Simultaneous Sr-Sr and U-Pb isotope ratio analysis in common geological reference materials

Assessment of performance of the ECHO split stream device

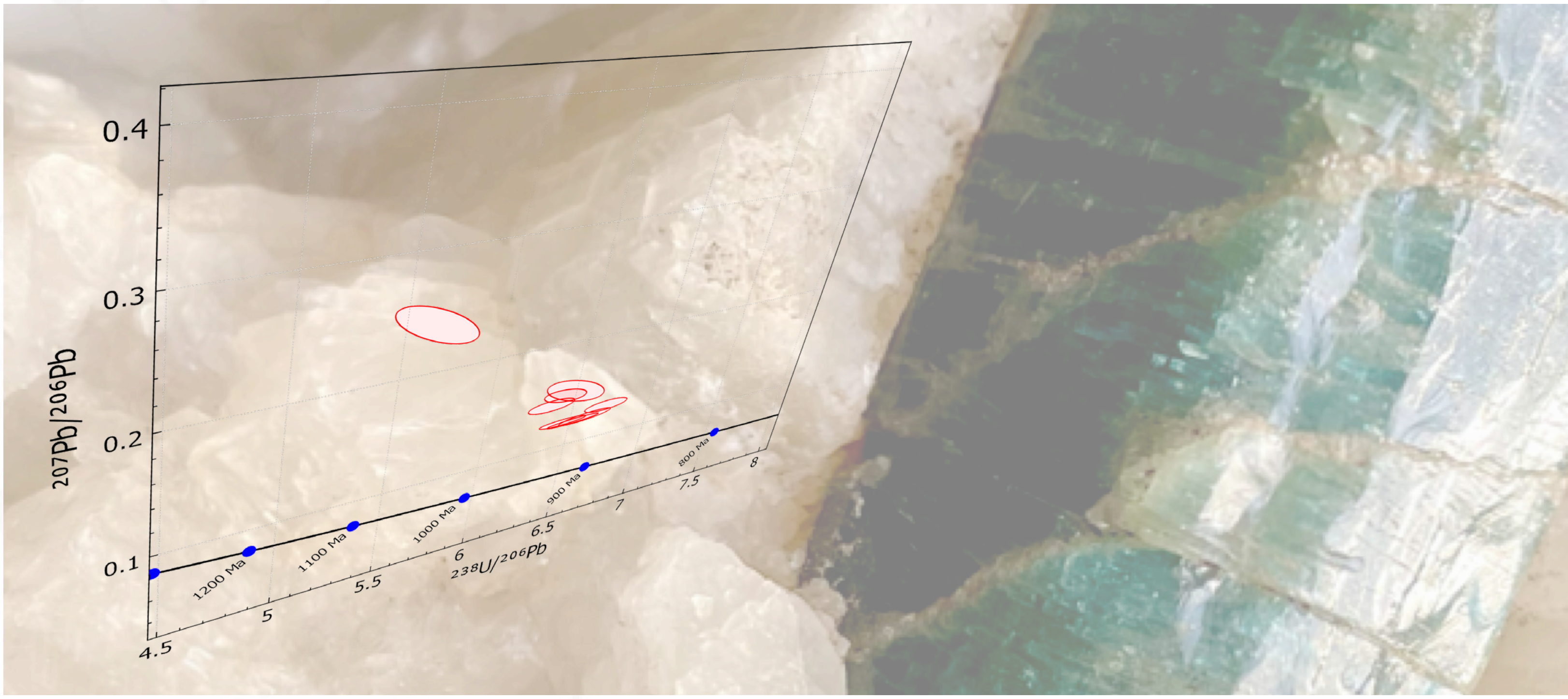

Photo Credit: Tamara Handl, Swedish Museum of Natural History Department of Geosciences.

Brief

Isotope ratios measured within geological samples are used within geochemistry and geochronology to give critical information about geological processes; however, more than one isotope system may need to be analyzed to give a full picture. Measuring two isotope systems, e.g. Sr-Sr and U-Pb, on a single ICPMS will negatively affect performance of the application by “bloating” the duty cycle to the detriment of analytical precision and accuracy; conversely, a multi-collector ICPMS will typically only offer sufficient mass range to monitor a single isotope system during a transient laser ablation; however, taking successive measurements of these different systems from different ablation sites assumes a degree of homogeneity that is unlikely to exist in a real sample.

Simultaneous measurement of both systems on more than one ICPMS from the sample ablation event is made possible by split stream sample handling to yield precise and accurate isotope ratios for both isotope systems from a single ablation event. Additionally, this allows measurement across a larger mass range than is typically possible for multi-collector ICPMS instruments.

ECHO – A robust, controllable split stream device for ICP/ICPMS analysis

Previous publications on split stream analysis have primarily relied on a simple Y-piece in the sample transfer line, whilst the balance of flow between the two or three detectors has been managed using a “choking” approach on individual lines (Kylander-Clark et al. 2013). This approach has been noted to be unstable and difficult to reproduce day-to-day within a single lab. A more reproducible approach is to sample directly from the sample-He gas stream via vacuum pumping (Oelze et al. 2021).

The new ECHO device from ESL (Figure 1) has been designed to maintain stable and controlled flows through each channel to either two or three detectors to give reliable and reproducible performance day-to-day. It can be installed in under 10 minutes and is plug and play with any ESL laser ablation system.

Figure 1. The ECHO split stream device from ESL is a compact, easy-to-use unit for laser ablation experiments with multiple ICP/ICPMS detectors.

ECHO is controlled via an AddIn within ESL's ActiveView2 software and different experiment profiles can be loaded from saved files (Figure 2). The He/sample gas flow can be divided down each channel from 10% to 90% of the total flow rate to enable the user to divert a greater sample load to the ICPMS that needs it the most. Tuning is made simple through the AddIn software interface, and ramping controllers on each channel protect the ICPs from sudden changes to flow rates.

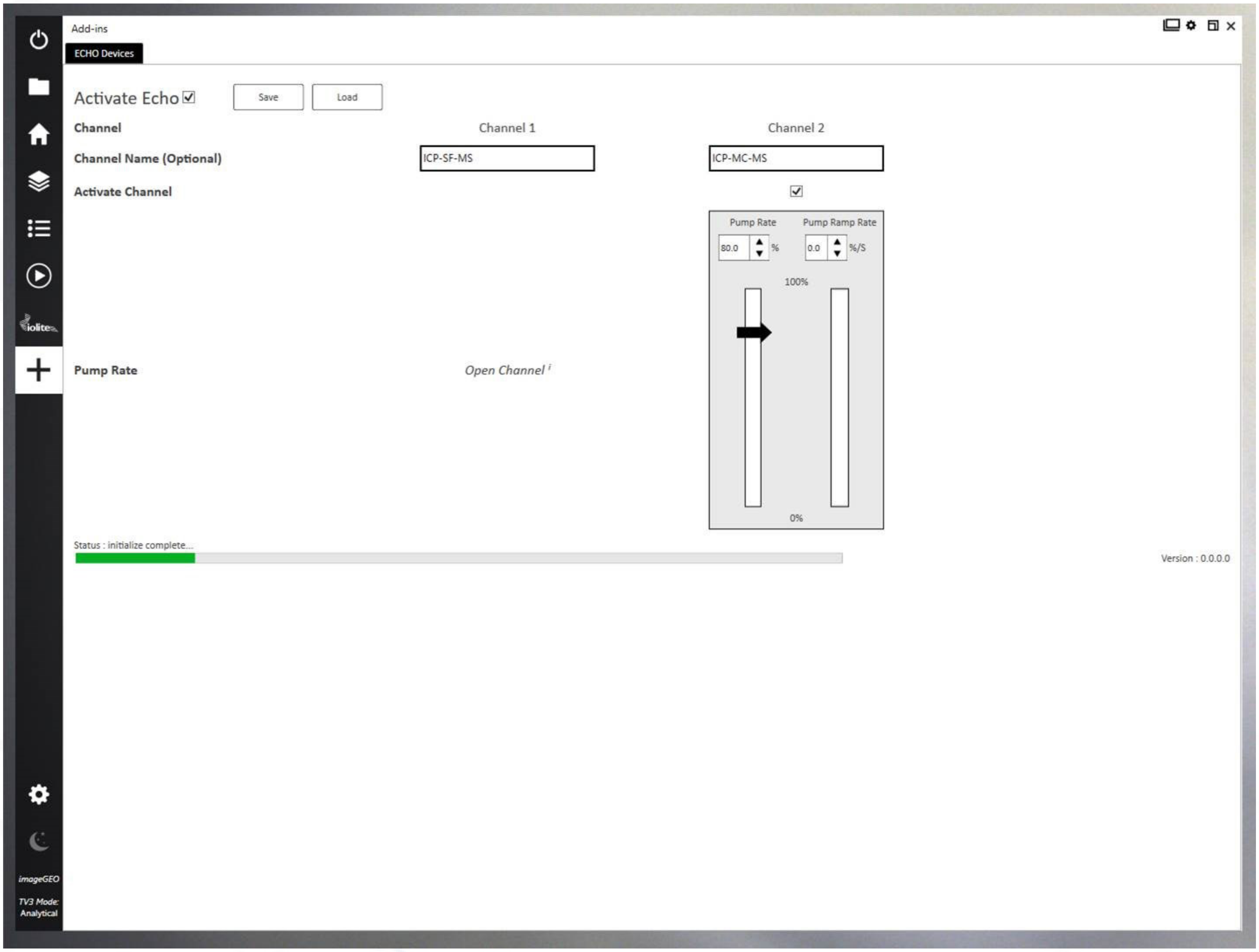

Figure 2. The ECHO split stream device is controlled via an AddIn launched within ActiveView2. Experiment profiles can be created, adjusted, saved and loaded from a single workspace, minimizing set up times and improving experimental reproducibility.

Experimental

Researchers at the Swedish Museum of Natural History (NRM, Stockholm, Sweden) analyzed a selection of apatite geological reference materials using an ESL193 excimer laser ablation system. A two-channel ECHO split stream device was used to connect the He/sample flow to a sector-field ICPMS (ICP-SF-MS, Attom, Nu Instruments) for determination of U-Pb isotope ratios/age and a multi-collector ICPMS (ICP-MC-MS, Plasma 3, Nu Instruments) for determination of Sr-Sr isotope ratios. Initial testing with NIST610 established the flow split between channels 1 and 2 to ensure adequate sensitivity on both systems for their respective applications. The Sr-Sr isotope ratios were standardised against a sperm whale tooth with reference $^{87}Sr/^{86}Sr$ ratio of 0.709155, determined by TIMS. The U-Pb ratios were standardised against Madagascar apatite (Thomson et al., 2012); as this contains variable amounts of common-Pb, NIST610 was employed for normalization of $^{207}Pb/^{206}Pb$. Table 1 outlines the major parameters for this experiment.

Table 1. Operating parameters for laser ablation with two channel split stream using the ECHO device from ESL with sector field ICPMS on channel 1 and multicollector ICPMS on channel 2.

ESL193	
Repetition rate	15 Hz
Fluence	2.2 J/cm^2
Spot size	130 µm
Scan speed	5 µm/s
Helium flow	400 mL/min
ECHO Split Stream	
Number of channels	2
Flow to Channel 1 (ICP-SF-MS)	80%
Flow to Channel 2 (ICP-MC-MS)	20%
ICP-SF-MS (Nu Attom) – Channel 1	
Ar nebulizer gas	800 mL/min
RF power	1300 W
Measured isotopes (and integration times)	202 (10 ms); 204 (10 ms); 206 (45 ms); 207 (45 ms); 208 (10 ms); 232 (10 ms); 238 (30 ms)
ICP-MC-MS (Nu Plasma 3) – Channel 2	
Ar nebulizer gas	500 mL/min
RF power	1300 W
Measured m/z	81.5, 82, 83, 84, 85, 86, 86.5, 87, 88
Integration time	0.5 s

Five certified apatite reference materials were used for this study due to having well-characterized ratios for Sr-Sr, and ratios and ages for U-Pb.

- Durango apatite. (DUR, Yang et al. 2014; Hou et al. 2013; McFarlane and McCullough 2008)
- Slyudyanka apatite (SLY, Yang et al. 2014)
- Otter Lake apatite (OTL, Yang et al. 2014)
- Madagascar apatite (MAD, Yang et al. 2014)
- Kovdor apatite (KOV, Amelin and Zaitsev 2002)

The Madagascar apatite was used as the primary age standard for U-Pb analyses.

Iolite Data Processing

All ICPMS data was imported into Iolite4 (Paton et al., 2011), which has been optimized for the multiple, overlapping data sources that are generated in split stream experiments using the unique DataSync tool (Figure 3). This allows separate data sets to be individually synchronized to the laser log file for accurate registration between ICPMS systems. The Sr-Sr isotope ratio data reduction scheme (DRS) in iolite4 was used to process the ICP-MC-MS data as per Mulder et al. (2023). The VizualAge_UComPbine DRS in iolite4 (Figure 3) was used to process the U-Pb data and calculate geological ages as per Chew et al. (2014).

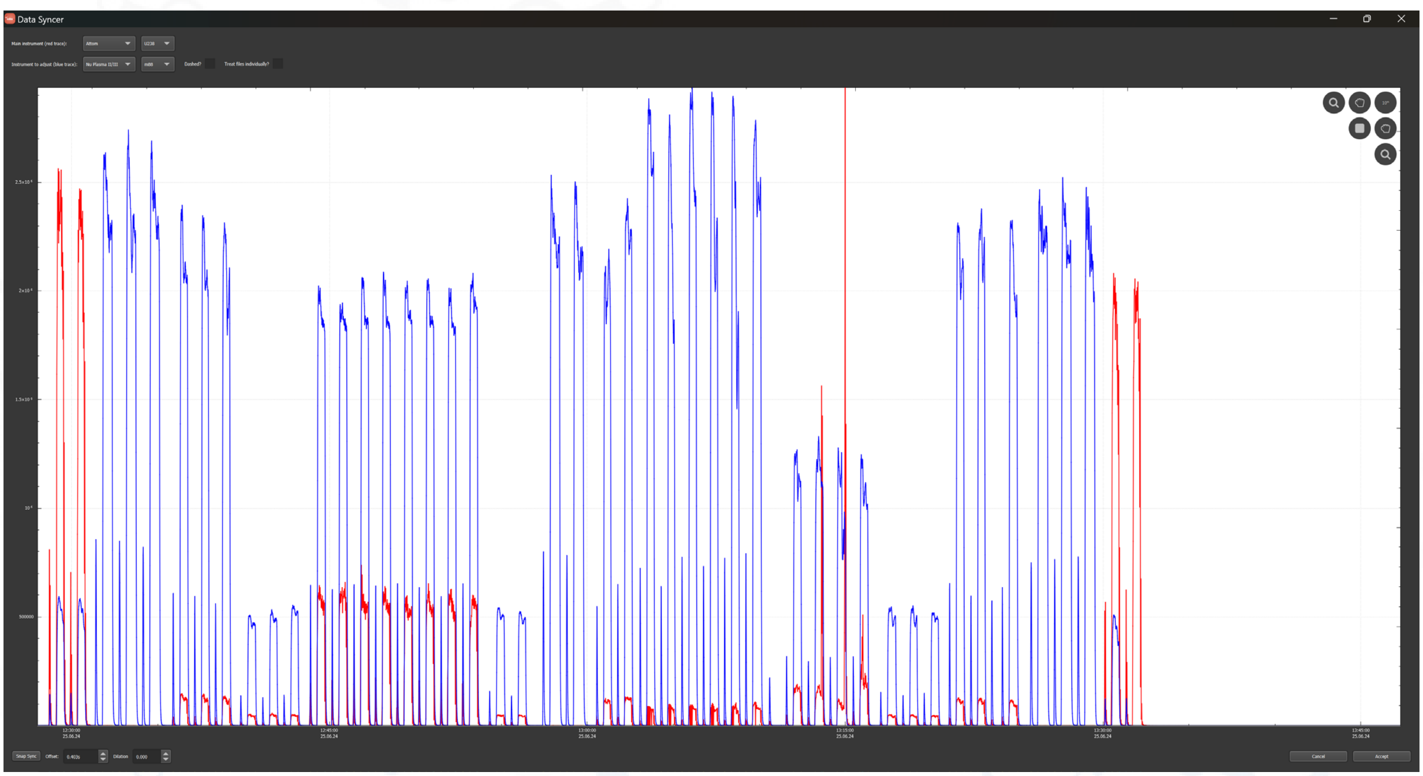

Figure 3. The DataSync tool in iolite allows multiple data streams from different ICPMS systems to be synched up in seconds.

Results

Table 2. Results and reference values for Sr-Sr isotope ratios measured on Channel 2 (ICP-MC-MS). All results show accurate ratios relative to the literature reference value.

Sample		Sr87/Sr86	2SE	Sr84/Sr86	2SE
MAD	Weighted Av (n=8)	0.71190	0.00006	0.0567	0.0003
	Reference (Yang et al., 2014)	*0.71180*	*0.00003*	*0.0565*	*0.0005*
	Measured relative to literature	+0.014%		+0.35%	
DUR	Weighted Av (n=8)	0.70626	0.00010	0.0565	0.0004
	Reference (Yang et al., 2014)	*0.70633*	*0.00002*	*0.0556*	*0.0010*
	Reference (Hou et al., 2013)	*0.70634*	*0.00003*	-	-
	Reference (McFarlane & McCulloch, 2008)	*0.70629*	*0.00002*		
	Measured relative to literature	-0.008%		+1.59%	
OTL	Weighted Av (n=8)	0.70424	0.00006	0.0565	0.0002
	Reference (Yang et al., 2014)	*0.70419*	*0.00003*	*0.0566*	*0.0010*
	Measured relative to literature	+ 0.007%		-0.18%	
KOV	Weighted Av (n=6)	0.70343	0.00007	0.0564	0.0002
	Measured relative to literature	N/A			
SLY	Weighted Av (n=4)	0.70777	0.00010	0.0567	0.0001
	Reference (Yang et al., 2014)	*0.70768*	*0.00003*	*0.0565*	*0.0007*
	Measured relative to literature	+0.013%		+0.35%	

Table 3. Results and reference values for U-Pb isotope ratios and age calculations measured on Channel 1 (ICP-SF-MS). All results show accurate ratios relative to the literature reference value.

Sample*		Age (Ma)	2SE (abs)
DUR	TW lower-intercept age	31.9	1.1
	Ref. age, Paul et al., 2021	*32.72*	*0.07*
KOV	TW lower-intercept age	383.2	5.5
	Ref. age, Amelin & Zaitsev, 2002, GCA	*377.5*	*3.5*
SLY	TW lower-intercept age	474	10
	Ref. age, Reznitskii et al., 1998	*460*	-

** Otter Lake (OTL) has been omitted due to the significant difference in alpha-dose versus the reference material.*

Conclusion

The ECHO split stream device from Elemental Scientific Lasers has enabled two distinct sets of isotope ratio experiments to be measured simultaneously on two different ICPMS systems from the same ablation pattern with no loss in precision or accuracy relative to performing the measurements separately, demonstrated over a range of apatite reference materials.

Real samples can be expected to exhibit a high degree of heterogeneity; therefore, the ability to measure these isotope systems simultaneously improves the data taken from real samples by taking results for both ICPMS detectors from the same ablation event. Without split stream analysis the user would be required to take data for each isotope system from separate ablations in separate locations – one for Sr-Sr and one for U-Pb. Acquiring two data sets from two different sample location increases the potential for error.

Split stream is currently the only feasible method for such an analysis. Attempting this on a single ICPMS would either not be possible due to limited mass range (e.g. ICP-MC-MS) or due to a loss of precision due to a bloated duty cycle (e.g. ICP-SF-MS, ICP-Q-MS). The approach would be applicable to other isotopic ratio systems measured in parallel (e.g. B-Mg-Ca, Zn, U-Th-series, etc.) or elemental data.

The approach ESL has taken to designing and implementing the ECHO split stream device has resulted in a simple-to-use, robust, reproducible unit that is quick to install and set up. The software-controlled interface allows experiments to be recreated without error. The software-based interface allows methods to be saved and recalled as needed. ECHO is the first commercial split stream device to offer such a convenient, useable workflow for multi-instrument analysis.

References

Kylander-Clark, A.R.C., Hacker B.R. and Cottle J.M., 2013. Laser-ablation split-stream ICP petrochronology. Chemical Geology, 345, pp. 99-112. https://doi.org/10.1016/j.chemgeo.2013.02.019

Oelze, M., Frick D.A. and Gleeson S.A., 2021. Laser ablation split stream for in situ sulfur isotope and elemental analysis. Journal of Analytical Atomic Spectrometry, 36, pp. 1118-1124. DOI https://doi.org/10.1039/D1JA00083G.

Yang, Y.H., Wu, F.Y., Yang, J.H., Chew, D.M., Xie, L.W., Chu, Z.Y., Zhang, Y.B. and Huang, C., 2014. Sr and Nd isotopic compositions of apatite reference materials used in U–Th–Pb geochronology. Chemical Geology, 385, pp.35-55. www.doi.org/10.1016/j.chemgeo.2014.07.012

Hou, K.J.,Qin, Y.,Li, Y.H.,Fan, C.F., 2013. In situ Sr, Nd isotopic measurement of apatite using laser ablation multi-collector inductively coupled plasma mass spectrometry (in Chinese with English abstract). Rock Miner. Anal. 32 (8), 547–554.

References *(continued)*

McFarlane, C.R.M.,McCulloch, M.T., 2008. Sm–Nd and Sr isotope systematics in LREE-rich accessory minerals using LA-MC-ICP-MS. In: Sylvester, P. (Ed.), Laser-Ablation ICPMS in the Earth Sciences: Current Practices and Outstanding Issues. Mineralogical Association of Canada Short Course, 40, pp. 117–133 (Vancouver, B.C.).Amelin, Y. and Zaitsev, A.N., 2002. Precise geochronology of phoscorites and carbonatites:: The critical role of U-series disequilibrium in age interpretations. Geochimica et Cosmochimica Acta, 66(13), pp.2399-2419.www.doi.org/ 10.1016/S0016-7037(02)00831-1

Paul, A.N., Spikings, R.A. and Gaynor, S.P., 2021. U-Pb ID-TIMS reference ages and initial Pb isotope compositions for Durango and Wilberforce apatites. Chemical Geology, 586, p.120604. www.doi. org/ 10.1016/j.chemgeo.2021.120604

Reznitskii, L.Z., Fefelov, N.N., Vasil'ev, E.P., Zarudneva, N.V., Nekrasova, E.A., 1998. Isotopic composition of lead from metaphosphorites and problem of the Slyudyanka Group age, the southern Baikal, Western Khamar Daban region. Lithology and Mineral Resources 33 (5), 432–441.

Thomson, S.N., Gehrels, G.E., Ruiz, J. and Buchwaldt, R., 2012. Routine low-damage apatite U-Pb dating using laser ablation–multicollector–ICPMS. Geochemistry, Geophysics, Geosystems, 13(2). www.doi.org/ 10.1029/2011GC003928

Chew, D.M., Petrus, J.A. and Kamber, B.S., 2014. U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb. Chemical Geology, 363, pp.185-199. www.doi.org/10.1016/j. chemgeo.2013.11.006

Acknowledgements

Elemental Scientific Lasers LLC would like to thank Dr Chris Mark of the Swedish Museum of Natural History, Stockholm, Sweden for independently running this experiment and for sharing the data. The NordSIMS-Vegacenter facility is financially supported by the Swedish Research Council.

Tel: 406-586-3159 | lasers@icpms.com | www.icpmslasers.com