Investigating two possible schemes of Laser Ablation – Cavity Ring Down Spectrometry for water isotope measurements on ice cores

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Background

- Thinning of the deep ice core layers is one of the biggest challenges to address when analyzing water isotopes on the Beyond EPICA-Oldest Ice Core, one of the most valuable paleoclimate archives.
- 'Cold' laser ablation[2] sampling using ultrashort laser pulses (femtosecond regime): laser pulse-material interaction time is shorter than the heat diffusion time leading to a negligible thermal effect that ensures no isotopic fractionation.
- A novel instrument that couples Laser Ablation (LA) sampling coupled with Cavity Ring Down Spectrometry (CRDS) is being built and it will allow for fast, continuous high-quality water isotope measurements with high spatial resolution.
- Coupling of two different Laser Ablation systems with a laser source operating at the nanosecond (ns LA) and the femtosecond (fs LA) regime was carried out. Both fs LA-CRDS and ns LA-CRDS experimental designs, which employ laser ablation sampling, ablation chambers, collection lines of the ablated mass, and a CRDS analyzer are being investigated.

LA – CRDS

University of Copenhagen

The laser ablation system[1] (1) comprises a high-energy pulsed laser that produces **fs pulses** enabling **'cold' laser ablation[2]**. Optical elements guide and focus the laser beam into the ice sample (**30mm x 30 mm x 550 mm**) which is placed on a sample holder (2) mounted on a motorized linear stage (3) for micro-metric translational movement. An enclosure (4) for the optics is inserted and attached to the ablation chamber (5), which faces both the ice surface and the CRDS analyzer inlet (6) through a collection line using dry air as the carrier gas.

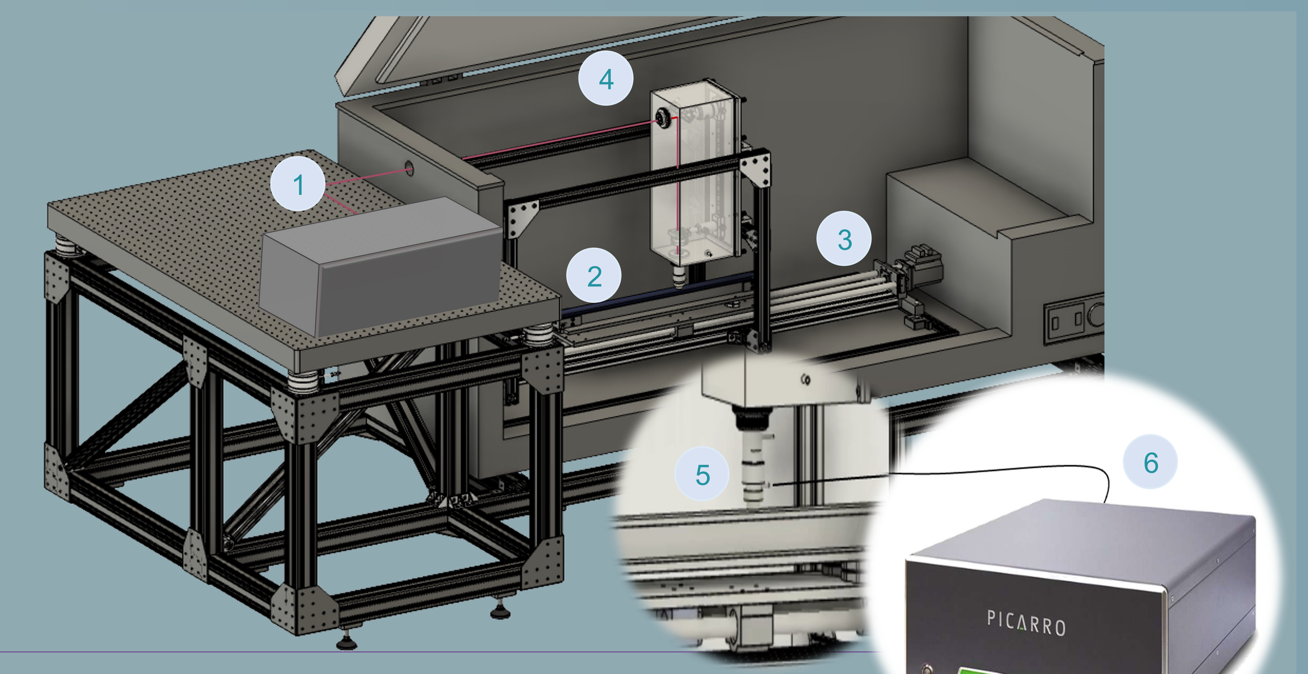

Figure 1: fs LA-CRDS system. Conceptual design of an ablation chamber coupled with the CRDS analyzer.

Laser source for LA

Ultra-fast pulsed laser	Wavelength Range	High pulse energy	High repetition rate
(200 fs)	1030 nm	0.1 – 40 μJ	50 – 500 kHz

Carrier Gas	Ablation chamber	
Dry air flow	Chamber with spring mechanism	Ablation Cup

Laser Ablation Craters on Ice

Laser ablation results in the formation of craters. Crater morphology indicates the physical processes that occured during the ablation and depends on the laser parameters, such as **pulse width, pulse energy**, **ablation time** and **repetition rate**. These parameters have to be optimized to achieve an adequate gas phase sample and prevent melting and recondensation when sampling ice.

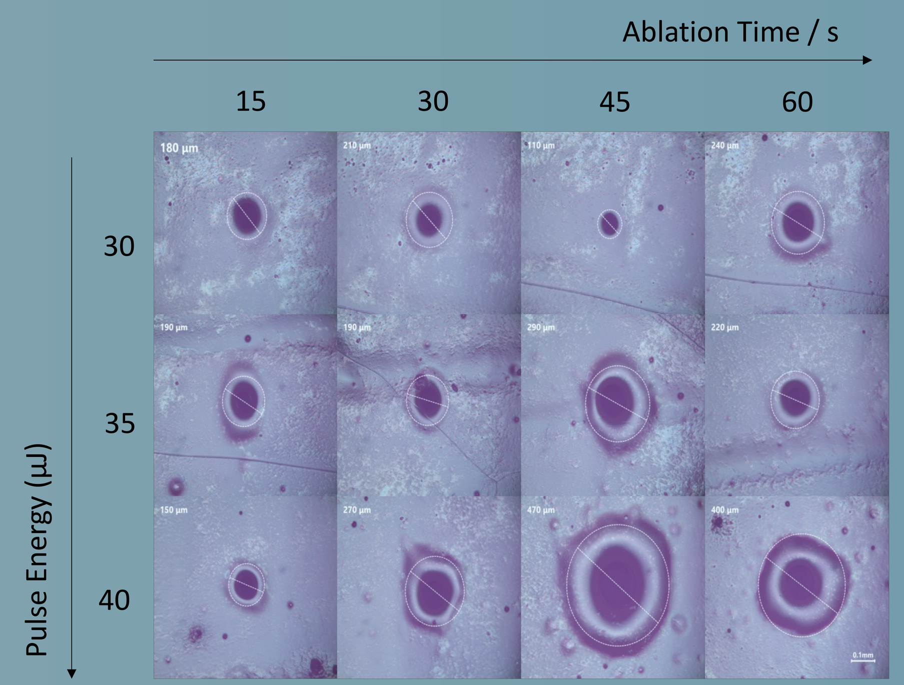

Figure 2: Laser ablation craters on artificial ice surface while using varying laser parameters of the fs-laser operating at 50 kHz.

Ablation Chamber

The ablation chamber and the transfer line are the two connecting parts of The wLA system and the CRDS analyzer. A specially designed ***ablation cup*** slides onto the ice surface when the ice sample moves during a continuous measurement, for robust gas phase sample delivery to the CRDS analyzer.

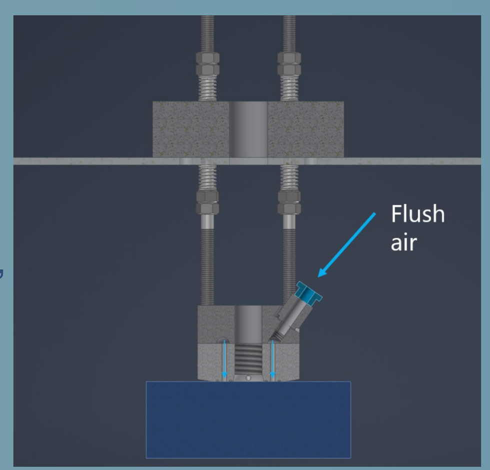

Figure 3: Ablation chamber (grey) for the fs LA-CRDS measurement on ice (blue).

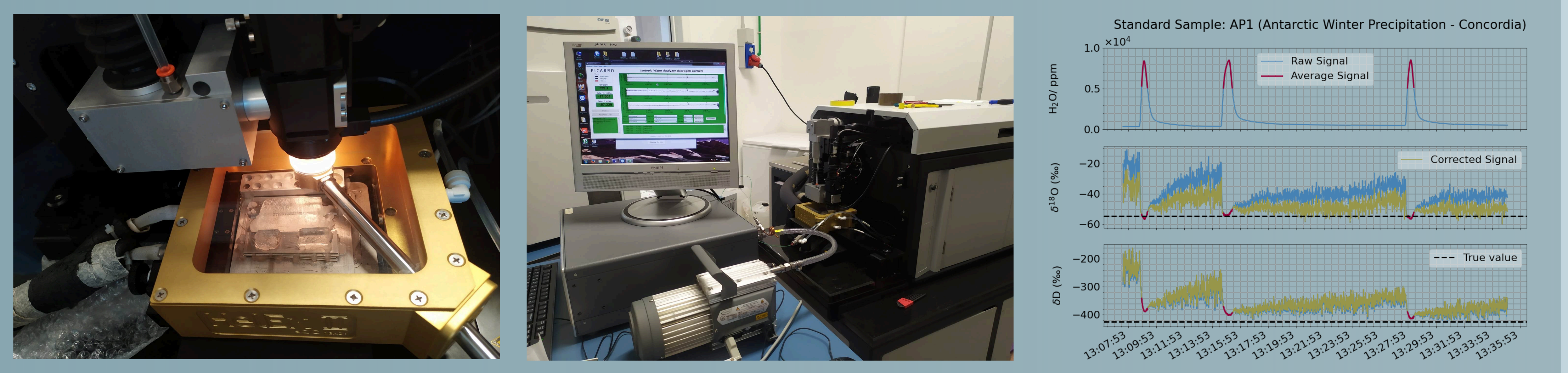

Figure 4: Two cell ablation system, ice holder with holes, ns LA-CRDS system (Ca'Foscari University of Venice), graph where the water (ppm) peak detected and water isotope signal δ[18]O, δD can be depicted. (from left to right)

LA – CRDS Coupling

University of Copenhagen (UCPH)

Proof of concept experiment carried out at DTU (Danmarks Tekniske Universitet) using a custom-made cryocell, a fs-laser and the L-2130i CRDS analyzer by PICARRO (***fig.5***).

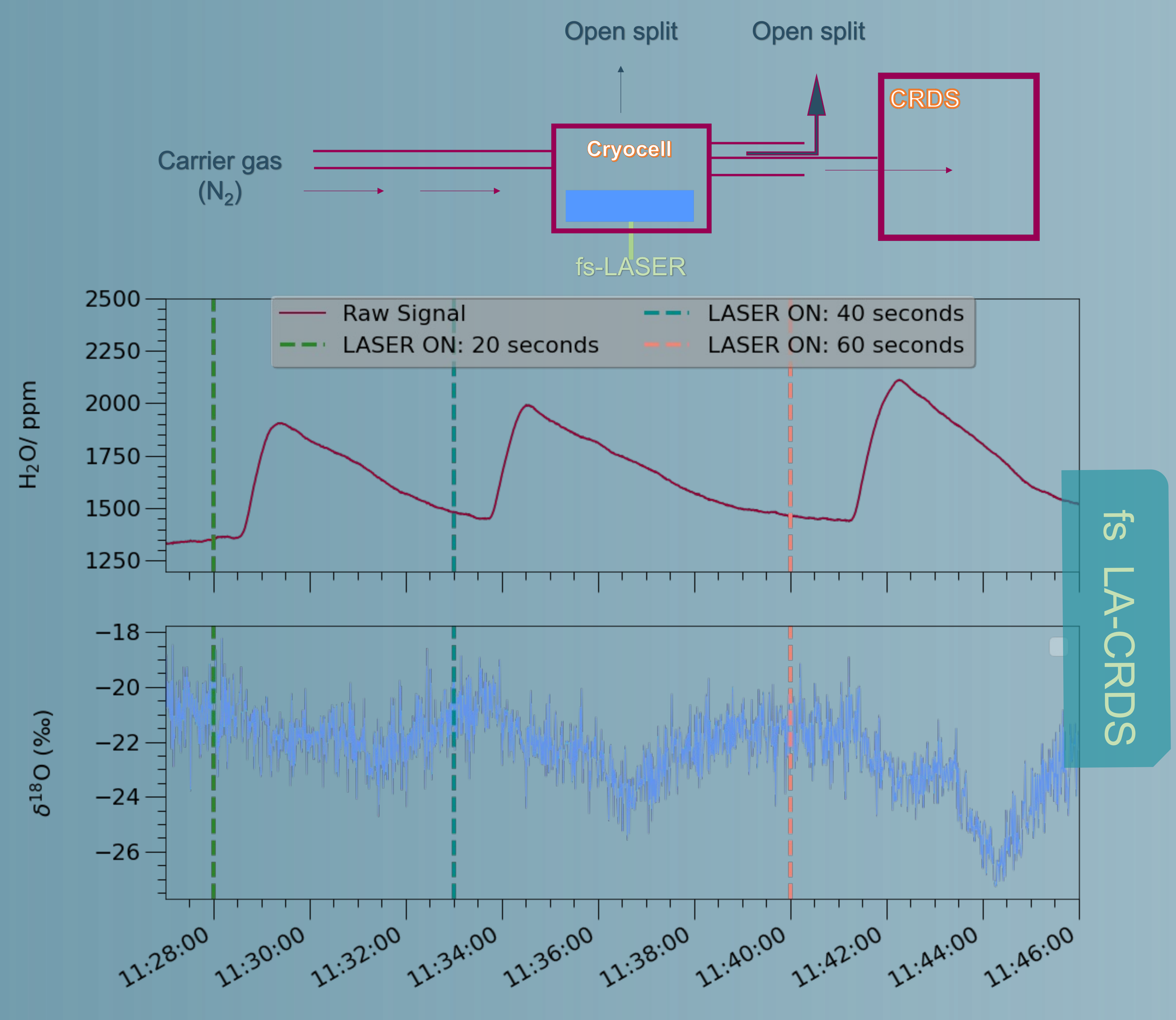

Figure 5: Water vapour level change as a response to different ablation time. (Proof of concept experiment at DTU)

Ca' Foscari University of Venice

The Laser Ablation system is used for impurities studies on ice cores[3] when coupled with ICP-MS. The same system was successfully coupled with the L-2130i CRDS analyzer (***fig.4***). Laser ablation using a laser beam spot size of 150μm in a raster scanning mode of a 4.2mm x 4mm surface area, resulted in a water concentration of 10000 ppm and water isotope signal values that approach the true value for the standard sample used (***fig.6***).

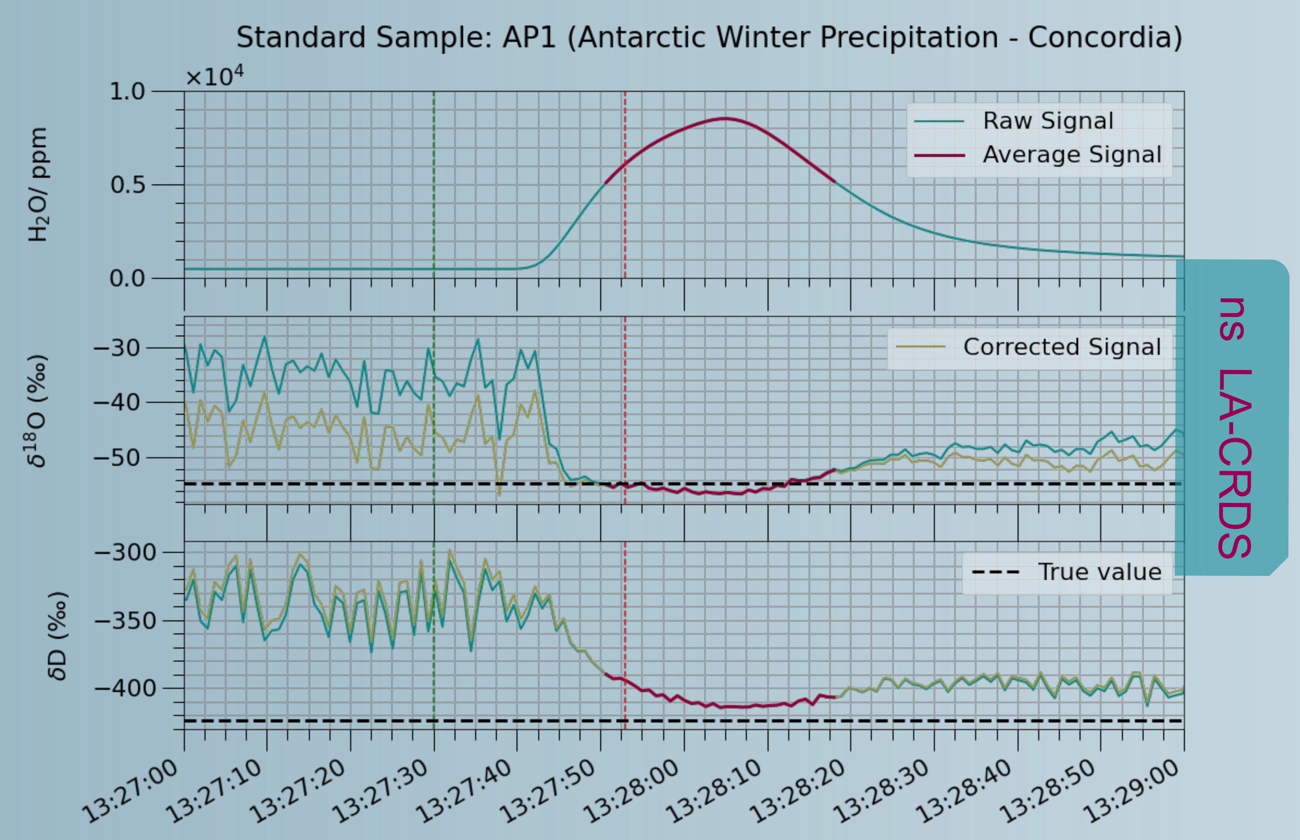

Figure 6: Water isotope signal acquired by the ns LA-CRDS system.

Outlook

- High quality ***crater imaging*** for their better characterization will lead to a better understanding of the ***cold ablation mechanism***.
- Integration of the new designed ***ablation chamber*** into the ***fs LA-CRDS (UCPH)*** while adding a transfer line to couple the LA-CRDS. Tests on the sampling and ablated mass transportation into the cavity towards a ***continuous water isotope measurement method***. Both crater characterization and water isotope signal evaluation will contribute to the optimization of the new system.
- Coupling optimization of the ***ns LA-CRDS (Ca' Foscari)*** for real ice measurements. Comparison of the two Laser Ablation systems, by the means of ice sampling and collection of the ablated material, will be of great importance to understanding the ablation mechanism and post-ablation processes on ice and further developing a system dedicated to water isotope measurements.

References and Acknowledgements

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