Institution: University of Reading		
Unit of Assessment: 8 - Chemistry		
Title of case study: Development of synchrotron facilities at Diamond Light Source for ambient pressure X-ray spectroscopy		
Period when the underpinning research was undertaken: Between 2008 and 2020		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Georg Held	Professor	2006 to May 2019
Roger Bennett	Associate Professor	2000 to Present
Period when the claimed impact occurred: Between 1 August 2013 and 31 July 2020		
Is this case study continued from a case study submitted in 2014? No		

1. Summary of the impact

Through the design, construction and operation of beamline B07 VerSoX at Diamond Light Source (DLS), Professor Held has addressed the demand for spectroscopy at vapour-solid, vapour-liquid and liquid-solid interfaces within technologically important systems maintained under realistic, *operando* conditions. He instigated and then, as a joint appointment between the University of Reading and DLS, led the beamline project, attracting circa GBP6.2M capital investment and 40 person-years of support. VerSoX is unique in the UK and the novel technologies he developed, self-cleaning mirrors and correction of distortions in large mirror optics, solve common beamline problems. These technologies, subsequently adopted by facilities worldwide, significantly reduce beamline downtime, save costs for replacing contaminated optics and ensure consistent, high-quality user experiences. VerSoX has delivered >6200h of user beamtime to academic and industrial users worldwide, including the multinational company Johnson Matthey PLC.

2. Underpinning research

The design, development, and construction of the B07 Versatile Soft X-ray beamline (VerSoX) at DLS has been spearheaded by Held, from the University of Reading, since 2010. He is now the principal beamline scientist, in charge of the entire VerSoX beamline operation and all future development of ambient pressure (AP-) soft X-ray spectroscopies, mainly X-ray photoelectron and X-ray absorption spectroscopies (AP-XPS and AP-XAS). The beamline provides a unique combination of sample environments (toxic or reactive gas mixtures at controlled pressures up to 10kPa H_2 / 5kPa H_2O) and photon energies between 250 and 2800eV. The straightforward user control (plus remote operation by external users, developed during the 2020 COVID-19 pandemic), in combination with multiple analytical capabilities to probe the chemical nature and composition of the near-surface regions of samples, make VerSox both internationally leading and distinctive. The beamline, a first in the UK, represents a step-change capability for the UK industrial and academic community [R1].

The need for an AP-XPS facility at DLS was first identified by Held and colleagues in a proposal to the STFC (ST/H0017431/1) in 2009 - led by G. Held (Principal Investigator) and R.A. Bennett (Co-Investigator, Reading), with M. Bowker (Cardiff), J.N. O'Shea (Nottingham) and T-L Lee (DLS). The intention was for a mobile analytical end station to be accommodated on existing X-ray beamlines I06, I09 or I10. Held was subsequently invited by DLS to co-lead a more ambitious proposal for not just an end station but a complete dedicated beamline at DLS. Held was one of three proposers (together with A. Evans (Aberystwyth) and S. Schröder (Manchester)) of the beamline project *'Versatile Soft X-ray Beamline at the Diamond Light Source (VerSoX)',* DLS Phase III Beamline Proposal 059 submitted to, and approved by, the DLS Science Advisory Committee (SAC, international peer review, March 2011). The DLS Industrial Science Committee also rated the proposal highly in light of national industrial priorities, and hence it was funded.

Held's research during this period was increasingly focussed on applying AP-XPS and AP-XAS to catalytic problems, such as identifying new hydrogen-stabilized enantioselective modifier geometries under H_2 [R2], understanding the influence of water solvation on surface reactions [R3] and probing methane partial oxidation catalysis [R4]. This was undertaken at international facilities worldwide (over 40d per year) and led to him becoming established as an expert in AP-XPS and AP-XAS. Following his joint appointment in January 2012 (60% University of Reading /

40% DLS FTE; 40% University of Reading / 60% DLS FTE from October 2013), he oversaw the conceptual and technical design of the beamline, its construction and commissioning [R1]. The AP-XPS branch C started user operation in July 2017 and a second high-throughput XPS and high-pressure XAS branch B is scheduled to start user operation in spring 2021. Held has also led the way in developing innovative new technologies to advance beamline performance, fully implemented on VerSoX and elsewhere. These include:

i. Self-cleaning mirrors [R5]: Contamination-free surfaces of mirrors and monochromator gratings are of the utmost importance for efficient use of synchrotron radiation [R5]. However, the intense synchrotron radiation decomposes carbon-containing molecules, present in the residual vacuum vessels of beamlines, and causes carbon contamination of optical surfaces. This usually results in large losses in X-ray transmission, particularly around the C K-edge energy, as well as generating fine structure in X-ray transmission. This distorts X-ray absorption data acquired in this key spectral region and severely limits or destroys the capability to measure the main constituent atoms of organic molecules and biosystems. Held's experiments with the Pt(111) surface at the Soleil synchrotron identified that photodissociation of O_2 in the high photon flux allowed adsorption of dissociated oxygen and hence oxidation of strongly adsorbed C and CO at low temperatures [R5]. The work went further to demonstrate that self-cleaning of beamline optics could be achieved by maintaining the same low-pressure oxygen atmosphere in the vacuum vessel containing the optics. Crucially the optics are continually cleaned by the oxygen and X-rays while the beamline is in operation. This avoids the build-up of carbon and improves beamline optics over long timescales. The photochemical mechanism [R1, R5] also enables even cryogenically cooled and chemically unreactive Au mirror surfaces to be cleaned in this way.

ii. Correction of focal length [R6]: Focussing and steering synchrotron radiation requires specific mirror and optical design. VerSoX uses large, 1.4m long toroidal mirrors which require active cooling. Thermal expansion and tension induced by clamping the mirrors introduces deformation of the radius of curvature, altering the focussing characteristics. On DLS beamlines B24 (Full field cryo-X-ray microscopy for the life sciences) and B07 (VerSoX) Held and colleagues found that by using standard facility cooling water of 20°C the mirror focuses up to 5m away from design position at the exit slit due to thermal and stress-induced distortion. Held et al. showed that modest changes to externally accessible parameters, involving tuning the cooling water temperature to within 0.1°C [R6], could compensate for the distortion of inaccessible components within the shield wall of the synchrotron ring. This significantly improves beamline transmission and energy resolution, restoring optimal design performance.

3. References to the research

The research resulted from competitive, peer-reviewed funding applications and secured substantial peer-reviewed beamtime. It has led to a unique beamline at an international facility and has been published in international, peer-reviewed journals in the field. It meets or exceeds 2* quality definitions in that it advances knowledge of processes occurring at surfaces and influences the way in which practitioners choose to undertake their research. The implementation of self-cleaning mirror technology at synchrotron facilities worldwide stemming from this research represents a significant change to practice. The research has had an influence on user engagement in extending the type of experiment conducted by the industrial and academic research base.

[R1] **Held G.** et al., (2020). 'Ambient-Pressure Endstation of the Versatile Soft X-ray (VerSoX) Beamline at Diamond Light Source'. *Journal of Synchrotron Radiation*. **27**, 1153-1166.

[R2] Nicklin, R. E. J., Shavorskiy, A., Aksoy Akgul, F., Liu, Z., **Bennett, R. A.**, Sacchi, M. and **Held, G**., (2018).' 'Pop-On and Pop-Off' Surface Chemistry of Alanine on Ni{111} under Elevated Hydrogen Pressures'. *The Journal of Physical Chemistry C*, **122** (14), 7720-7730.

[R3] Shavorskiy, A., Aksoy, F., Grass, M. E., Liu, Z., Bluhm, H. and **Held, G.** (2011). 'A step toward the wet surface chemistry of glycine and alanine on Cu{110}: destabilization and decomposition in the presence of near-ambient water vapor.' *Journal of the American Chemical Society*. **133** (17) 6659-6667.

[R4] Price, R., Eralp-Erden, T., Crumlin, E., Rani, S., Garcia, S., Smith, R., Deacon, L., Euaruk-sakul, C. and **Held, G.** (2016). 'The partial oxidation of methane over Pd / Al_2O_3 catalyst nanoparticles studied in-situ by near ambient-pressure X-ray photoelectron spectroscopy.'

Topics in Catalysis, **59** (5-7), 516-525.

[R5] Risterucci, P., **Held, G**., Bendounan, A., Silly, M. G., Chauvet, C., Pierucci, D., Beaulieu, N. and Sirotti, F. (2012). 'Preventing carbon contamination of optical devices for X-rays: the effect of oxygen on photon-induced dissociation of CO on platinum'. *Journal of Synchrotron Radiation*. **19** (4), 570-573.

[R6] Hand, M., Wang, H., Harkiolaki, M., Venturini, F., Arrigo, R., Ferrer-Escorihuela, P., Alcock, S., Nistea, I., Marshall, A., Scott, S., Duke, L., **Held, G.** and Sawhney, K. (2019). 'Compensation of X-ray mirror distortion by cooling temperature control.' *Proceedings of the 13th International Conference on Synchrotron Radiation Instrumentation – SRI2018*, AIP Conference Proceedings 2054, 060044.

Grant Information:

Held has had 484d synchrotron beamtime awarded through competitive peer review at facilities in Europe and the USA since 2007 and approximately GBP940,000 income from EPSRC, EU Marie Curie Network and industrial funding from DLS and Johnson Matthey PLC for synchrotron-based soft X-ray spectroscopy research.

'Versatile Soft X-ray Beamline at the Diamond Light Source (VerSoX).' DLS Phase III Beamline Proposal 059 - A proposal prepared for the DLS SAC, March 2011. Funded since 2012.

4. Details of the impact

Investment by Diamond: DLS is funded by STFC (60%) and The Wellcome Trust (40%). Since its inception in 2001, it has had investment of approximately GBP1bn. The development of the 39 beamlines now in operation at DLS was divided into three phases. The VerSoX project started in 2012 and was one of the last beamlines to be built in Phase III (between 2008 and 2017). DLS capital investment is approximately GBP4.2M (August 2020) into the front end, branch C beamline, end station, control systems, gas handling and sample environments [E1], and a further GBP2M (August 2020) into the branch B beamline and end stations [E2]. The planning, design, engineering, and construction took approximately 40 person-years of engineering support [E1]. Beamline B07 currently supports seven permanent beamline staff (Held as Principal Beamline Scientist, four senior beamline scientists, one PDRA and one technician) [E2].

Meeting beamline community demand: VerSoX is unique in the UK, offering tuneable, soft X-ray spectroscopy under controlled gas environments, and is enabling a wide range of systems and processes to be studied as close as possible to real-life, *operando* conditions, meeting unmet demands of UK and international chemists. The AP-XPS branch C has been operational since 2017. Branch B, high-throughput XPS and high-pressure X-ray absorption spectroscopy, is currently in the final stages of construction. Branch C had delivered >6200h of academic and industrial user beamtime by August 2020 [E2]. So far, over 30 user groups from the UK, Europe, America, Asia, and Africa have benefitted from beamtime allocations. Requested beamtime typically exceeds the available time by two to three times, despite being in the early years of building a user community. Its novelty has successfully brought in new users to the DLS, particularly from within the catalysis community, like the UK Catalysis Hub at Harwell [E2]. DLS has stated that "*the critical partnership for this success has been with the University of Reading through Prof Held, who has provided a rare and invaluable combination of expertise in both the measurement science and engineering and in the scientific drivers to lead the design of some of our cutting edge beamlines."… "Put simply, VerSox, or a beamline with a similar performance and impact in the areas it serves, would not have happened without this collaboration"* [E2].

i. Self-cleaning mirrors: Widespread adoption of the research [R5] has led to the implementation of self-cleaning optics at six beamlines at international facilities (there are approximately 36 synchrotrons worldwide) and is specified for deployment at several more. By eliminating cleaning cycles and increasing mirror lifetime, approximately 900d instrument downtime has been saved at these facilities since 2013. In addition to VerSoX, at DLS the 'self-cleaning' mirror technology has been implemented on the insertion device beamline I09 (Surface and Interface Structural Analysis) and has been specified for the aberration-corrected Photo Emission Electron Microscope (PEEM) upgrade to beamline on I06 (Nanoscience), where measurements on graphene and other 2D materials will benefit from C K-edge XAS. This technology will also feature on many more beamlines, both at DLS II, as part of the proposed upgrade programme, and internationally; for example, at the new Thai SPS-II synchrotron, where it has already been specified for the High-

Resolution Soft X-ray Spectroscopy beamline [E3]. This innovation has also been adopted by the following beamlines: PolLux Swiss Light Source, since 2014 [E4]; Hermes, since 2012 [E5] and Tempo, since 2011 [R5, E6] - both Soleil Synchrotron in France; ID32 European Synchrotron Radiation Facility in France, since 2014 [E7a,b]; and MAX-IV HIPPIE beamline Swedish National Synchrotron, since 2016.

The Tempo beamline (Soleil) was the testbed for the operation of the self-cleaning mirrors and due to continuous operation since 2011, provides an exemplar of the value of the system to facilities that adopt the methodology. Soleil staff found that *"In the last year of operation, we have not observed significant carbon contamination in contrast to the experience before when no oxygen was introduced"* [R5]. More recently, they detail that the self-cleaning mirrors significantly extend mirror working lifetime (perhaps indefinitely), and hence lengthen the time between replacements [E6]. Mirrors were previously replaced every five years due to damage caused by oxygen plasma cleaning, and now there is a saving of "*50 k€ in replacements and 15 days of downtime and commissioning*" [E6]. Plasma cleaning, required every three months, takes at least a week to perform and roughens the mirror surface. The cumulative damage degrades the optical performance across all X-ray wavelengths. Since adopting self-cleaning technology, Soleil have not had to plasma clean their mirror, saving this beamline approximately 210d of facility time since August 2013, in addition to the time and cost involved in exchanging the roughened mirrors [E6]. Hence, the technology demonstrably increases lifetime, shortens instrument downtime by around 30d per year, per instrument, and gives a more consistent user experience over both the medium- and long-term, because: carbon does not build up over time [E7b]; mirror roughness is constant; and experiments that need high-quality X-rays at the carbon K-edge do not need to be scheduled soon after plasma cleaning. Dr. A. Bendounan, Beamline Scientist at the Soleil synchrotron in France, stated: *"The improved performance of the beamline around the C K-edge has allowed us to undertake new and more challenging experiments with our academic and industrial users"* [E6].

ii. Correction of focal length: DLS beamline B24 and B07 (VerSox) both employ large toroidal mirrors, necessarily located within the structure containing the storage ring itself, before the concrete radiation 'shield' wall. This hard X-ray environment is inaccessible whilst the synchrotron is running and requires specialist and expensive instrumentation to operate reliably within it. Held's elegant solution [R6] to compensate for mirror distortions by modulating the cooling water temperature allows optimisation of beamline transmission without opening the storage ring. It has been successfully adopted on B24 and B07. Distortions due to thermal expansion and clamping of large mirrors are unavoidable, so this problem will likely manifest itself in many beamlines. The correction method restores the beamline to its design performance without the need to open the mirror module, remove the mirror from the beamline, or indeed shut the storage ring. Thus, the facility is saved much effort and time in making unnecessary repairs and alterations or building complex engineering solutions in a harsh X-ray environment.

Commercial use: At DLS, beamlines generally become available for proprietary use after at least one year of full user operations; however, DLS's CEO Professor Andrew Harrison has said: *"In the case of VerSoX the interest from industry was so great that we decided to offer access much earlier for experienced users"* [E2]. As an exemplar of this type of access, the relationship between the beamline with Johnson Matthey PLC (JM) demonstrates its value to industry. JM is a global leader in sustainable technologies and '*maintains its leading science position in emission control catalysis, chemical synthesis catalysis, PEM fuel cell and lithium ion battery materials through continuous investment in R&D based on achieving insight and designed improvement through advanced characterisation'* [E8]. As a key strategic partner for DLS, JM can use VerSoX through direct access for open research and can also buy time for proprietary research including several days for collaborative research with staff across DLS per annum. JM have spent 23d at VerSox to date, which they equate to approximately 100d of R&D activity [E8]. JM's Dr Peter Ash states: *"The direct impact of the work has been a significant shift of our understanding of the relationships between surface oxidation states, temperature and gas composition. This has not been possible before and has impacted on our modelling of the behaviour of our materials"* [E8]. The close relationship with JM has grown throughout the assessment period [E8] through the development of analytical techniques by Held that directly address the generic pressure [R3] and materials gaps

[R4] that are inherent in JM's work. Dr Ash adds: *"In many areas of characterisation, current trends in instrumentation and facilities have allowed in-situ and 'operando' measurements to be made that enhance insight through observations of active materials close to their duty cycle. Until recently this has been very difficult in one of our key measurement goals, that of surface spectroscopies*" [E8]. VerSoX is influencing how JM chooses to undertake its research, since the company became a regular commercial user of the beamline. Dr Tuğçe Eralp-Erden (Principal Scientist X-ray Photoelectron Spectroscopy, JM) explains the science undertaken at VerSoX that drives innovation in catalytic materials: *"…we've been learning a lot about new characterisation techniques that are used at Reading University and what the fundamentals of these techniques are. JM has very complex materials and we wanted to apply these methods on JM's materials"* [E9]. *"Since the start of operation in July 2017, the beamline has delivered circa 6,200 hours of beamtime to users, of which 4,200 hours (68%) were for research with direct industrial links."* – DLS CEO, Andrew Harrison [E2]. This is a higher percentage of commercially relevant beamtime than the average of 40% of projects with an industrial partner seen across DLS as a whole – demonstrating that VerSoX allocations underpin a high level of industrial research activity.

Development of an expert community: Bringing unique capabilities to scientists, engineers, and industrialists in the UK, VerSoX is beginning to make widespread contributions to new, industry-facing centres of excellence. Locally, VerSoX has strong links to the UK Catalysis Hub [E2, E8] with members of the beamline team contributing to training and arranging conferences (e.g. 3rd International Workshop on Ambient Pressure X-Ray Photoelectron Spectroscopy 2016). VerSox is also currently forming strong bonds to the Faraday Institute (through R. Weatherup, Oxford) with a studentship and a PDRA co-hosted by VerSoX. The unique capabilities of VerSoX provide insights into batteries and electrochemistry in general, since measurements in electrolytes are now possible, as highlighted in the first reference of [E2]. The dispersal of trained and aware scientists into industrial sectors strengthens those sectors. Alumni from the Held group, who were instrumental in early AP-spectroscopy or have worked at VerSoX, now hold prestigious roles in industry (Dr Eralp Erden, Principal Scientist JM) and at other facilities (Dr Andrey Shavorskiy, Beamline Manager Max IV in Sweden; Dr Chanan Euaruksakal, Thai synchrotron in Thailand).

Summary: The demand for spectroscopy at interfaces within systems maintained under realistic, *operando* conditions has been met with the B07 VerSoX beamline at DLS, a unique beamline in the UK. VerSoX has delivered >6200h of user beamtime already, with significant engagement with industry leaders JM. Held has also created solutions for self-cleaning mirrors and the correction of distortions in large mirror optics. These technologies have been adopted by facilities worldwide and have significantly reduced beamline downtime, generated costs savings for replacement parts and ensured consistent, high-quality user experiences.

5. Sources to corroborate the impact

[E1] Technical Design Report for the B07 VERSOX PART- B, Project Planning Document 2012.
[E2] Letter from Chief Executive Officer, Diamond Light Source Ltd., August 2020.
[E3] Testimonial from Synchrotron Light Research Institute, Thailand, June 2020.
[E4] Watts B., Pilet N., Sarafimov B., Wittea K. and Raabe J. (2018). Scanning Transmission X-Ray Microspectroscopy beamline, "Controlling optics contamination at the PolLux STXM", *Journal of Instrumentation.* **13**, C04001.
[E5] Swaraj S., Belkhou R., Stanescu S., Rioult M., Besson A. and Hitchcock A. P. (2017). ' X-ray microscopy beamline, 'Performance of the HERMES beamline at the carbon K-edge', *IOP Conference Series: Journal of Physics*: **849**, 012046.
[E6] Testimonial SOLEIL SYNCHROTRON, France, June 2020.
[E7] (a) N. B. Brookes et al. (2018). 'Soft X-ray spectroscopy beamlines employing common cryogenic Au mirror 'The beamline ID32 at the ESRF for soft X-ray high energy resolution resonant inelastic X-ray scattering and polarisation dependent X-ray absorption spectroscopy', *Nuclear Inst. and Methods in Physics Research*. **903**, 175–192.
(b) email from Nicholas Brookes, ESRF, June 2020.
[E8] Testimonials from Johnson Matthey PLC, August 2020.
[E9] University of Reading "Shedding new lights on catalysts – VERSOX: An X-ray beamline…" Video and YouTube plus accompanying transcript, June 2020.