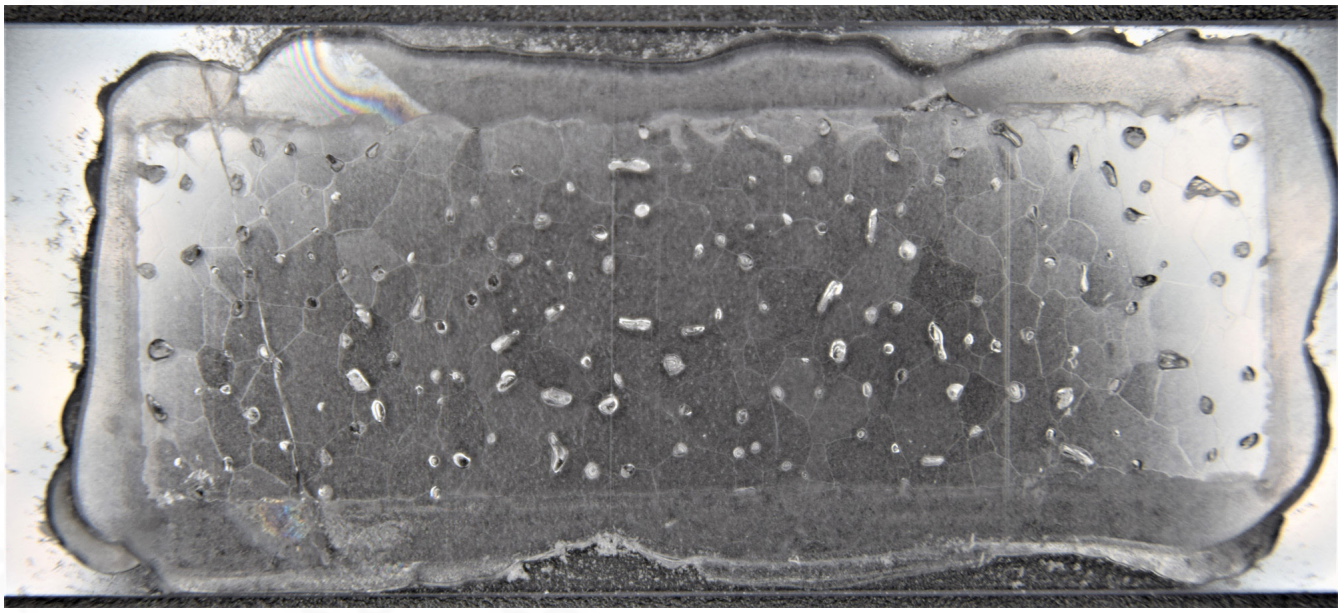
Elemental Scientific LASERS
INNOVATION TO ILLUMINATE

Applications Note

High Temporal Resolution of Arctic Ice Cores

With ESL's Peltier CryoCell



Facilitating the Analysis of Frozen Samples

Mapping the spatial distribution of impurities within ice cores provides a means to build temporal models and understand past climates for future climate prediction. Continuous Flow Analysis ICPMS (CFA-ICPMS) has been used extensively to analyze ice and study past events, however, the technique suffers from poor resolution ca. 1.0-3.5 cm and thus provides limited temporal information. LA-ICPMS provides resolution down to 100-200 µm and, as such, allows resolving of microstructures, impurities and highly compressed layers of older ice – all important for more accurate modeling and observation of changes over seasonal periods.

Samples must remain frozen during the analysis to retain spatial information and allow for physical recovery of samples for record keeping. ESL has developed the CryoCell, a Peltier-cooled drawer, to address these needs and facilitate the analysis of frozen samples such as Arctic ice cores.

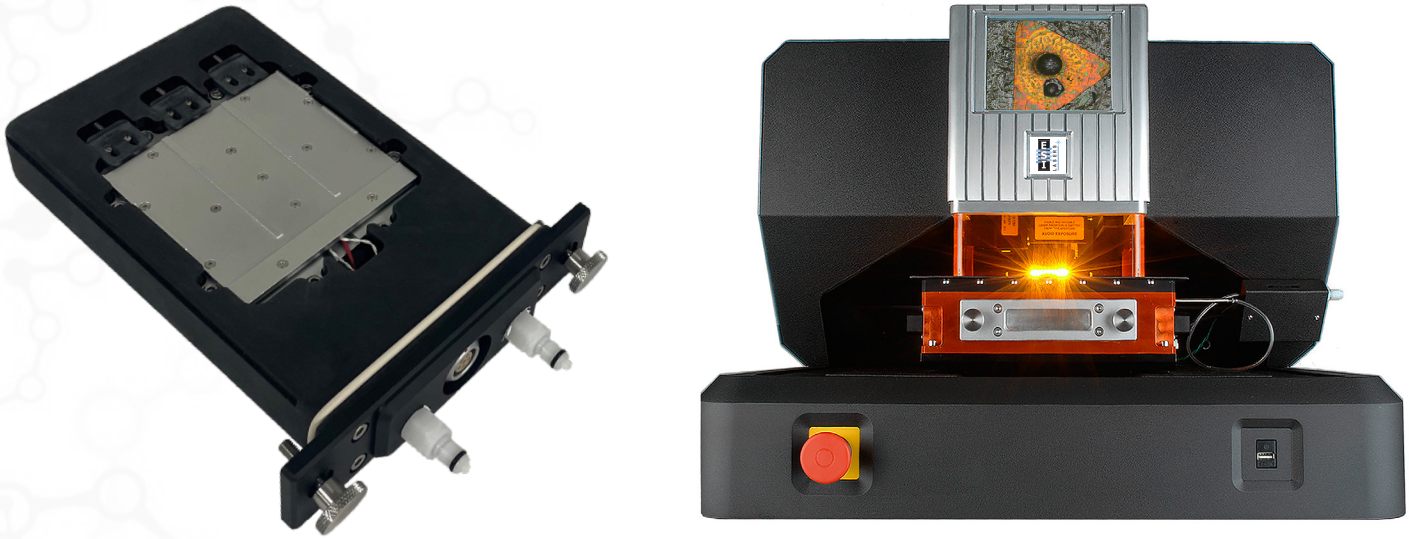


Figure 1. Peltier CryoCell sample drawer (left) and the TwoVol2 and ESL193 (right).

Methods and Instrumentation

Sections, *ca.* 20 x 50 mm, were cut from ice cores at the British Arctic Survey (BAS) using a band saw and affixed to standard microscope slides (25 × 75 mm). The mounted ice core sections were shaved to a thickness of 1 mm to remove surface contamination and provided a flat surface for ablation. The Peltier CryoCell can accommodate up to 3 standard microscope slides, providing space for both samples and matrix matched standards, reducing the need for sample change over and allowing for quantitative analysis. Samples were placed in the CryoCell under dry N_2 gas to avoid condensation on the sample surface.

ESL's NWR193 was equipped with the TwoVol2 peltier CryoCell and coupled to an ICPMS via a standard Y-piece and Tygon tubing. Table 1 contains the instrumental conditions used in these experiments. The CryoCell, controlled by ActiveView2 (laser control software) was set to -20°C. The temperature at the sample was recorded throughout the analysis.

Table 1. Instrumental Conditions

Laser Ablation – NWR193	
Spot size	150 µm
Stage speed	Ablation 40 µm/s Pre-ablation 150 µm/s
Fluence	5 J/cm2
Repetition rate	20 Hz
He sample gas	0.8 L/min
Peltier CryoCell	-20°C 3 slides

ICPMS – NexION 350D	
Power	1300 W
Argon make-up gas	0.9 L/min
Isotopes	^{23}Na, ^{24}Mg, ^{27}Al, ^{43}Ca, ^{55}Mn and ^{88}Sr
Dwell time	50 ms for Na 100 ms for all other isotopes

The onboard wide-angle camera of the ESL193 (25 mm FOV) was used to map the ice core sections within the TwoVol2 and facillitated the placement of unbroken line ablation patterns from one edge to the next. Ablation was completed across the entire length of each ice core section (direction relative to increasing depth of the core) in duplicate.

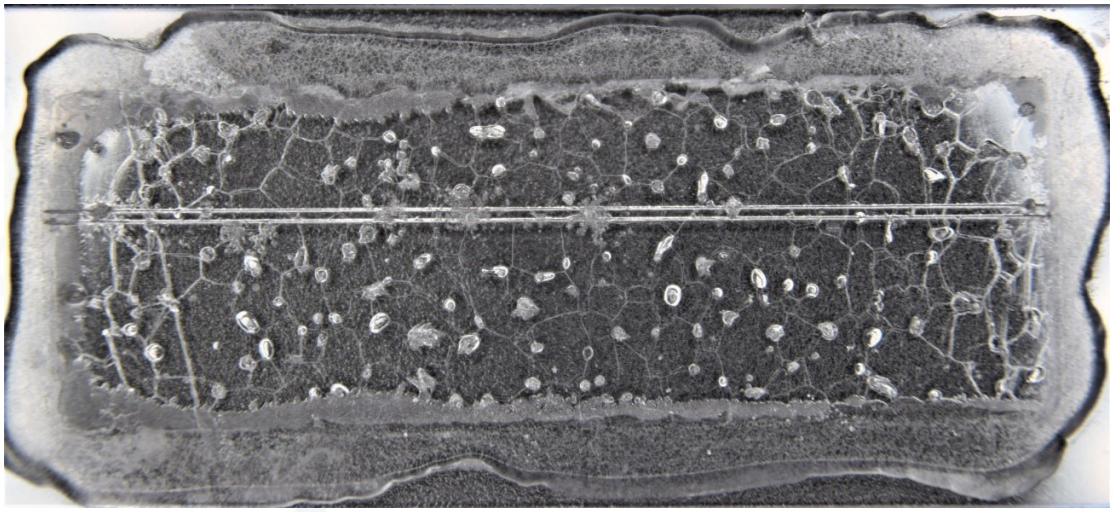


Figure 2. Ice core section post analysis, shows the 2 replicate laser ablation transects.

In total 16 consecutive ice sections were analyzed and the data combined to provide a depth profile across 80 cm of ice core from a depth of 83.2 to 84.0 meters.

Temperature Stability

Analytical improvements have been reported for many sample types (e.g. tissue, plants, ice) when kept frozen during laser ablation.[1-2] Analysis of these samples can take many hours, especially when mapping large sections, and as such the temperature must remain constant to ensure a stable signal while avoiding any possible elemental diffusion from temperature cycling. The CryoCell runs uninterrupted and provides stable temperatures, between -5 to -20 °C (selectable in 0.1 °C increments), as shown in Figure 3. The CryoCell was set to -15 °C, which provided an average measured temperature at the sample of 15.001 °C over 24 hours of analysis with a drift of 0.02% and variation of only 2.3 %RSD.

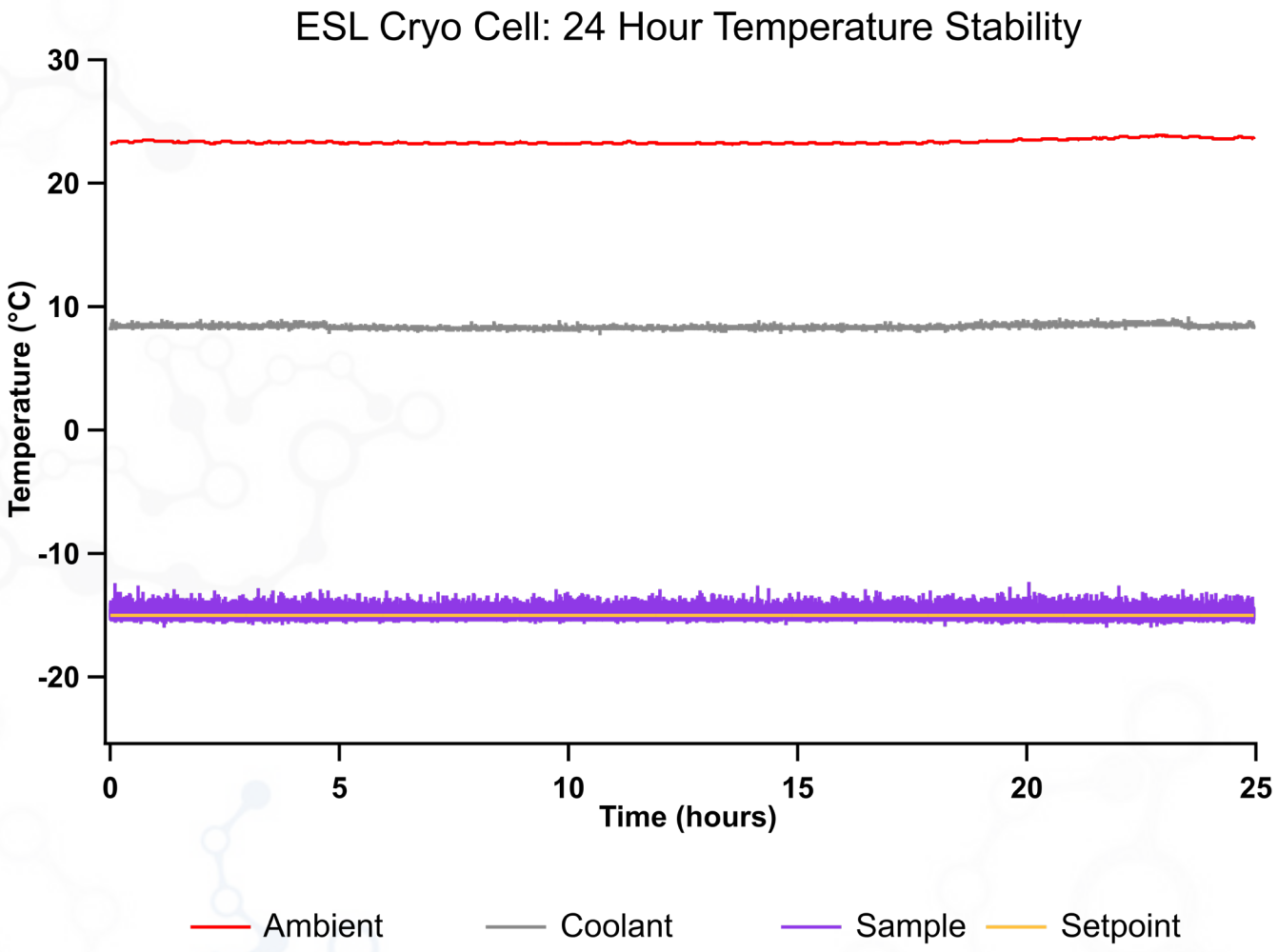


Figure 3. CryoCell stability over a 24 hour period; set point = -15 °C, average temperature at the sample = -15.001 °C with a 2.3 %RSD.

Results

The transient data from 16 consectutive sections were stiched together to provide a temporal profile over 80 cm of ice. At a resolution of 200 µm the laser ablation data provides sub-annual information of the Na distribution throughout the ice core.

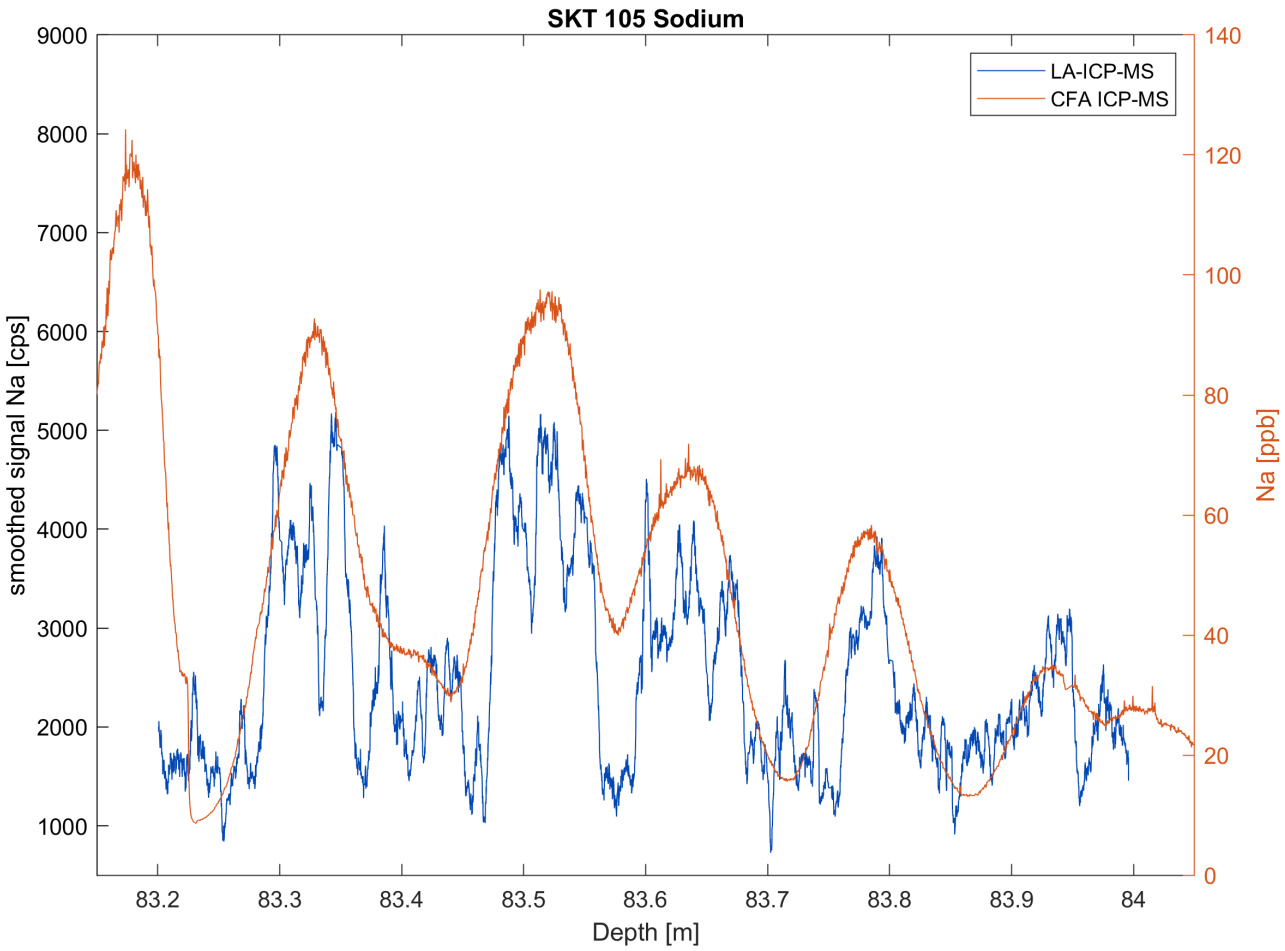


Figure 4. Transient profile of Na distribution across 16 ice sections from a core at 83.2 to 84.0 meters depth using LA-ICPMS [Blue] and CFA-ICPMS [Red]. A medium smoothing filter was applied to the LA-ICPMS data for clarity.

Applying a high degree of smoothing to the laser ablation data yields excellent agreement with the annual Na profile signal obtained by CFA-ICPMS (Fig. 5).

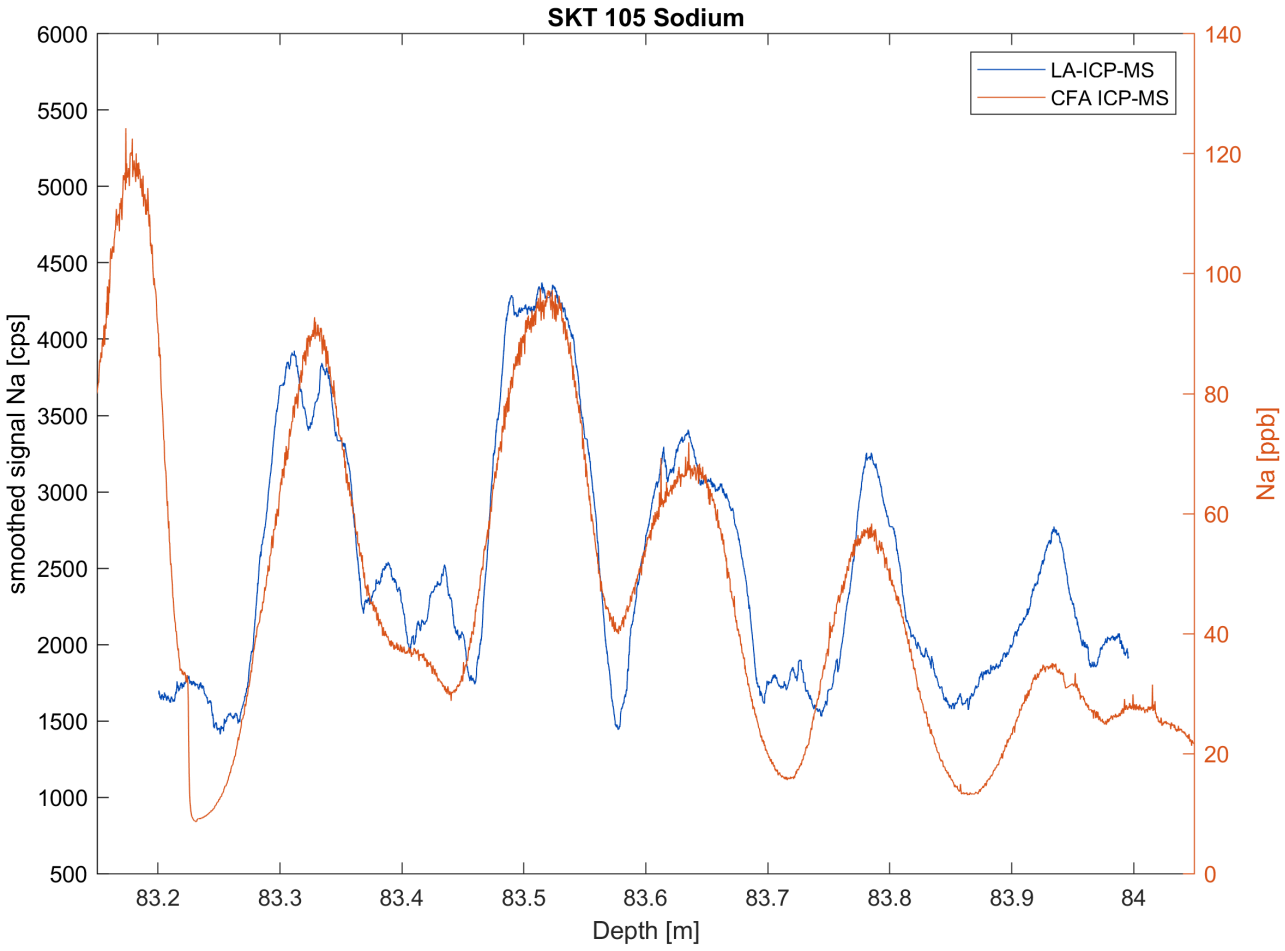


Figure 5. Transient profile of Na distribution across 16 ice sections from a core at 83.2 to 84.0 meters depth using LA-ICPMS [Blue] and CFA-ICPMS [Red]. A high smoothing filter was applied to the LA-ICPMS data for clarity.

Conclusion

The peltier CryoCell facilitates stable LA-ICPMS analysis of ice core sections and the visualization of elemental profiles at a sub-annual resolution, a significant improvement compared to CFA-ICPMS analysis. A constant and stable -20 °C provided optimum conditions to keep the sections frozen during the analysis and rentention of the samples for future records.

References

1 D. Pozebon, G. L. Scheffler and V. L. Dressler, J. Anal. At. Spectrom., 2017, 32, 890-919

2 I. Konz, B. Fernández, M. L. Fernández, R. Pereiro and A. Sanz-Medel, Anal. Chim. Acta, 2014, 809, 88-96

Acknowledgements

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