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# A New Multielement Method for LA-ICP-MS Data Acquisition from Glacier Ice Cores

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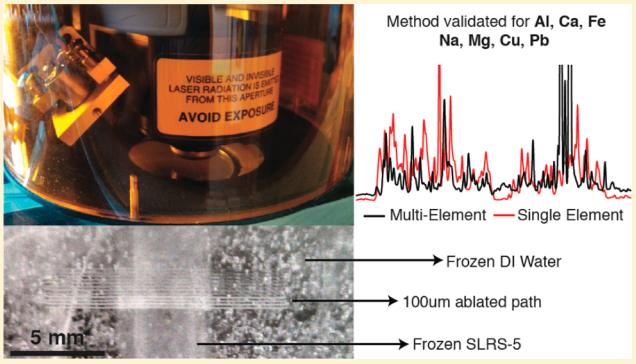
**ABSTRACT:** To answer pressing new research questions about the rate and timing of abrupt climate transitions, a robust system for ultrahigh-resolution sampling of glacier ice is needed. Here, we present a multielement method of LA-ICP-MS analysis wherein an array of chemical elements is simultaneously measured from the same ablation area. Although multielement techniques are commonplace for high-concentration materials, prior to the development of this method, all LA-ICP-MS analyses of glacier ice involved a single element per ablation pass or spot. This new method, developed using the LA-ICP-MS system at the W. M. Keck Laser Ice Facility at the University of Maine Climate Change Institute, has already been used to shed light on our flawed understanding of natural levels of Pb in Earth's atmosphere.




## INTRODUCTION

To reveal the valuable climate information contained in glacier ice at sites where annual layers are thin (i.e., only 5 mm thick) ultrahigh-resolution sampling by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is necessary. Originally introduced for ice core analysis by Reinhardt et al.,[1,2] the technique was further improved by Müller et al.[3] and has more recently been extended by Della Lunga et al.[4] and Sneed et al.[5] The increase in resolution afforded by LA-ICP-MS does come at a cost, as in stark contrast with traditional geochemical methods of ice core analysis, thus far, only a single chemical element is routinely measured per preprogrammed ablation pass or spot. Although additional elements can be measured in parallel tracks or spots, the potential offset given spatial variability at the ice sample surface makes precise investigation of the relative phasing of elements on a submillimeter level (e.g., over abrupt climate transitions, a primary target of the ice core community) difficult to accomplish accurately. In this article, we introduce a more robust procedure for ice chemical analysis using a multielement LA-ICP-MS method, wherein an array of chemical elements is simultaneously measured from the same ablation area. Such methods are commonplace in the characterization of high-concentration materials (see the review by Limbeck et al.[6]) but have yet to be used on ultrapure (i.e., microgram or nanogram per liter for most chemical elements) glacier ice. Here, we report on this new methodological addition to the LA-ICP-MS system described originally by Sneed et al.[5]

## METHODS

**Multielement LA-ICP-MS Analysis of Glacier Ice.** A new multielement method was developed and tested using samples from an ice core drilled at the Colle Gnifetti (CG) glacier saddle (Swiss-Italian Alps) in 2013. Use of CG ice core samples for these experiments was motivated by the glacier's relatively low net snow accumulation and high rate of annual layer thinning (see ref 7 and references therein), which provide ideal experimental conditions for the development of ultrahigh-resolution analytical methods. All of the work was conducted using the LA-ICP-MS system of the W.M. Keck Laser Ice Facility (KLIF) at the University of Maine Climate Change Institute. This system, the design of which is outlined and depicted in ref 5, is unique among those used to study ice in that it includes a cryocell (the Sayre Cell) chamber capable of holding 1 m of ice at a temperature of −20 °C, equipped with a small-volume (~5 $cm^3$) open-design ablation chamber, thereby allowing continuous ablation of ice core samples at close to their original length (Figure 1). Ablation and analysis are accomplished using a standard New Wave UP 213 laser and Thermo Element 2 ICP-MS instrumentation, respectively. See Table 1 for a complete list of applied parameters. In the series

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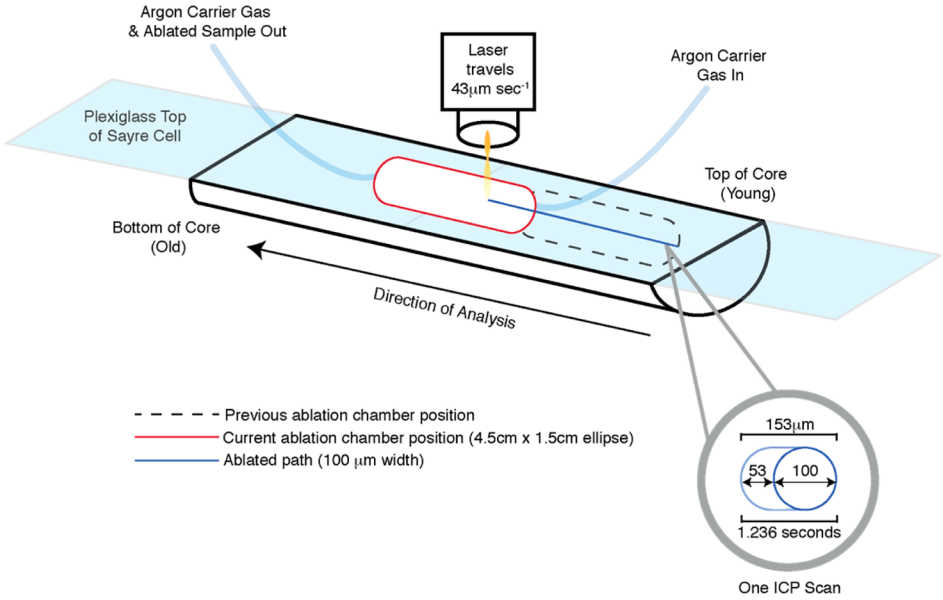


**Figure 1.** Sayre Cell consists of an open-cell ablation chamber centered in a plexiglass window above a moveable cryocell. A servomotor, Kevlar belt, and programmable logic controller (not shown) are used to reposition the cell (and the ice within it) after the laser module has traversed the length of the ablation chamber. The top of the ablation chamber is a round laser window 5 cm in diameter. The bottom is covered in gasket material with a 4.5 × 1.5 cm ellipse cut out of it. Mechanical risers within the Sayre Cell lift the ice sample into contact with the gasket material to form the seal needed to ensure that the ablated material is transferred to the ICP region. Transport is achieved with an argon carrier gas, which enters and exits through the inlet and outlet ports, respectively, at opposite sides of the ablation chamber. Argon is used because it is available in bulk in our laboratory. Each data point in the multielement method is the result of one ICP scan, lasting 1.236 s. The laser stage travels at 43 $\mu$m per second, thus moving 53 $\mu$m (light blue inset) over the course of one ICP scan. This is added to the 100-$\mu$m beam size (dark blue inset) to calculate the nominal resolution of 153 $\mu$m.

**Table 1. KLIF LA-ICP-MS Operating Conditions**

| ICP-MS system | | laser | |
|---|---|---|---|
| instrument | Thermo Element 2 | instrument | New Wave UP-213 |
| RF power | 1300 | carrier-gas flow rate | 1.2 L/min |
| cooling-gas flow rate | 17.04 L/min | firing mode | continuous |
| auxiliary-gas flow rate | 0.9 L/min | output level | 100% |
| sample-gas flow rate | 0.75 L/min | repetition rate | 10 Hz |
| additional-gas flow rate | 0.25 L/min | spot size | 100 $\mu$m |
| scan optimization | speed | fluence | 31 J/cm$^2$ |

of experiments reported here, the laser was operated at a repetition rate of 10 Hz (rather than the 20 Hz used by Sneed et al.[5]), which is closer to the natural frequency of the system's Nd:YAG crystal (New Wave Research Inc., Fremont, CA). This modification reduces vibration, thereby limiting excessive heat formation at the surface of the ice sample, but it has the auxiliary consequence of increasing the nominal resolution of the system (see example calculation below) to 143 $\mu$m under normal operating conditions (85 $\mu$m s$^{-1}$ scan speed, 100-$\mu$m spot size, single element per ablation path). To collect profiles of multiple elements within a single ablation pass, the scan speed is reduced from 85 to 43 $\mu$m s$^{-1}$. This reduction in speed is necessary to ensure that an ice volume adequate for robust measurement of impurities in glacier ice can be collected, but it must be balanced against the potential entrapment of ablated material within the deepened ablation path (Sneed et al.[5]). Observation of the depth of the ablated path at multiple points along a test line showed that the paths produced at 43 $\mu$m s$^{-1}$ are twice as deep as those produced at 85 $\mu$m s$^{-1}$ (60 versus 30 $\mu$m) and vary by $\pm 2$ $\mu$m in depth on average ($1\sigma$). This method assumes that the volume of ablated material is constant. The fluence (energy per area) used is well above what is deemed necessary for most materials in the Earth Sciences (31 versus up to 8 J/cm$^2$); thus, we do not expect significant variation in the ablation depth as a result of changes in microstructure or impurity content. The KLIF LA-ICP-MS system includes a magnified visual feed of the ablation path, and in our experience, it is rare to observe any deviation from the 100-$\mu$m diameter (i.e., jagged boundaries along the ablation path or subsumption of surrounding ice grains).

An additional change from the single-element method is that the Scan Optimization settings of Element 2 must be set for "Speed" instead of "Mass Accuracy". This change eliminates the magnet's high and low jumps [i.e., the magnet cycles only between the lowest and highest masses measured, rather than starting at a "zero mass" (typically Li) for each new scan and ending at a high mass (typically U)]. This setting reduces the analysis time for each element, thereby maintaining sub-millimeter resolution. To further avoid increases in analysis time, a low-resolution (LR) method is used for $^{23}$Na, $^{25}$ Mg, $^{63}$Cu, and $^{208}$Pb, and a separate medium-resolution (MR) method is employed for $^{27}$Al, $^{44}$Ca, and $^{56}$Fe. These elements were selected for their climatologic and environmental implications within the CG ice core. It should be possible to use the same technique for other elements as needed. In both the MR and LR methods, the mass window is set to 100 (with the exception of that for $^{27}$Al, which requires a slightly larger window of 110), and 20 samples per peak are measured, resulting in a scan duration per isotope of 0.20 s (or 0.22 s in the case of $^{27}$Al). When settling times (these vary for each element) are included, the time per pass is 1.236 s for the MR


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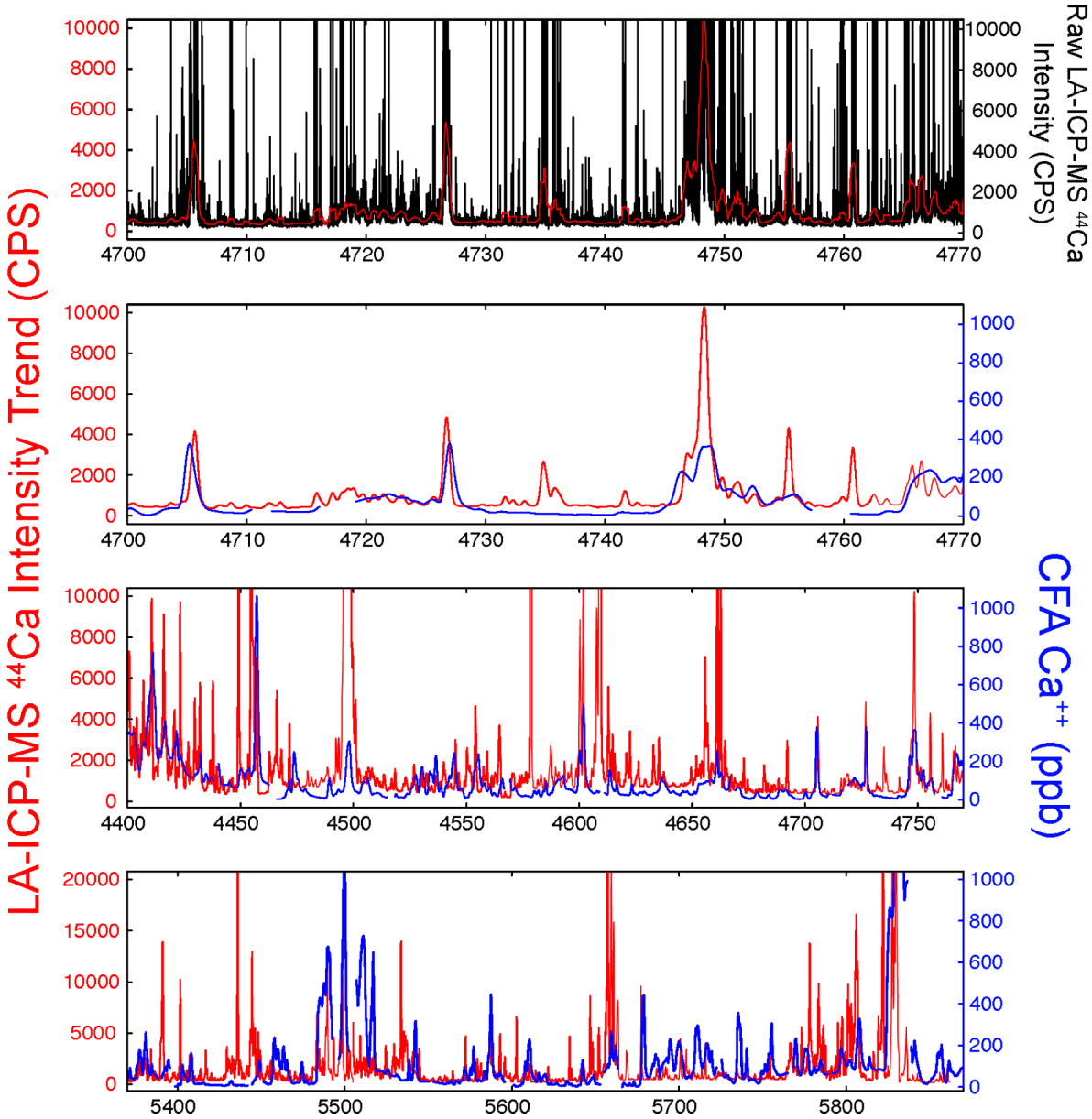


**Figure 2.** Short sections of $^{44}$Ca data from the KLIF LA-ICP-MS single-element method (top panel: raw, black; smoothed, red) were compared with traditional melt-based chemistry derived from continuous flow analysis (CFA, second panel) as a means of validating the LA-ICP-MS signal. These data were shared in ref 5. This validation has been extended over a continuous distance of ∼30 m throughout the bottom of the CG ice core. The bottom two panels present exemplary comparisons of smoothed LA-ICP-MS data for $^{44}$Ca (red) and CFA data for $Ca^{2+}$ (no filtering or detrending; blue). Establishing the link between an accepted geochemical method of ice core analysis (CFA) and the KLIF LA-ICP-MS single-element method allows validation of the new multielement method through comparison with the single-element method alone (Figure 3). Smoothing of single-element LA-ICP-MS $^{44}$Ca data was achieved using the "ksmooth" kernel regression smoother in R with a bandwidth of 0.5.

method and 1.246 s for the LR method, resulting in a nominal resolution of ∼153 $\mu$m per isotope (∼53-$\mu$m depth change + 100-$\mu$m beam size; Figure 1).

**Impulse Response of the KLIF LA-ICP-MS System.** Our nominal resolutions of 143 $\mu$m for single-element methods and 153 $\mu$m for the multielement method take into consideration the size of the laser beam, its speed of travel (area sampled during ICP-MS analysis), and the repetition rate of the laser pulse, but it does not address the convolution (true signal + impulse response) inherent in all recorded signals. This convolution is manifested as a dispersion of the original signal, which must be quantified, as only peaks separated by a distance greater than the dispersion limit can be characterized as individual events. In previous studies, signal dispersion within LA systems (and indeed continuous melter systems) has been discussed as a function of mixing within the sample/ablation chamber, drag within transport tubing, and incomplete transport of the generated aerosols from the chamber to the ICP.[8] Changing the shape (and therefore volume) of the opening to the ice within the ablation chamber yields significant changes in the intensity of peaks analyzed; thus, we assume that the chamber is the primary source of dispersion within the KLIF LA-ICP-MS system.

Previously, on continuous melter-based systems, an impulse was created through injection of a high-concentration standard into a melt stream (e.g., Breton et al.[9]). We simulate this


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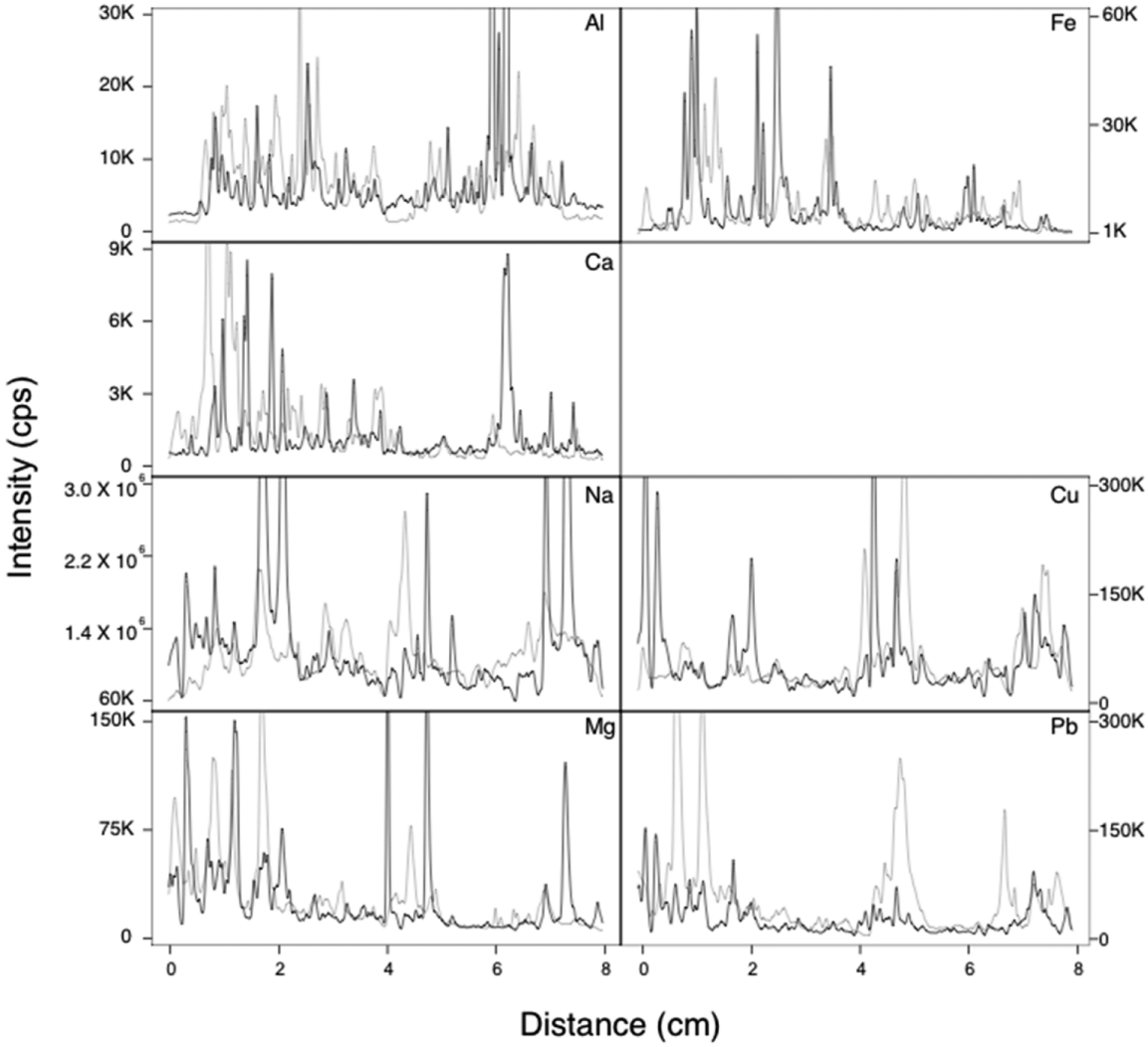


**Figure 3.** Single-element data (intensity in counts per second, CPS), resampled to the resolution of multielement method data and smoothed (gray line) are compared to smoothed multielement data (black line). Smoothing of both data sets was achieved using the ksmooth kernel regression smoother in R with a bandwidth of 0.05. The two methods produce comparable results. Small offsets in peak placement and errant spikes likely result from the spatial variability of the ice surface, as there is a small lateral distance between the ablation paths used in this comparison. Note that, for elements collected at low resolution or LR (Al, Fe, and Ca; top two rows), the intensities derived from the multielement method are approximately half those obtained by the single-element method, which were divided by 2 for this comparison. This is not unexpected, given the limited sample volume used in the multielement method and the particulate nature of these elements.

injection of material by ablating sticks of pure frozen distilled water into which SLRS-5 (a river water certified reference material for trace metals and other constituents from National Research Council Canada) is rapidly frozen into two channels that are 3 mm wide and 1 mm deep. The transition from one concentration to the other models a Heaviside step function, or an infinitely sharp step; thus, we can quantify the magnitude of signal dispersion by fitting an exponential decay function to the trailing side of the impulse peak and calculating the time constant, $\tau$. $\tau$ represents the elapsed time required for the system response to decay to zero if the system had continued to decay at the initial rate; because of the progressive change in the rate of decay, the response will have actually decreased in value to 1/e or ∼36.8% of the initial intensity in this time.

## ■ RESULTS AND DISCUSSION

**Multielement LA-ICP-MS Analysis of Glacier Ice.** In ref 5, short sections of $^{44}$Ca data (<1 m) from the KLIF LA-ICP-MS single-element method were compared with data from traditional melt-based chemistry derived from continuous flow analysis (CFA[10]) at the University of Bern's Climate and Environmental Physics Department as a means of validating the LA-ICP-MS signal. Although a perfect match between the two methods is not expected, given the differences in measurement techniques (melting versus ablation), parameters (dissolved versus total Ca), and inhomogeneities in particle distributions within a given "layer", we undertook an effort to extend this crucial validation over even longer depth intervals, comprising the most highly thinned sections of the core. Doing so adds fundamentally to the validation of the KLIF LA-ICP-MS system, and no other laboratory has yet produced such a long comparison. Figure 2 depicts nine of the ∼30 continuous meters that were compared throughout the bottom sections of the CG ice core (bottom two panels) and includes the data comparison shown in ref 5 (top two panels). Notably, the success of this comparison was foundational for the annual layer counting of the LA-ICP-MS $^{44}$Ca signal, which now extends nearly to bedrock.[11] The established link between an


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accepted geochemical method of ice core analysis (CFA) and the KLIF LA-ICP-MS single-element method allows validation of the new multielement method through comparison with the single-element method alone (Figure 3). The two methods produce comparable results. Small offsets in peak placement and errant spikes likely result from the spatial variability of the ice surface, as there is a small lateral distance between the ablation paths used in this comparison. For those elements measured in a LR method (Al, Fe, and Ca), the decreased sample size of the multielement method results in lower intensity values than those derived from the single-element method. This is particularly evident for elements already found in low concentration in the samples (e.g., $^{44}$Ca, which has a natural abundance of only 2.09%). Despite this change, the variability within the signal remains interpretable for all elements. Detection limits for multielement analysis using the KLIF LA-ICP-MS system are reported in Table 2. Minimum concentrations observed within the CG ice core by liquid ICP-MS analysis of discrete samples are provided for comparison.

**Table 2. Limits of Detection for the KLIF-LA-ICP-MS Multielement Method**

| element | limit of detection[a] | CG min[b] |
|---|---|---|
| Pb (ng/L) | 0.19 | 0.43 |
| Na (μg/L) | 1.46 | 0.30 |
| Mg (μg/L) | 0.02 | 1.59 |
| Fe (μg/L) | 0.01 | 0.11 |
| Cu (ng/L) | 12.13 | 1.83 |
| Ca (μg/L) | 0.30 | 6.95 |
| Al (μg/L) | 0.00 | 0.16 |

[a]10 ablation passes on frozen DI water − 3 × std dev (3σ). [b]As determined by liquid ICP-MS of discrete samples.

**Impulse Response of the KLIF LA-ICP-MS System.** Following a series of 10 trials (five ablation paths across the two wells of SLRS-5; Table 3), the mean time constant ($\tau$) for dispersion within the KLIF LA-ICP-MS system was determined to be −10.5 ± 0.2 s (1σ). Within mass spectrometry, the depth resolution of a system is typically defined by its 10% valley (i.e., the distance at which two peaks of equal magnitude can be separated by a valley just 10% below the peak height[12]), We thus used $\tau$ to calculate that 1.1 s is required to achieve a 10% reduction of the initial value. This corresponds to a distance traveled of 94 μm for a scan speed of 85 μm s$^{-1}$. Including the 100-μm beam diameter, the true resolution of the system is determined to be 194 μm. As most of the dispersion results from mixing within the ablation chamber, limiting its volume could reduce the impulse response.

**Table 3. Mean Time Constant ($\tau$, s) for Dispersion within the KLIF LA-ICP-MS System at 85 μm s$^{-1}$**

| | peak 1 | peak 2 |
|---|---|---|
| | −10.5 | −9.2 |
| | −10.3 | −10.3 |
| | −11.8 | −10.9 |
| | −10.6 | −9.7 |
| | −10.4 | −11.6 |
| mean | −10.7 | −10.3 |
| SD (1σ) | 0.6 | 1.0 |

**Implications for Ultrahigh-Resolution Ice Core Analysis.** This study presents the latest evolution in the process, begun nearly two decades ago by Reinhardt et al.,[1] of establishing LA-ICP-MS for ice core analysis. With the multielement method present here, LA-ICP-MS technology can now be fully brought to bear on pressing new research questions about the rate and timing of abrupt climate transitions, as it allows the relative phasing of elements over abrupt climate transitions to be investigated more precisely than methods using multiple lines or spots with potential offsets (e.g., Della Lunga et al.[13]). Abrupt events are one of the primary future targets of LA-ICP-MS-based ice core analysis, and so, this method is of direct relevance to the broad scientific community. Additionally, multielement LA-ICP-MS data allow precise consideration of elemental ratios. Not only does using ratios essentially remove the complicated steps required to produce accurately calibrated concentrations from the counts per time data produced by ICP-MS (see a review of this issue in ref 14), it also allows new avenues of proxy development at ultrahigh resolution. For example, preliminary analyses of Si/Fe and Ca/Al ratios from coarse-resolution liquid-based measurements of the CG ice core were interpreted as changes in dominant atmospheric circulation pathways. These findings can now be investigated in greater detail using the KLIF LA-ICP-MS system. Finally, the ability to measure elements additional to those reported by Sneed et al.[5] at ultrahigh resolution has already allowed new and exciting investigations of historical environmental change. More et al.[15] showed that Pb levels in Medieval Europe (as determined using this multielement method on the CG ice core) dropped precipitously at the time of the Black Death (ca. 1349−1353 CE), concurrent with decreased mining activity upwind of the ice core site. This four-year period is the only time within the past 2000 years in which Pb levels fell below what is often considered to be "natural background", leading the authors to conclude that current assumptions about safe levels of Pb in the atmosphere are misleading.

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### Notes

The authors declare no competing financial interest.

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