

## An attempt at determination of calcium in ice by laser induced breakdown spectroscopy

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### Abstract

In order to develop a continuous and non-destructive technique to analyze chemical constituents in ice, we have applied LIBS (Laser Induced Breakdown Spectroscopy) to ice. We have detected emission of Ca in artificial ice when focused laser pulses are irradiated. The observed sample consumption was only about 1 mm in diameter and 1 mm in depth. The optimum conditions for laser irradiation and timing of spectral detection were examined. Under the optimum conditions studied, we found a linear relationship between emission intensity and Ca concentration in the range of 2.2–20  $\mu\text{g g}^{-1}$ . The detection limit was estimated to be 2.2  $\mu\text{g g}^{-1}$ . These results indicate that LIBS can be used to analyze Ca in ice cores from low and mid latitudes, where Ca concentrations are relatively high. This shows the potential of LIBS as a continuous, high spatial resolution and non-destructive technique in analyzing ice cores.

### 1. Introduction

Variations of chemical constituents in ice cores reflect past environmental and climatic changes (*e.g.* Oeschger and Langway, 1989). To reconstruct these changes on a global scale, ice cores have been drilled in low and mid latitudes, as well as in polar regions. They have been analyzed for various chemical species and have provided new insights into our understanding of the climatic and environmental changes (*e.g.* Oeschger and Langway, 1989; Thompson *et al.*, 1995; De Angelis *et al.*, 1997). It has been recognized that continuous analyses with high sampling resolution are desirable to extract more detailed information from the chemical analyses of ice core samples. Conventional chemical analysis techniques, such as ion chromatography, atomic absorption spectroscopy and inductively coupled plasma - mass spectrometry (ICP-MS), are not suitable for continuous high-resolution analyses, because these techniques cannot be applied directly to solid ice and require liquid samples. To use these techniques, we generally need to cut ice cores,

remove the sample surface for decontamination, and melt the decontaminated samples in pre-cleaned bottles. This pretreatment procedure makes it difficult to obtain a sampling resolution of less than 1 cm. In addition, this laborious and time-consuming pretreatment procedure limits the measurable number of samples, and thus leads to the reduction of sampling resolution. Although a few attempts have been made to solve these problems (Hammer, 1980; Moore *et al.*, 1989; Moore, 1993; Sigg *et al.*, 1994), none of the previous techniques have succeeded to analyze chemical constituents in ice rapidly and continuously with a high sampling resolution.

We have been trying to develop such a technique. Our final goal is to establish a rapid and continuous method to analyze different chemical species in ice cores with a mm sampling resolution. In this paper, we report our first attempt to apply Laser Induced Breakdown Spectroscopy (LIBS), one of the laser spectroscopy techniques, to ice samples and show the potential of this technique to reach our goal. LIBS has already been used to determine chemical constituents in solid,

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liquid and gas samples (Kagawa and Yokoi, 1982; Cremers and Radziemski, 1983; Radziemski *et al.*, 1983; Cremers *et al.*, 1984; Kitamori *et al.*, 1989; Iida, 1990; Kagawa *et al.*, 1995; Ito *et al.*, 1995; Nakamura *et al.*, 1996), but has not been applied to ice samples so far.

The principle of LIBS is as follows: When a sample is irradiated with a focused laser pulse with high peak power, a bright plasma is produced at the irradiated point. The plasma includes a small amount of atomized sample and constituent atoms and/or ions that radiate luminescence. Elements are identified from their characteristic emission lines in the luminescence spectrum and their concentrations are determined from their peak intensities. If we know the relation between concentration of a specific element and its emission intensity, its unknown concentration can be determined from measured intensity (Radziemski and Cremers, 1989). In principle, chemical constituents in ice can be determined with little sample consumption using LIBS.

While our final goal was mentioned above, the following procedure is necessary before we apply this technique to real ice cores: (1) Preparation of standard samples containing given concentrations of a chemical species, which have homogeneous distribution within the samples; (2) detection of the characteristic emission spectrum corresponding to the chemical species from laser induced breakdown plasma; (3) investigation of optimum conditions for laser irradiation and spectral measurement; (4) investigation of the relationship between emission intensity and concentration of chemical species in standard ice samples; (5) application to different chemical constituents.

So far we have carried out processes (1)–(4) with artificial ice samples containing calcium (Ca) or sodium (Na), and investigated the possibility of determining their concentrations by LIBS. We have chosen Ca and Na in our first approach, since Ca and Na are major chemical species originated from continental dust and sea salt, respectively; both are important indicators of climatic changes. Their emissions are also expected to be relatively strong. In this paper we focus on processes (2) to (4), using the results for Ca. Process (1) and the results for Na will be written elsewhere (Takata *et al.*, in preparation).

## 2. Experiment

Figure 1 shows a schematic drawing of the experi-

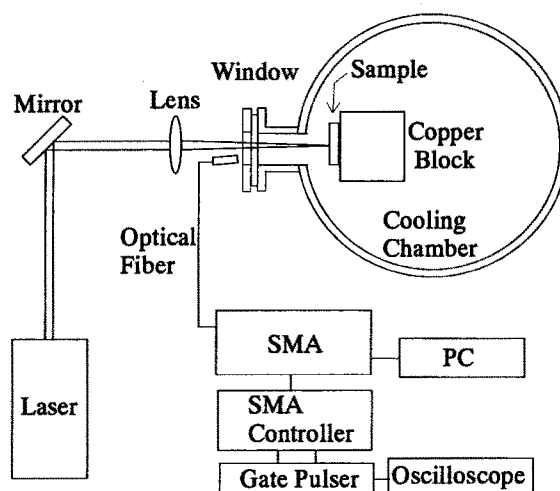


Fig. 1. Schematic drawing of experimental setup.

mental set-up. The ice sample was mounted on a copper block in a cooling chamber where the temperature was kept at about  $-5^{\circ}\text{C}$ . Artificial ice samples, which were presumed to have homogeneous distribution of Ca, were prepared from Ca solutions of known concentration using  $\text{CaCO}_3$ , HCl and ultra pure water (Takata *et al.*, in preparation). A Q-Switched Nd:YAG laser (DCR-3G, Spectra Physics Inc.) of 8 ns pulse width was operated at its fundamental wavelength (1064 nm) at 5 Hz. The laser pulse was focused by a lens (focal length 200 mm) placed about 200 mm from the sample surface. The spot size of the laser pulse at the sample surface was about 1 mm in diameter.

Luminescence from a spark ignited on the ice surface by a focused laser pulse was picked up by a single core optical fiber and its spectrum was recorded by a multichannel photodetector (SMA, Princeton Inc.) mounted on a 32-cm polychromator with a 1200 grooves  $\text{mm}^{-1}$  grating. The nominal wavelength resolution of the system was 1 nm. The SMA was operated in a gate mode and data were accumulated for 20 to 1000 laser pulses. The spectra were analyzed using a data-processing program developed previously (Ito *et al.*, 1995; Nakamura *et al.*, 1996). The program was capable of determining emission peak intensity in both height and area above the background signal. The signal to noise (S/N) ratio, where S is the peak height above the background and N is noise level, was used in optimizing the measurement conditions, and the peak area was used in determination of Ca concentration.

### 3. Result and discussion

Figure 2 shows the emission spectrum from a laser induced plasma at the surface of ice containing  $500 \mu\text{g g}^{-1}$  of Ca. It was taken from 500 to 3500 ns after the laser pulses, and accumulated for 100 pulses. Laser energy was  $300 \text{ mJ pulse}^{-1}$ . We could identify peaks at 393 nm and 396 nm. The 393 nm and 396 nm peaks coincide with ion emissions of Ca in a published wavelength table of elements (Reader and Corliss, 1987). We used the 393 nm peak, the strongest emission of Ca (Reader and Corliss, 1987), to evaluate its emission intensity and the S/N ratio for optimization of the experimental conditions. The observed sample consumption after measuring the spectrum was only about 1 mm in diameter and 1 mm in depth.

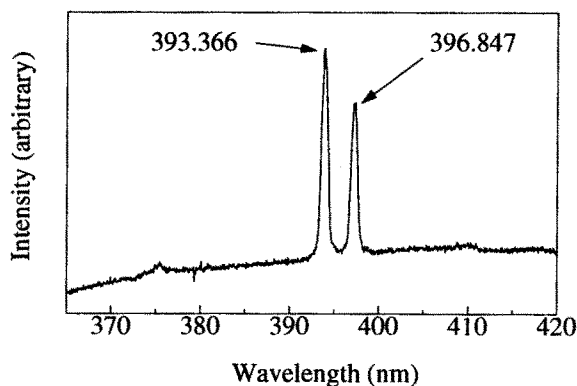


Fig. 2. Luminescence spectrum obtained for  $500 \mu\text{g g}^{-1}$  Ca in ice.

A laser induced plasma changes very quickly after laser irradiation: the plasma expands out into the surrounding gas, forming a shock wave, and its temperature varies with time and position (*e.g.* Radziemski *et al.*, 1983; Cremers *et al.*, 1984). Therefore, luminescence from the plasma also changes with time, and timing of spectral measurement needs to be studied. Optimum conditions of delay time and gate width must be determined so as to obtain high S/N spectra. Here, delay time means the interval between the laser pulse and opening of the multichannel photometer gate, and gate width means the spectrum measuring time. Thus the spectrum measurement started at the delay time after the laser pulse and continued during the gate width. They were controlled by the SMA gate controller and monitored by a digital oscilloscope.

First, we varied the delay time from 200 to 2500 ns with a fixed gate width of 2000 ns using ice samples

containing  $500 \mu\text{g g}^{-1}$  Ca. The laser was operated at  $400 \text{ mJ pulse}^{-1}$  and data were accumulated for 150 laser pulses. Fig. 3a shows S/N as a function of the delay time. The optimum delay time, where S/N showed the largest value, was determined to be 600 ns. Then we varied the gate width from 500 to 3400 ns with the optimum delay time of 600 ns (Fig. 3b). The optimum gate width was determined to be 2500 ns.

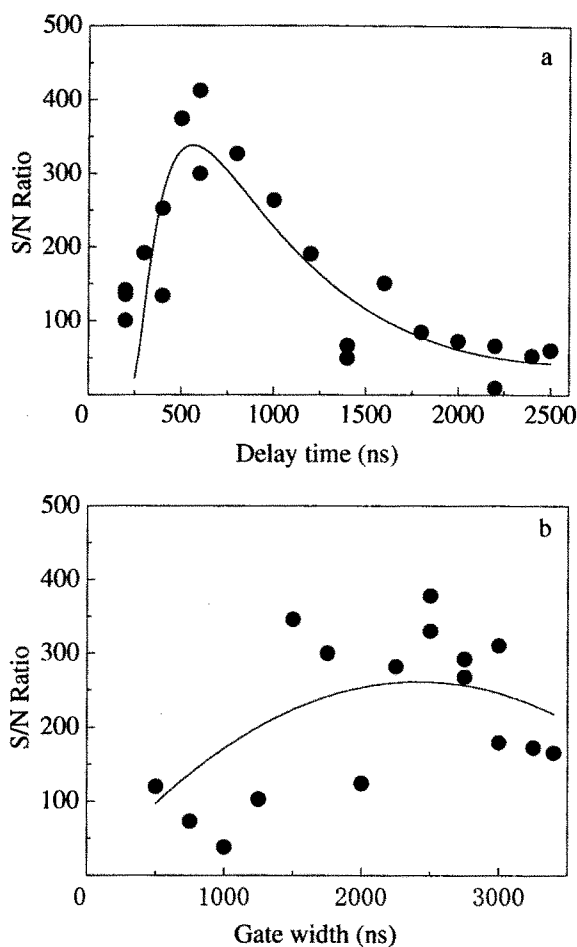


Fig. 3. Temporal changes of the S/N ratio at 393 nm using Ca samples. (a) changes by delay time and (b) changes by gate width.

The laser-induced plasma and the emission from the plasma fluctuate, since laser pulse intensity fluctuates significantly and laser induced breakdown is a highly non-linear phenomenon. Therefore, spectrum quality should become more stable as the number of accumulated laser pulses increases. In addition, fluctuations of the background emission, which contribute

to noise, occur randomly and will be smoothed out as accumulated laser pulses increase, while the real signal accumulates and adds up. This means that the larger the pulse number, the better the S/N ratio and the lower the detection limit. On the other hand, since the laser induced breakdown at the surface of the ice causes a small amount of ablation of the ice, a larger number of pulses may consume the ice near the focal point. This leads to a decrease of emission intensity. Therefore, we should seek out the optimum number of laser pulses.

Figures 4a and b show the S/N ratio and the emission intensity (peak area) against the number of accumulated laser pulses, respectively. The laser energy was  $110 \text{ mJ pulse}^{-1}$ . The irradiated area was about 1 mm in diameter and thus the energy fluence EF at the sample surface was estimated to be  $13 \text{ J}(\text{cm}^2 \text{ pulse})^{-1}$ . This EF was just enough to generate a plasma. When the EF was larger than  $26 \text{ J}(\text{cm}^2 \text{ pulse})^{-1}$ , the sample sometimes cracked after a few laser pulses. The experiment was carried out using samples containing  $20 \mu\text{g g}^{-1}$  Ca, with the optimum delay time and gate width of 600 ns and 2500 ns,

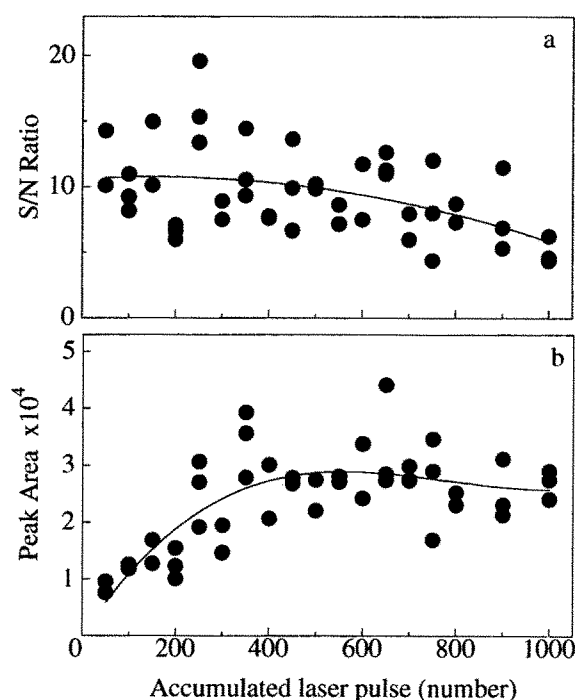


Fig. 4. Effect of accumulated laser pulse on 393 nm peak intensity (peak area) and S/N ratio for samples containing  $20 \mu\text{g g}^{-1}$  Ca: pulse energy of  $110 \text{ mJ pulse}^{-1}$ , spot size 1 mm in diameter.

respectively. Emission intensity increased with accumulation of laser pulses up to 250–300 pulses and showed little change afterward. The S/N ratio showed a high value up to 250–300 pulses and decreased with increasing number of pulses. The optimum number of accumulated laser pulses was determined to be 250–300, where both the intensity and the S/N ratio indicated large values.

The relation between Ca concentration and emission intensity was examined using ice samples with the following Ca concentrations:  $1.0 \mu\text{g g}^{-1}$ ,  $2.5 \mu\text{g g}^{-1}$ ,  $5.0 \mu\text{g g}^{-1}$ ,  $7.5 \mu\text{g g}^{-1}$ ,  $10.0 \mu\text{g g}^{-1}$ ,  $12.5 \mu\text{g g}^{-1}$ ,  $15.0 \mu\text{g g}^{-1}$  and  $20.0 \mu\text{g g}^{-1}$ . Experiments were carried out under the optimum conditions discussed above: The laser was operated at  $110 \text{ mJ pulse}^{-1}$ , the irradiated area was about 1 mm in diameter, the delay time was 600 ns, the gate width was 2500 ns, and data were accumulated for 300 pulses.

Figure 5 shows the emission intensity (peak area) of Ca ions at 393 nm *v.s.* Ca concentration. We measured more than 5 samples for each concentration. Filled dots denote data for individual samples and open dots represent averages at the same concentrations. The straight line represents the result of linear fitting by the least mean square method. Correlation was linear, and the correlation coefficient between the averaged value and the concentration was 0.99. The emission intensity of Ca at 393 nm was detectable for all samples of Ca concentrations larger than  $2.5 \mu\text{g g}^{-1}$ , while it was not detectable for those with Ca 1

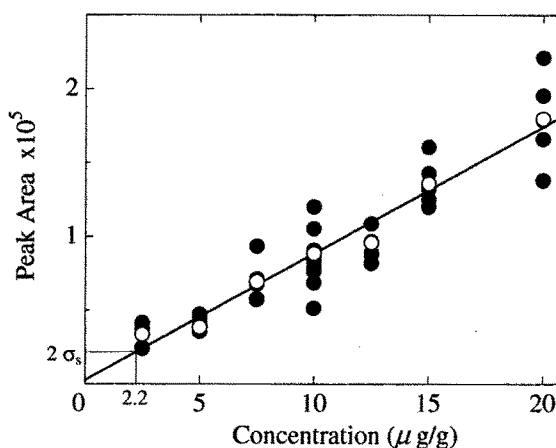


Fig. 5. Correlation of 393 nm peak intensity (peak area) and Ca concentration. Filled dots represent individual results and open dots represent averages at the same concentrations.

$\mu\text{gg}^{-1}$ . To evaluate the detection limit, we have calculated the standard deviation ( $\sigma$ ) of emission intensities (peak area) at 2.5 and 5  $\mu\text{gg}^{-1}$  with respect to the fitted line. The detection limit was estimated to be 2.2  $\mu\text{gg}^{-1}$  from the  $2\sigma$ . Although a high correlation coefficient between the average emission intensities and concentration was obtained, intensities for different samples at the same concentration were scattered. These rather scattered results could be attributed to the non-uniform distribution of Ca in ice samples, unevenness of ice density in the irradiated area or uneliminable fluctuation of emission intensity. We considered inhomogeneous distribution of Ca in ice samples and unevenness of ice density to be the major causes of the scattering, because fluctuation of each measurement point around the average values seems to be larger than that for the case of solution samples (Ito *et al.*, 1995; Nakamura *et al.*, 1996), and also because preparation of standard ice samples with uniform impurity distribution and density is rather difficult (Reid *et al.*, 1992). If this scatter is attributed to the samples, we can apply LIBS to the high-resolution analysis of Ca distribution in ice cores using a regression curve which is obtained with averaged values, since the high correlation coefficient between averaged emission intensity and Ca concentration suggests that several measurements average out the causes of fluctuation such as inhomogeneous Ca distribution and unevenness of density. We, however, need to improve the method to prepare standard ice samples by using a technique such as more rapid quenching of liquid samples. We also need more investigation of the reason for the data fluctuation.

Figure 5 indicates that we can determine Ca concentration in the range of 2.2–20  $\mu\text{gg}^{-1}$  in ice samples by LIBS. This concentration range for Ca corresponds to that in ice cores from low and mid latitudes (Jenkins *et al.*, 1987; Wake *et al.*, 1990, 1992; Zhang, 1996).

#### 4. Conclusions

Emission of Ca in ice samples was detected by the LIBS technique for the first time. We have investigated the optimum conditions for laser irradiation and timing of spectral measurement to obtain high S/N ratio and low detection limit. The optimum delay time and gate width for Ca measurements were 600 ns and 2500 ns, respectively. We studied the relation between emission intensity and concentration of Ca in ice, and

found a linear relationship in the concentration range of 2.2 – 20  $\mu\text{gg}^{-1}$  with the detection limit of 2.2  $\mu\text{gg}^{-1}$ . Thus our results, though preliminary, indicate that LIBS can be used to determine Ca concentration in low and mid latitude ice cores containing relatively high concentration of Ca. LIBS has a great potential as a continuous and non-destructive analysis technique for ice core chemistry. More work, however, is necessary in order to analyze polar ice cores that contain lower concentrations of chemical constituents.

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