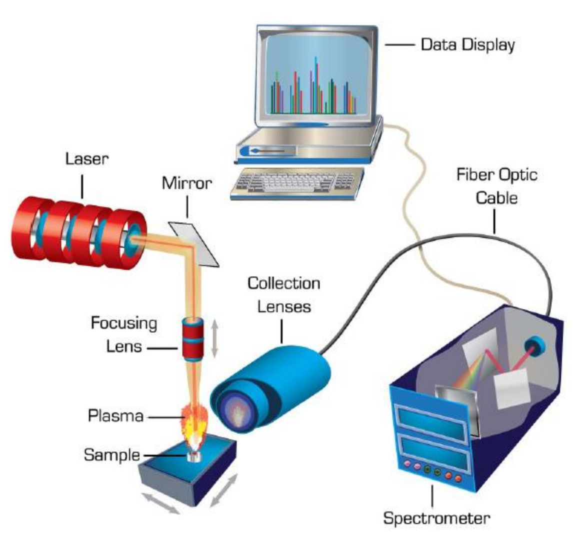
Laser induced breakdown spectroscopy (LIBS) was being evaluated for its suitability as a detector of paleo-climate proxy (atmospheric circulation) indicators while operating in a polar environment. The focus is on detection of paleo-climate proxy indicators such as Ca, K, Mg, and Na to eliminate the logistical need of shipping ice-core samples out of the field. A secondary objective is to determine if a higher degree of spatial precision is possible with LIBS such that the age interval can be narrowed (<0.5 years corresponding to ~7 cm interval) to see abrupt climate change events. LIBS analysis was performed on an ice-core from Greenland, which was previously analyzed by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS). ICP-MS analysis establishing elemental concentrations of parts-per-trillion. Preliminary results using a commercial LIBS system built by Applied Spectra Inc. (ASI) indicate detection of peaks of C, N, and O consistent with the presence of organic material as well as major ions (Ca, K, Mg, and Na) and metals (Al, Cu, Fe, Mn, Ti). Analysis was performed on the ice-core itself using a thermoelectric Peltier Cooler kit to maintain ice integrity. In addition, split samples of the ice-core were melted and sublimated and filtered through 0.45 micron nylon filters. Both solid particulates on the filter as well as material dissolved and sorbed/precipitated to the filter were analyzed.

Additionally, LIBS detection capability for analysis of ice-entrapped oil was tested. The spectra (C, N, O) consistent with heating oil was detectable.

INTRODUCTION

- Laser induced breakdown spectroscopy (LIBS) involves use of laser energy to ablate a material (laser ablation) and simultaneously measure spectral emissions of elements and some cases isotopes and species
- LIBS is capable of real-time, multi-element, molecular, isotopic analysis with a single instrument for ice, air, water, soil, and other surfaces without need for sample preparation
- LIBS has been investigated for military, environmental, industrial, geological, archeological, and planetary applications
- Ice-core analysis using LIBS has not been previously reported in the peer-reviewed literature.

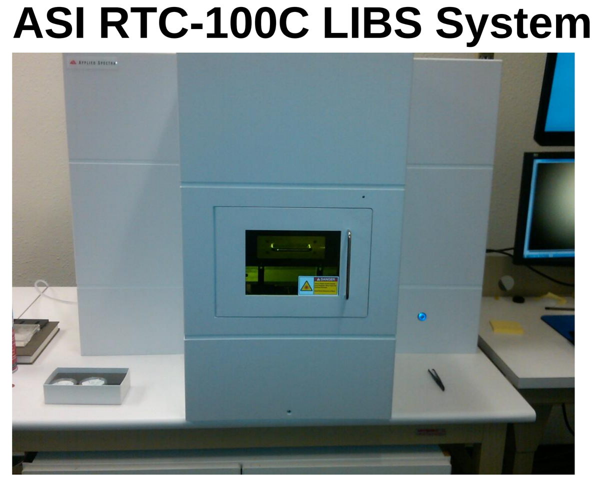




METHODS

- Ice-cores split into fourths
  - Conventional melting and laser ablation ICP-MS analysis
  - Melting and sublimating followed by filtering (0.2 micron nylon filter paper) and LIBS analysis of particles and filter paper
  - Direct LIBS ice-core analysis of ice and particulates
- Applied Spectra RT-250 LIBS instrument used initially, includes a 266 nm laser. Insufficient power so switched to 1064 nm research laser.
- Later work conducted on commercial ASI RT-100C system with 50 MJ laser at 1064 nm
- Five locations per ice core sample were interrogated with 25-500 shots per location, which resulted in a depth profile of the ice core
- To prevent melting during analysis. ASI developed a Peltier cooler platform chamber allowing ice stabilization during analysis

ASI RTC-100C LIBS System



Pelletier Cooler

Experimental Parameters and Procedures

Table 1: Instrument and Experimental Parameters

Instrument: RT250-EC 6 Channel	
Laser	Nd:YAG
Wavelength	266 nm
Energy output	100 %
Spectrometer	6 channels
Gate delay	1.3 μs
Number of shots per location	500
Number of locations	5 per sample
Spot Size	~200μm

•Alaskan intact ice core #33 was cut into 17 subsection samples. The ice core was removed from a test hoop where oil was injected under the ice.

•The samples were sequentially labeled top to bottom as core#33-1 to core#33-10 and core#33-15 to core#33-21.

•Beginning from core#33-16, the ice samples were visibly contaminated by oil.

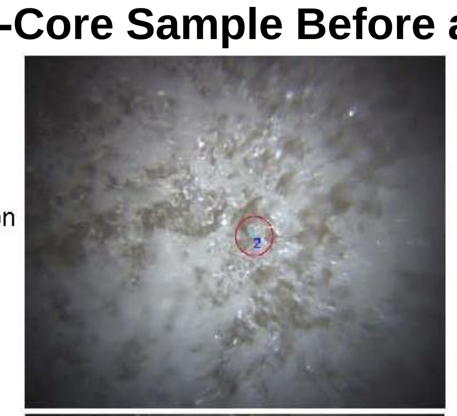
•The samples were analyzed by LIBS using the RT250 system with a Peltier cooler.

•Five locations on each sample were chosen to include both relatively clean and contaminated spots.

•Ice samples were stabilized with dry ice (CO_2) for transportation and custody. They were handled using nitrile gloves during analysis.

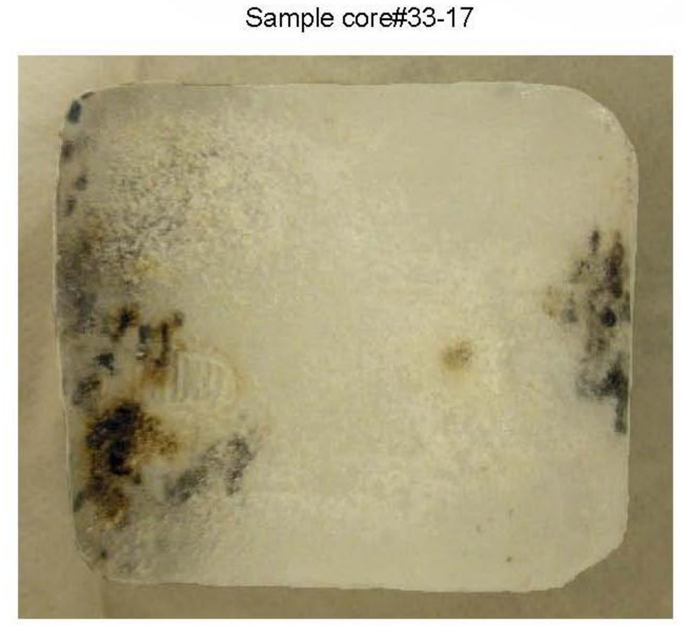
Ice-Core Sample Before and After Ablation

•Before ablation with the laser focused inside the red circle.



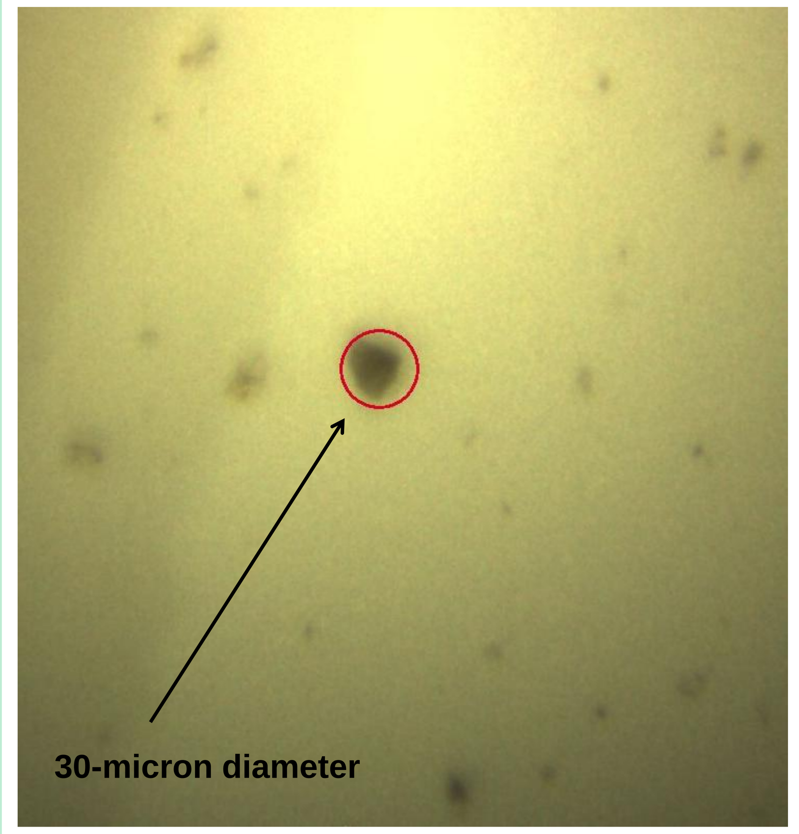
•After ablation a crater was formed.

Sample core#33-17

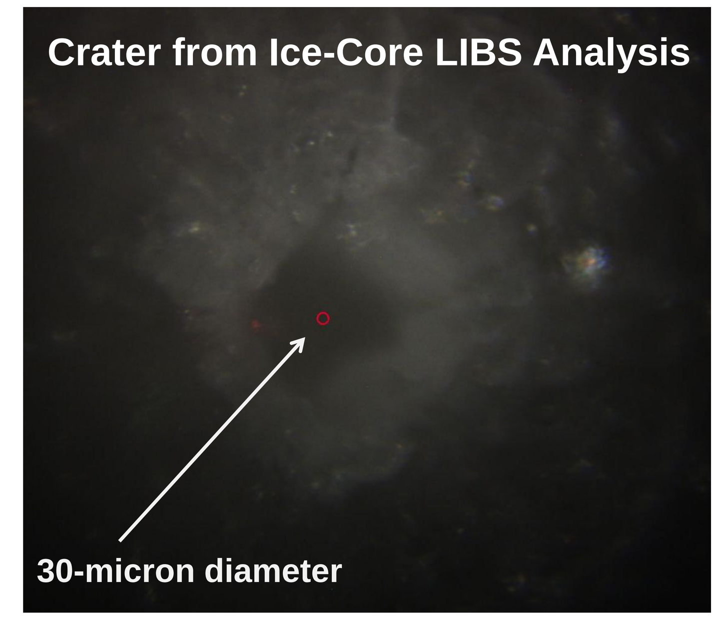


Oil inclusions are visible

Particulate on Filter Paper Analyzed

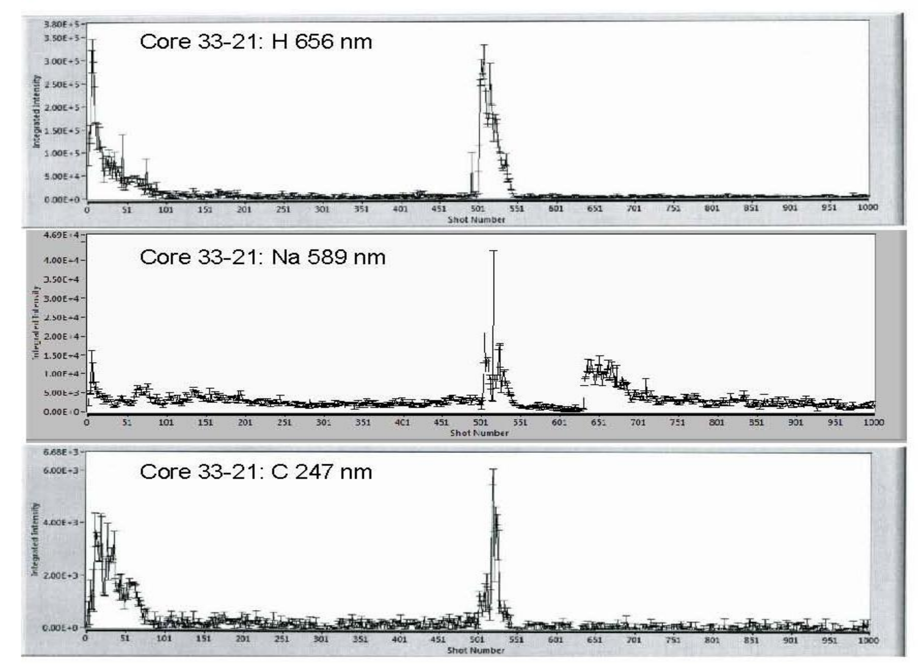


Ice-Core Sample



Examples of Ice Surface Scanning

In this example, the ice sample #33-21 was probed by LIBS at two locations using 500 laser shots at each of them (overall 1000 laser shots). Three spectral lines (H, Na, C) were monitored.



•The intensity of hydrogen indicated that LIBS plasma were becoming weaker as ablation progressed (probably, because of ice melting inside the developing laser ablation crater).

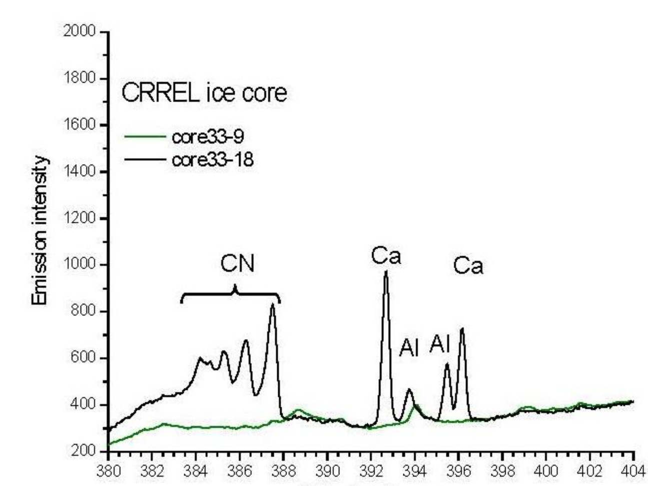
•Even a weaker plasma at the higher laser shot numbers was able to detect a high sodium-containing inclusion below the ice surface (as evidenced by the Na intensity between shot numbers 630 to 700).

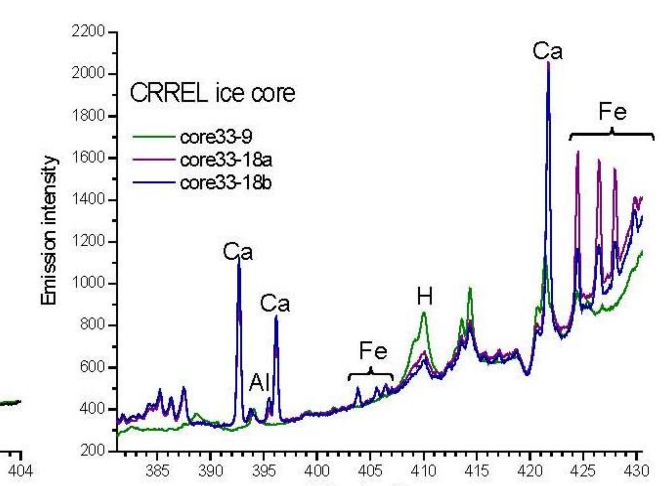
•Carbon emission intensity did not correlate with sodium emission but behaved differently at different locations.

•In most cases, a visibly clean ice did not produce any emission from carbon.

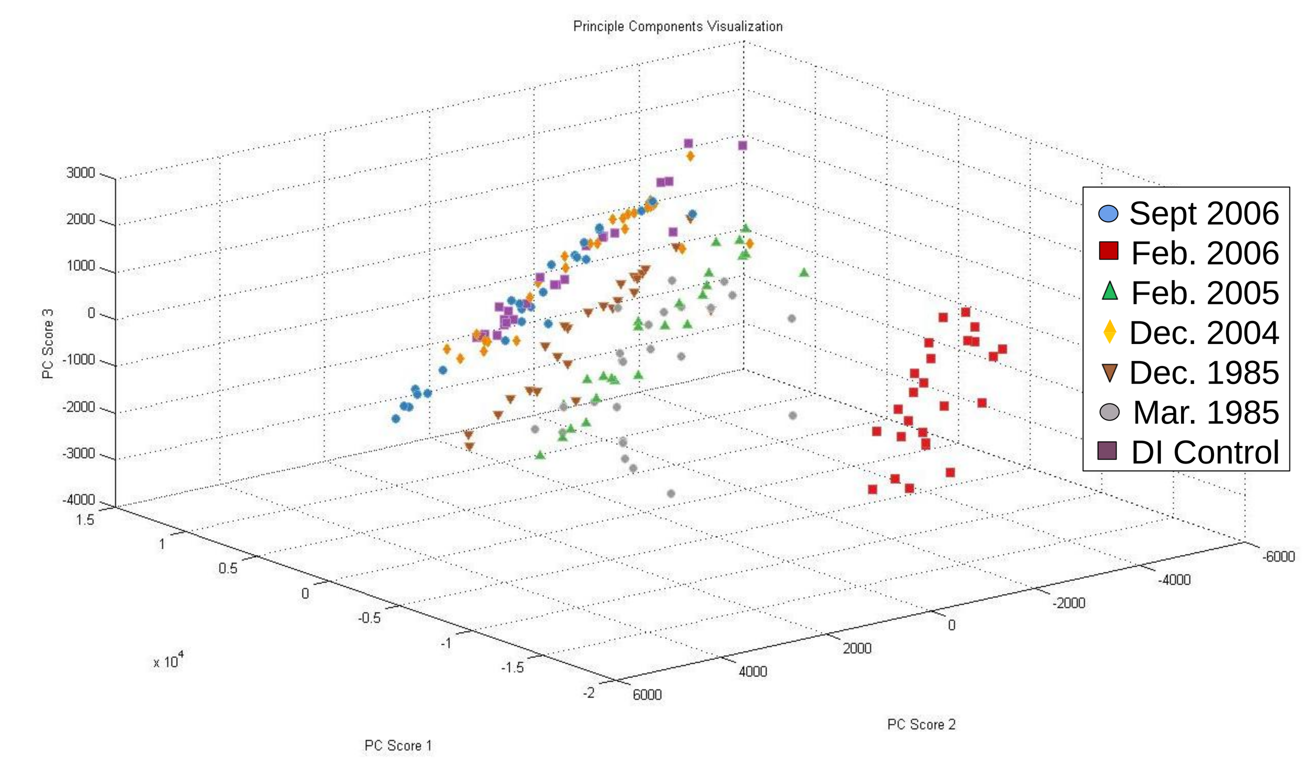
Elements Detected and Examples of Spectra

- Substantial content of Na and Ca was detected in the ice core samples without any significant correlation to the oil inclusions.
- Spectral lines of atomic carbon and emission of molecular radicals CN and C_2 were intense at those spots which were visibly contaminated with oil and in their vicinity - not necessarily visibly contaminated areas.
- Other elements detected in some of the ice samples were K, Al, Fe, and possibly Sr.





Principal Component Analysis for Paleo-Climate Proxy) Indicators in Greenland Ice-Core Samples



Comparison of LIBS to other Analytical Technologies

	SIMS	AES	SEM/EDS	XRF	GD-MS	LIBS
Depth profiling resolution	1 – 20 nm	10 -100 A	0.5 – 3 micron	> 1 micron	100 to 300 nm	30 to 100 nm
Lateral resolution	> 10 micron	0.01 – 2 micron	0.2 to 2 micron	10's micron to 1 mm	>1000 micron	10 micron
Measurement time for 2 micron film	hours	hours	minutes	minutes	10's minutes to hr	seconds
Detection limit	ppb	1000 to 10000 ppm	1000 to 10000 ppm	100 to 1000 ppm	Sub-ppm	ppm
Sample preparation	Minor sectioning to put into the sample holder	Little sample prep but the sample needs to be conductive	Coating with Ir or Au	Minor palletizing or little prep	Minor surfacing cleaning or little sample prep; mainly conductive sample	Little sample prep
Measurement environment	High vacuum	High vacuum	High vacuum	In air	High vacuum	In air/ in chamber with buffer gas
Elemental coverage	Most of elements in the periodic table	Most of elements in the periodic table (except H & he)	Difficult for elements lighter than Carbon	Difficult for elements lighter than Sodium	Most of elements in the periodic table	Most of elements in the periodic table
Instrument cost	500K to 1 Mil USD	350 to 500K USD	500 to 750K USD (with SEM)	80 to 150K USD	400 to 800 K USD	120 to 170K USD

CONCLUSIONS

- First direct analysis of ice-cores using LIBS
- LIBS identified presence of elevated levels of C, N, and O indicative of an organic compound, i.e. oil.
- Detection of paleo-climate proxy indicators (K, Na, Ng, Ca)
- Elemental metal detection (Al, Fe, Mn, Zn) at ppt levels
- Melting of cores and analysis of particulates and precipitates/sorbtive material on filter paper viable
- Analysis of sub 50-micron particulates on filter paper conducive
- Direct analysis of particulates in ice-core difficult due to auto-focusing issues and ability to visually locate
- Pelletier cooler to maintain frozen samples worked relatively well

Acknowledgments

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