

<p>Institution: Royal Holloway, University of London</p>
<p>Unit of Assessment: Earth Systems and Environmental Sciences</p>
<p>Title of case study:</p> <p>Development of a custom-designed laser-ablation system for high-resolution chemical and isotopic analysis</p>
<p>1. Summary of the impact</p> <p>Wolfgang Müller “...developed with Resonetics (USA) and Laurin Technic (Australia) an instrument...designed to be the ultimate, no compromises, laser ablation...” system (Gabay, President/Director, Resonetics). Crucially featuring a two-volume laser-ablation-cell available commercially for the first time, the new “RESolution-series product-line” has since development and installation of the Royal Holloway-prototype (2007/08) been sold worldwide to 20+ laboratories. When coupled to (MC-)ICPMS (plasma mass spectrometers), RESolution LA-systems yield the most accurate and precise isotopic/trace element data at the μm-scale for a wide variety of solids. Economic and societal impact included (a) employment of eight technical specialists at Resonetics and additional staff at worldwide suppliers, (b) direct technological spin-offs linked to monitoring diabetes and stents production, and (c) a turnover of US\$7M (2011). This new partnership has shaped the LA market worldwide and remains a key innovation driver with the recent addition of a Royal Holloway-designed cryogenic cell for analysis of ice cores or frozen biological samples.</p>
<p>2. Underpinning research</p> <p>Direct <i>in-situ</i> isotopic and elemental analysis at the μm-scale is a fast growing area in geochemistry with diverse applications in the Earth and related sciences. The development of both the electron microprobe in the 1950-60s and the ion microprobe in the 1970-80s paved the way for spatially-resolved analysis of element concentrations and/or low-precision isotope ratios, respectively. However, only the coupling of laser-ablation systems with (MC-)ICPMS (multicollector inductively-coupled-plasma mass spectrometers) during the 1990s facilitated analytical breakthroughs, allowing for rapid accurate trace elemental and/or high-precision isotopic analysis at the μm-scale with applications across the sciences.</p> <p>At Royal Holloway, the appointment of Wolfgang Müller in late 2004 spawned a new initiative in <i>in-situ</i> geochemical analysis, because the then commercially available laser-ablation systems comprised unsophisticated laser-ablation (LA) cells despite their UV-laser sources. The LA cell represents the core of any LA system because it is where the laser interacts with the sample, and as such defines its key performance characteristics. The SRIF3-funded LA prototype system was developed at Royal Holloway between 2006-2007. The Royal Holloway-led design was realized as a new joint venture between Royal Holloway (idea, research, overall design, consortium setup), Laurin Technic (Australia; LA cell developer, supplier & design-consultant) and Resonetics LLC (USA; overall system integration) and is now marketed as the RESolution series and available to the geochemical community worldwide. Resonetics had previously not been active in the geoscience market.</p> <p>The RESolution series is the first commercially available LA system featuring a two-volume LA sample cell (Laurin cell). Due to its rapid signal washout (<1.5 s/99% signal drop) and uniform signal response, this LA cell gives unprecedented signal stability and allows rapid acquisition of precise and accurate data using depth and compositional profiling, ‘normal’ spot analysis and 2D mapping (Müller et al 2009, Tomlinson et al 2011, Evans & Muller 2012, Rittner & Müller 2012). Besides the LA cell, long-distance imaging lens and off-axis viewing system, further technological developments achieved in this collaboration include:</p> <p>a) A user-friendly, graphic-user-interface (GUI)-based, fully image-controlled LA software (‘GeoStar’) ideal for a multi-user environment</p>

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- b) A rotating, variably-sized rectangular aperture that combines highest-spatial resolution with high-sensitivity, facilitating analysis of curved layered samples such as speleothems or corals
 c) A unique peltier-cooled sample holder compatible with the two-volume LA cell that allows analysis of frozen samples (ice cores, biological tissues)

The new laser-ablation facility is the cornerstone of a palaeoenvironmental research group at Royal Holloway Earth Sciences (1 postdoc; >5 PGR students) including:

- (1) Seasonally-resolved Palaeogene Mg/Ca thermometry and 'deep-time' Mg/Ca seawater reconstruction using large benthic foraminifera as newly-developed proxies (*Evans & Müller, 2012*).
- (2) In-situ chemical analysis of Greenland ice cores at ~100µm resolution across rapid climate change events (*Müller et al 2011*)
- (3) Seasonal-resolution of Miocene Caribbean palaeoenvironments using corals (*Griffiths et al., 2013*) and Indonesian Throughflow using giant clams
- (4) High-resolution time-series studies of human tooth enamel (*Müller et al 2009*) and Ca-isotope systematics in bioapatite (*Dr Qiong Li, Leverhulme PDRA*).

The new LA-ICPMS facility designed and installed at Royal Holloway has been fundamental to a multi-university, multi-disciplinary NERC **RES**ponse of humans to abrupt **ENV**vironmental Transitions Consortium (RESET, £3M, 2008-2012, Royal Holloway [Menzies], Oxford, Southampton, NHM). Volcanic ash trace element fingerprinting was undertaken entirely on the LA-ICPMS system. NERC-based research at Royal Holloway utilising the laboratory includes elemental analyses of annual growth laminae in speleothems (Mattey) and olivine trace elements (Thirlwall). In addition, within the REF period a large number of researchers from leading international institutions are conducting collaborative research with Müller utilizing the Royal Holloway LA-ICPMS instrumentation (eg Harvard, Oxford, UCL, Durham, Barcelona, Innsbruck, Manchester, Edinburgh, Zürich, Oviedo).

3. References to the research: All outputs available from the HEI on request.

Research Quality:

1. Müller, W., Shelley, M., Miller, P., Broude, S., 2009. Initial performance metrics of a new custom-designed ArF excimer LA-ICPMS system coupled to a two-volume laser-ablation cell. *Journal of Analytical Atomic Spectrometry* **24**: 209-214. DOI: 10.1039/B805995K
2. Tomlinson, E. L., Thordarson, T., Müller, W., Thirlwall, M. & Menzies, M. A. 2011 Microanalysis of tephra by LA-ICP-MS - Strategies, advantages and limitations assessed using the Thorsmork ignimbrite (Southern Iceland). *Chemical Geology* **279** (3-4): 73-89. DOI: 10.1016/j.chemgeo.2010.09.013
3. Müller, W., Shelley, J.M.G., Rasmussen, S.O., 2011. Direct chemical analysis of frozen ice cores by UV-laser ablation ICPMS. *Journal of Analytical Atomic Spectrometry* **26**: 2391-2395. DOI: 10.1039/C1JA10242G

RESolution LA-ICPMS prototype applications:

4. Evans, D. & Müller, W. 2012. Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca. *Palaeoceanography* **27**(4): PA4205, DOI:10.1029/2012PA002315.
5. Griffiths, N., Müller, W., Johnson, K. G. & Aguilera, O. A. 2013. Evaluation of the effect of diagenetic cements on element/Ca ratios in aragonitic Early Miocene (~16 Ma) Caribbean corals: Implications for 'deep-time' palaeo-environmental reconstructions. *Palaeogeography, Palaeoclimatology, Palaeoecology* **369**: 185-200. DOI: 10.1016/j.palaeo.2012.10.018
6. Rittner, M. & Müller, W. 2012: 2D mapping of LA-ICPMS trace element distributions using R. *Computers & Geosciences* **42**: 152-161. DOI: 10.1016/j.cageo.2011.07.016

2) Key research grants (Total £900k):

Müller, W.: **SRIF3** (2006-2007) "Human Environment Initiative" for establishing the new custom-designed LA-ICPMS system at Royal Holloway. (~£370k).
 Müller, W.: **NERC Small Grant** (2010-2011) *A new method for dating brittle deformation: U-Pb*

Impact case study (REF3b)

dating of carbonate fibres. (£63k), NE/H012702/1

Müller, W.: Royal Holloway-PI of EU FP7 **Marie Curie Initial Training Network (ITN)** (2010-2013) *“Throughflow”: Cenozoic evolution of the Indonesian Throughflow and the origins of Indo-Pacific marine biodiversity: Mapping the biotic response to environmental change.* (lead-PI: K. Johnson, NHM). €216k (~£173k) at Royal Holloway (total ~€3M), FP7-PEOPLE-ITN-2008-237922

Müller, W.: **Industry-funded research grant**, Resonetics LLC (USA) and Laurin Technic (Australia) for 3 years (2010-2013), (£43k).

Müller, W. & Thirlwall, M.F.: **Leverhulme Trust Research Project Grant** (2012-2015) *Spatially-resolved Ca isotope systematics in vertebrates by LA-MC-ICPMS.* (£251k), RPG-156.

4. Details of the impact

The research and instrumental development described above gave rise to a new tool for the Earth Science community – namely the laser-ablation system ‘RESolution series’. A laser-ablation system utilizes high-energy (up to GW/cm²), deep-UV (e.g. 193 nm) photons for the controlled removal (ablation) of material at μm -spatial resolution (<10 - >300 μm). Ablation takes place in a He-atmosphere inside a gas-tight LA cell that contains variously shaped and sized samples and produces nanometer-sized particles. These are transported into a plasma-based ion source (ICP), where they are atomized and ionized, and then analysed in the attached mass spectrometer (MS), hence (MC-(ICPMS). **The geometry and (small) volume of the LA sample cell is critical as the LA system must maintain exactly the same performance characteristics irrespective of sample size / shape (e.g. a long stalagmite, a tiny zircon or a single foraminifer). For the first time, the RESolution LA systems with their two-volume LA cells guarantee such a performance for a commercially available instrument** (Müller et al., 2009), applicable to essentially all solids (diamonds, ice, minerals (carbonates, phosphates, silicates, ores), metals, wood, polymers etc.).

The performance metrics of the new system include superior analytical precision via much improved LA-ICPMS signal stability (~fivefold; Müller et al. (2009)), excellent accuracy especially for high-precision isotope ratio analysis (e.g. Hf; Sr isotopes), and significantly shortened analysis time due to very rapid signal washout of the two-volume LA cell. The latter also enables reliable and routine depth-profiling (e.g. Griffiths et al., 2013), which facilitates *sub- μm* spatial resolution since a single laser pulse removes <100 nm (<0.1 μm) of material.

The leading role of Royal Holloway Earth Sciences in LA system development is highlighted by having been invited to organize and host the forthcoming (12th) European Workshop on Laser Ablation (EWLA) in July 2014, a biennial international conference on laser-based microanalysis (<http://ewla.rhul.ac.uk/>). Müller chairs the organizing committee.

The impact of this instrument development can be clearly demonstrated in several areas:

1) Resonetics (USA) & Laurin Technic (Australia)

The commercialization and continued development of the Royal Holloway prototype via the joint venture between Laurin Technic (*Canberra, Australia*) and led by Resonetics LLC (*Nashua, NH, USA*) **has created an entirely new area of commercial activity for Resonetics (The President/Director of Resonetics 2011/12)**. Resonetics was previously not active in the Geoscience sector but since ~2009 are considered a key player, driving innovation in laser-ablation. The laser-ablation market since 2007 has changed almost beyond recognition, because the new competitors such as Resonetics or Photon Machines (on the market with their two-volume cell ~2 years after Resonetics) have removed the earlier market dominance of NewWave Research and driven innovation significantly forward.

For Resonetics, this has resulted in a US\$7 million turnover and the direct support for eight to ten employees to manufacture the “RESolution series“ LA-ICPMS based on the Royal Holloway prototype, with research money being returned to Royal Holloway (see Sections 3 & 5). The continued construction of highly specialized two-volume LA cells in Canberra by Laurin Technic also strongly supports the local specialist engineering and machining

industry there. Further impact at Resonetics is evident in their biomedical application areas, as documented in a letter from the *President/Director of Resonetics* in 2013: ‘...Resonetics was able to utilize some of the core technology from the RESOLUTION on laser manufacturing equipment for CGM devices. CGM devices are utilized to allow diabetics to monitor their blood sugar levels [...]. [...] use some of the technology developed for the RESOLUTION and expand it for use with producing next generation stents. Stents are used to heal either blocked or damaged arteries [...].’

2) Geochemical microanalysis worldwide

The new instrumentation had significant impact in the analytical Geoscience community through the introduction of much more sophisticated hardware integrated with (MC-)ICPMS and controlled by user-friendly software. In addition this high-end instrument has resulted in 20+ sales worldwide in ~3 years and the details are documented in section 5 below. Apart from the two-volume LA cell, further instrumental breakthroughs that substantially enhance the types of material that can be analyzed and the analytical capabilities include

- (a) a cryogenic sample holder compatible with the two-volume cell,
- (b) a rotating rectangular aperture for analysis of curved, layered samples (e.g., speleothems, corals) at maximum spatial resolution combined with maximum sensitivity,
- (c) development in sophisticated gas plumbing including a debris exhaust valve activated during pre-analysis cleaning.

5. Sources to corroborate the impact

Reports, web links in the public domain

Statements on the Resonetics Web-site confirm the impact of this research on the development of the Resonetics RESOLUTION product line <http://www.resonetics.com/la/?p=history> :

“.....RESOLUTION Instruments: When Dr Wolfgang Müller moved from the Australian National University (ANU) to Royal Holloway University of London (RHUL), he needed a LA-ICPMS instrument to continue his work on geosciences.....and on high resolution (palaeo) environmental records (teeth, speleothems etc.). He developed with Resonetics of Nashua USA and Michael Shelley of Laurin Technic Pty. Ltd. (Canberra, Australia) an instrument with a medium-sized excimer laser operating at a maximum repetition rate of 100 Hz. This instrument was designed to be the ultimate, no compromises, laser ablation instrument. The RESOLUTION Series is the developed result.....”

Company executives who will corroborate this Case Study

Resonetics LLC

The then President, now Director of Resonetics LLC will confirm that Royal Holloway not only initiated this new innovative analytical instrument but also provided the design specifications and established the joint venture between the two companies in Australia and the USA. Resonetics can also confirm sales figures.

Laurin Technic

The Director will confirm the leading role of Royal Holloway in establishing this new initiative and the ensuing and ongoing cooperation between Royal Holloway, Resonetics and Laurin Technic.

Selected users of RESOLUTION M-50 systems

Users of the RESOLUTION M-50 systems will confirm how successful the new prototype has been and its broad applicability in the sciences:

1. Leader of the Technology Programme, CODES-ARC Centre of Excellence in Ore Deposits, University of Tasmania, Australia
2. Centre for Geobiology, Department of Earth Sciences, University of Bergen, Norway
3. Equipe de Geochimie, University of Clermont-Ferrand, France