



# Chemistry

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Transforming silica into silicate - pilot scale removal of problematic silica from geothermal brine

Modern techniques for the discovery of marine natural products

Elementary history

Biodegradable magnesium in temporary medical implants

The fading of acetylene's bright light

Ruby gold glass: early nanotechnology in art and science

Brian Halton, 1941 - 2019

Robin Clark, 1935 - 2018



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# The International Symposium on Macrocyclic and Supramolecular Chemistry

On behalf of the local organising committee, you are invited to participate in the International Symposium on Supramolecular and Macrocyclic Chemistry (ISMSC-2020) to be held in Sydney, Australia from July 12 – 16, 2020.

ISMSC-2020 will provide a forum for the discussion of all aspects of macrocyclic and supramolecular chemistry, including nanoscience and materials science. It will follow the style of the preceding meetings in the series with a single scientific session running throughout the conference.

ISMSC, the International Symposium on Macrocyclic and Supramolecular Chemistry, came from a fusion of the International Symposium on Macrocyclic Chemistry (ISMC) and the International Symposium on Supramolecular Chemistry (ISSC). These meetings combined in 2006 and since then have been held on an annual basis in a different location. Join us for the meeting in Sydney in 2020!

<https://www.ismsc2020.org/home>



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## Comment from the President

Welcome to the April issue of *Chemistry in New Zealand*. As I mentioned in the last issue, 2019 sees another big change for the Institute; we have a new treasurer following Colin Freeman's retirement. I am delighted to announce that Hamish McDonald has been appointed as the new NZIC treasurer. Hamish has been a member of NZIC for 35 years, and although now based in Sydney retains very close connections with NZ through family, friends and investments. After completing an MSc in Organic Chemistry at the University of Auckland, he initially worked as a QC chemist, and has since progressed through a broad range of operational, commercial, and strategic senior management roles in quality, manufacturing, logistics, information technology and financial services. Additionally he has held directorships with a number of corporate superannuation funds and was treasurer/community elected director of The Kolling Foundation, a research charity associated with the Royal North Shore Hospital in Sydney. Hamish has considerable experience in financial administration and management. He attended his first NZIC Council meeting in February in Christchurch and has already proved a very valuable addition to the governance team. I hope you will all make Hamish welcome as he settles into his new role within the NZIC.

The good news for Distinguished Professor Margaret Brimble (University of Auckland) kept coming at the end of 2018 with the announcement in the New Year Honours List of her appointment as Dame Companion of the New Zealand Order of Merit (DNZM) for services to science. A reminder that in 2018 Distinguished Professor Brimble was the first New Zealand woman to be elected Fellow of the Royal Society (London). On behalf of all the Institute many congratulations Margaret, these high level international recognitions are richly deserved.

Continuing the theme of celebrating women in science, and chemistry, on 12<sup>th</sup> February many of you will have attended a local Global Women's Breakfast event. The event was titled "Empowering Women in Chemistry: A Global Networking Event". The New Zealand events,



hosted across the branches, had the privilege of being the initiators of a global handshake from Palmerston North and the AMN9 Conference (first cabs off the rank) around the world to Honolulu, Hawaii, who had to wait and follow the event on Twitter before bringing the proceedings to a close. I organised and attended a breakfast in Perth, Australia as part of the organising committee of the RACI PhysChem 2019 conference! The Global Women's Breakfast was designed to assist women chemists to expand their network of contacts, both locally and internationally. Women at different stages of their individual careers were encouraged to inform each other about their career progress, and together explore opportunities, in professional development and in research or teaching horizons. The feedback received so far is that this was a phenomenally successful event. Please check out <https://iupac.org/100/global-breakfast/> for more information and pictures from the various events worldwide.

The breakfast event was heavily publicised and followed on social media, and I'm delighted to report that NZIC has recently joined Facebook (search New Zealand Institute of Chemistry) and Twitter (our handle is @\_NZIC). Please follow us. On Twitter, please tag @\_NZIC in chemistry related tweets, and use the hashtag #nzchem to build up a record of exciting NZ chemistry related news.

Media interaction for the International Year of the Periodic Table 2019 has begun apace. I had a Saturday morning chat with Charlotte Graham-McLay from The Weekend show about the curious history of the periodic table, whilst the Element of the Week discussion on Radio New Zealand has started. I hope you have all been tuning into the Sonic Tonic and subsequent discussion on the Friday evening Nights show with Bryan Crump. As I write this we've had Cather Simpson discussing the periodic table (Sonic Tonic Theme – Periodic Table), Dave McMorrnan discussing helium (Sonic Tonic Theme – Balloons), Christian Hartinger discussing platinum (Sonic Tonic Theme – Blonde) and Matt Cowan discussing silver (Sonic Tonic Theme – Cutlery). All of the interviews are available on the Radio NZ website in the Nights section. Continuing the engagement with radio, Professor Allan Blackman (AUT) is also doing a series of podcasts, called *Elemental*. These have just launched on the Radio NZ website and can be found here <https://www.radionz.co.nz/programmes/el->

*emental*. I encourage you to listen to all of the interviews and podcasts, and let friends and family know about them.

Finally, on a sad note I acknowledge the loss of several valued members of the NZIC in recent weeks. Professor Brian Halton passed away in February 2019. Brian was an active member of the NZIC, serving a term as president and being instrumental in revitalising our *Chemistry in New Zealand Journal*. Lilly Taylor passed away at the end of January. Still near the start of her chemistry career, Lilly made a large impact on many people and was a strong advocate for women in STEM subjects. She was the secretary of the Canterbury branch. Professor Robin Clarke passed away at the end of 2018. Robin was a leading figure in experimental physical and inorganic chemistry. Obituaries and tributes can be found in this edition of CiNZ. Our thoughts are with all the families at this time.

**Sarah Masters**  
NZIC President

## New Zealand Institute of Chemistry

*supporting chemical sciences*

### April News

#### AUCKLAND

##### The University of Auckland

##### Events

##### *Naming of the Kathleen Curtis atrium*

The atrium of the new Science Centre (Building 302) at the University of Auckland was renamed the Kathleen Curtis Atrium, in honour of the first woman to receive a DSc in New Zealand and who became the first female Fellow of the Royal Society of New Zealand (Royal Society Te Aparangi). There is now a plaque and a portrait of Dr Kathleen Curtis in the atrium, the painting being a replica of one held by the Royal Society Te Aparangi. Distinguished Professor Margaret **Brimble** gave an address on Kathleen's life and achievements and gifted the portrait to the Uni-



Professor Emeritus Dame Charmian O'Connor giving a speech at the opening of the renaming ceremony of the Kathleen Curtis Atrium

versity of Auckland on behalf of the Royal Society. Professor Emeritus Dame Charmian O'Connor also gave a speech at the opening, as did the Minister for Research, Science and Innovation, Dr Megan Woods, who was very supportive of science and equity initiatives.

### **Global Women's Breakfast**

Dr *Melissa Cadelis* organised the Auckland leg of the Global Women's Breakfast at the University of Auckland. The Global Women's Breakfast was designed to assist women chemists to expand their network of contacts, both locally and internationally. The event was initiated by IUPAC, and the University of Auckland event was sponsored by the NZIC Auckland Branch.

### **Farewell to Professor Penny Brothers**

In February 2019, we farewelled Professor *Penny Brothers* as she takes up the Directorship of the Research School of Chemistry at ANU. Penny has been with the School of Chemical Sciences at the University of Auckland since 1986 (and was a student earlier still), and has contributed to the activities and success of the School and University in very many ways. A farewell event was held at the Old Government House on 7 February. Associate Professor *Gordon Miskelly*, Professor *James Wright* and Professor *John Hosking* acknowledged Penny's contributions as a colleague and as a citizen of the University during the event.

### **School of Chemical Sciences seminars**

The School of Chemical Sciences at the University of Auckland hosted several seminars between December 2018 and January 2019:

Professor Peter Behrens (Leibniz University Hannover, Germany): *Metal-organic frameworks and electrical conductivity: three cases*

Professor Marcus Rose (Technische Universität Darmstadt): *Catalysis engineering – from materials to process design for the utilization of bio-based feedstock*

Professor Ernst-Walter Knapp (Free

University of Berlin, Germany): *Bivalent and multivalent ligand binding*

Professor Michael Fröba (University of Hamburg, Germany): *Periodic mesoporous organosilicas: porosity meets functionality*

Dr Carlos Romero-Nieto (Heidelberg University, Germany): *Fused six-membered phosphorus heterocycles as highly fluorescent and stable materials*

Dr Vanessa Li (University of Hong Kong, Hong Kong): *Structuring and interfacing nanomaterials for electrochemical application and ion exchange*

Professor Rhett Kempe (University of Bayreuth, Germany): *Catalysis for a more sustainable chemistry*

Dr Matthew Cliffe (University of Cambridge, UK): *Disorder, dynamics & magnetism in molecular frameworks*

Dr Adam Perriman (University of Bristol, UK): *Enzymes out of water: reengineering protein surfaces for non-aqueous activity*

### **NZIC Auckland Branch seminars**

The University of Auckland hosted the following NZIC Auckland Branch seminars between November 2018 and February 2019:

Dr Matthew Cook (Montana State University, USA): *Palladium catalysed allylic rearrangements of N-alloc imides,ynamides and enamines*

Dr Tobias Gruber (University of Lincoln, UK): *From supramolecular methyllysine receptors to bridged caprolactams*

Dr *Jóhannes Reynisson* (The University of Auckland): *Known drug space as a navigational tool*

### **Staff successes**

#### **Dame Companion of the New Zealand Order of Merit**

Distinguished Professor *Margaret Brimble* has been made a Dame Companion of the New Zealand Order of Merit for her services to science. Distinguished Professor Brimble's citation is as follows, and shows

the wide range of contributions she has been making to New Zealand and international science:

"Distinguished Professor Margaret Brimble has made world-class contributions to research in medicinal chemistry and has been a key driver of the creation of a nascent drug discovery and development industry in New Zealand. Professor Brimble is Chair of Organic Chemistry and Director of Medicinal Chemistry at the University of Auckland. She discovered the drug candidate NNZ2566, named Trofinetide by the World Health Organisation, which is currently in phase three human clinical trials for treatment of Rett Syndrome and Fragile X syndrome. She established New Zealand's first Good Manufacturing Practice Peptide Active Pharmaceutical Ingredient Manufacturing Facility that was licensed by Medsafe NZ and produced clinical grade antigens for the MELVAC melanoma vaccine trial in 2014. She is Principal Investigator in the Maurice Wilkins Centre for Molecular Biodiscovery. She was Chair of the Royal Society of New Zealand Rutherford Foundation from 2009 until 2016. She has supported the L'Oreal-UNESCO Women in Science Programme. Since 2014 she has held the roles of Vice-President and President of the Organic and Biomolecular Division of the International Union of Pure and Applied Chemistry (IUPAC). She has been a panel member of the European Research Council Synthetic Chemistry and Materials Science Advanced Grants Scheme since 2015. In 2018 Professor Brimble was the first New Zealand woman to be elected Fellow of the Royal Society (London)."

#### **Dean's Award for Teaching Excellence (Early Career)**

Dr *Kaitlin Beare* won the 2018 Dean's Award for Teaching Excellence (Early Career). Dr Beare's citation states, "For responsive, student-focused teaching and dedication to building communities of practice and enhancing the culture of teaching and learning". Dr Beare's knowledge and enthusiasm is a real boost for the School.

#### **IUPAC Periodic Table of Young Chemists**

Dr *Erin Leitao* has been named as “Lanthanum” in the IUPAC Periodic Table of Young Chemists, which recognises outstanding younger chemists from around the world who embody the mission and core values of IUPAC. The IUPAC Periodic Table of Young Chemists is part of the celebrations of the 150th anniversary of the periodic table.

### Student successes

#### **ANBUG/AINSE Neutron Scattering Symposium, Lucas Heights, NSW, Australia**

PhD student Nur Maizura Mohd Darbi, who works with Associate Professor *Duncan McGillivray*, won second place in the poster contest for her work titled, *The attack of antimicrobial peptide on cell membrane*.

PhD student Joseph Vella, who works with Associate Professor *Tilo Söhnel*, won third place prize for his poster titled, *DFT studies of  $Fe_4Si_2Sn_7O_{16}$* .

#### **Massey University (Auckland Campus)**

The Albany chemists farewelled technician Danny Maloney as he returns to Dunedin.

*John Harrison* returned from a visiting professorship at Stanford University’s chemistry department where he continued his long standing collaboration with Professor Richard Zare. While there (apart from experiencing the worst air quality in the world due to the California wildfires) he was involved in successful experiments aimed at pioneering photon catalysis, where an intense pulsed electric field from a non-resonant laser directly influences the potential energy surface and the outcome of chemical reactions. John also continues his role as head of chemistry and physics in the newly renamed School of Natural and Computational Sciences at Albany. John welcomes to his group *Jade Pope*, a PhD candidate working on catalytic remediation of the earth’s atmosphere.

Professor *Peter Schwerdtfeger* was awarded a Catalyst Fund Dumont d’Urville grant to collaborate on atomic structure calculations for superheavy elements with the atomic

physics group at CNRS (CE), Laboratoire Kastler Brossel in Paris, led by Professor Paul Indelicato. It includes an active student and postdoctoral exchange program and finances two workshops, one in Auckland and the other one in Paris. This nicely coincides with the 2019 Year of the Periodic Table.

*Jon Kitchen* was awarded a Catalyst Seeding grant to collaborate on the development of lanthanide-containing molecular machines with Professor Steve Goldup in the UK. Jon welcomes *Alex O’Neil* into his group as a PhD candidate working on the development of luminescent lanthanide supramolecular materials.

In mid January Albany Chemistry (led by *Debbie Jordan* and *Erin Moffet*) hosted 6 groups of 30 students from The Rotary National Science & Technology Forum.

#### **Auckland University of Technology**

#### **NZ-Italy Meeting on Supramolecular and Materials Chemistry**

AUT hosted the NZ-Italy Meeting on Supramolecular and Materials Chemistry (NZIMSMC), sponsored by a Catalyst Seeding grant held by Dr *Jack Chen*. This two day event brought together researchers from Italy and New Zealand working in supramolecular and materials chemistry and featured a diverse array of talks covering topics from systems chemistry through to nanomaterials.

### New faces

We welcome a new MPhil student, *Bhavana Kapila*, who will be working with Dr *Cameron Weber* and a new third year research project student, *Jessica Robinson*, who will be working with Professor *Nicola Brasch*. *Bronte Carr* and *Chloe Ren* return to AUT, *Bronte* to do her BSc(Hons) with Professor *Allan Blackman* and *Chloe* is commencing her PhD with Dr *Jack Chen*.

Professor *John Goodwin* from Coastal Carolina University, USA joins AUT on sabbatical to work with Professor *Nicola Brasch*.

### Events

#### **First-Year Science Educator’s Colloquium**

The 9th annual First-Year Science Educator’s Colloquium (FYSEC) was hosted by Auckland University and Auckland University of Technology on 3-4 December 2018. Many interesting and thought-provoking sessions were presented with major themes encompassing:

Transition to university/ tertiary study (NCEA, subject, assessment, delivery, background, expectations)

Reflection on implementation of emerging pedagogies (inclusion of puzzles, videos, collaboration, flipped classroom, blended learning)

Impact of learning space design (alternatives to lecture theatres for teaching and learning in science)



Visitors from the University of Padua at the NZ-Italy Meeting on Supramolecular and Materials Chemistry

Chemistry featured as an area that is often perceived as ‘the difficult’ subject area in first year university study. VUW and AUT lecturers of the large first year chemistry papers identified common hurdles and barriers to students in large first year chemistry classes and reflected on the incorporation of less traditional teaching methods (in chemistry) that have been successful. The videoing of laboratory techniques, lecture question and answer sessions and collaborative work were but a few of the alternatives responded to favourably by students.

This annual colloquium is an opportunity for educators at the tertiary level to share and reflect on innovative ideas and practices evolving throughout universities and polytechnics in New Zealand in the teaching and learning of science. The colloquium was originally established as a biology colloquium but has expanded to encompass all areas of science which experience common issues and developments.

FYSEC will be hosted by Lincoln University, Christchurch, in 2019.

#### **NZIC Auckland Branch Seminars**

AUT hosted the following NZIC Auckland Branch Seminars between November 2018 and February 2019:

Dr Gareth Cave (Nottingham Trent University): *Nano-rust: from therapeutic vectors to potatoes*

Dr Alvin Orbaek White (Swansea University): *How to turn plastic waste into a commodity by using nanotechnology*

#### **Podcast**

Starting on 20 February, **Allan Blackman** and Alison Balance (RNZ) have been presenting a podcast titled, *Elemental*, in which they discuss all 118 elements in the Periodic Table, in celebration of its 150<sup>th</sup> birthday. 2 to 3 episodes per week are being broadcast.

#### **Invited talks**

Professor **Allan Blackman** presented an invited talk at the FYSEC: *First year chemistry – the pariah subject*.

Professor **Nicola Brasch** gave an invited talk at the University of Otago: *Exploring the mechanism of HNO release from photoactive molecules incorporating the (hydroxynaphthalenyl)methyl phototrigger*.

Dr **Cameron Weber** gave an invited talk at NZIMSMC: *Using the nanostructure of amphiphilic ionic liquids to control reactivity*.

Dr **Jack Chen** gave an invited talk at NZIMSMC: *Self assembled photoresponsive catalysts*.

Dr **Marcus Jones** gave an invited talk at NZIMSMC: *Exploiting exciton plasmonic coupling to enhance optical transitions in colloidal quantum dots*.

#### **Congratulations**

Ruth Cink and Dominique Rwizinkindi, PhD students of Professor **Nicola Brasch**, both received awards for their poster presentations at the Dodd-Walls Centre Symposium.

## **CANTERBURY**

### **University of Canterbury**

#### **Awards and appointments**

Professor **Bryce Williamson** has been appointed as the new Dean of Postgraduate Studies.

#### **New arrivals - visiting academics**

Professor Dr Thisbe Lindhorst is from Christiana Albertina University of Kiel Otto Diels Institute of Organic Chemistry (for more information see: [https://de.wikipedia.org/wiki/Thisbe\\_Lindhorst](https://de.wikipedia.org/wiki/Thisbe_Lindhorst)). Thisbe comments (from <http://www.academia-net.org/profil/prof-dr-thisbe-k-lindhorst/1133909>): “My research focuses on a basic understanding of molecular interactions with glycoconjugates on eukaryotic cell surfaces, or glycocalyx. Synthetic modelling systems are employed in combination with biophysical and biochemical methods.”

Dr Thomas Douglas Bennett is a Visiting Cambridge Scholar. Thomas comments: “I was born in South Shields, in the North-East of England, in 1986. I read the Natural Sciences Tripos at the University of Cambridge as an undergraduate, specialising

in chemistry and gaining a 1st class MSc (Hons) in 2008. I then completed a PhD in the Materials Science and Metallurgy Department on the physical properties of porous materials under Professor Anthony K. Cheetham FRS. After completing my PhD, I spent the 2012/2013 academic year in secondary school education as a chemistry teacher. A 3 year independent Research Fellowship at Trinity Hall, University of Cambridge followed, where I started a Royal Society University Research Fellowship in 2016. I now lead a research group of 14 researchers. Past awards include the Woldemar A. Weyl International Glass Science Award (2019), ISIS Rutherford Appleton Laboratory Science Impact Award (2018), the PANalytical Award (2013), and making the shortlist for the Chemical Communications lectureship and European Young Chemist award (2018). Our research centres on the thermo-mechanical properties of porous materials (or ‘sponges’), and specifically those used in clean air technologies, water desalination, drug delivery, catalytic and harmful gas storage. Recently, the group has also commenced work on new types of liquids and glasses, resulting in the discovery the first new glass family found since metallic glasses in the 1970s. These ‘hybrid’ glasses are meltquenched glasses which exhibit characteristics of organic and inorganic compounds, and importantly demonstrate superior chemical properties to existing glass categories. They possess mechanical properties intermediate between brittle inorganic glasses, and scratch prone organic polymers. This work is pursued in close collaboration with major glass industries for protective coatings, screens and communications technologies. I am particularly interested in establishing international links and hold a visiting professorship at the Wuhan University of Technology, China, alongside a visiting scientist position at CSIRO Melbourne. In addition, I chair the new Royal Society of Chemistry interest group on porous materials, organise the annual UK porous materials conference, and sit on the International Zeolite Association Advisory Board on metal-organic framework structures. Personally, I am passionate regarding science and university

outreach activities, and frequently give talks on access to higher education in the UK.”

Professor Mark Distefano, University of Minnesota, Department of Chemistry, Lloyd Reyerson Professorship 2016 (for more information see: <https://chem.umn.edu/profiles/mark-distefano>). Mark comments: “Our group is interested in molecular recognition and catalysis in the context of proteins. Current research is focused on the process of protein prenylation, a key modification that occurs on proteins involved in cellular signalling. Part of the group is studying the enzymes responsible for this process with the ultimate goal of facilitating the development of new anti-cancer, anti-bacterial and antiviral agents. The other major focus concerns the use of protein prenylation to selectively modify proteins for therapeutic applications. Group members use a combination of small molecule and macromolecule-based methods including organic synthesis, peptide chemistry, enzyme assays, proteomics, recombinant DNA methods and mammalian cell culture.”

### Women in Science Breakfast

On February 12, like other NZIC branches in New Zealand, the Canterbury branch hosted one of the IUPAC Global Breakfasts to celebrate Women in Science. These breakfasts were one initiative to celebrate IUPAC's 100<sup>th</sup> anniversary. Our event, from 08:30 – 09:30, was held in the new Earnest Rutherford building at UC. It was attended by women of a wide range of ages and from a number of organisations including ESR, AgResearch, high schools and UC staff and students. After watching Mary Garson's welcoming speech, a lively round table discussion encompassing challenges, highlights and many positive suggestions carried on until we ran of time. Everyone agreed that it was a very worthwhile event and we look forward to more in the future. The New Zealand breakfasts were the first in the world and although our wave to the group in Australia fell through at the last minute we did manage one to the huge group in Wellington. From the feedback, the same positivity was felt everywhere and now there is

much consideration of the best way to carry momentum out of this event and continue to support Women in Science.

### Sad loss

We were very saddened by the passing of Lillian Rose Marie Taylor, aka Danielle Lily Donnelly (10 August 1993 – 30 January 2019). Lilly was a first year PhD student in the School working in organic synthesis. She started her academic career at Massey University, where she completed her undergraduate degree. After stints at ANU and the University of Auckland, Lilly decided to relocate to Christchurch for her PhD. In the short time that Lilly was in the School, it became clear that she was a very talented and enthusiastic scientist. Lilly was always happy to help and to find ways to assist her fellow students both in and out of the lab. Lilly was passionate about outreach and was involved in a number of national initiatives including South Sci and Inspiration Education. She had already been in contact with *Jan Wi-*

*kaira* and the Maori development team about outreach activities involving Maori high school students. She was awarded the AMP Regional award in 2018 for promoting diversity in science and sustainability in New Zealand. Lilly had a number of interests outside science. She was a keen baker, an amazing cook, very keen on fashion and could often be found providing food and dinner for her colleagues. Lilly's enthusiasm, kindness and willingness to help will be sorely missed. Some of her awards and achievements included:

- AMP Regional Award Winner (2018) Awarded for work promoting diversity in science and sustainability in New Zealand
- Homeward Bound Participant (2018/19) One of 3 NZ based woman in STEM selected for the HB leadership initiative that includes a 3 week expedition in Antarctica
- Governor General's Science Forum (2018) Selected to partake in the forum at Government House, hosted by Dame Patsy Reddy to talk with scientists and industry members about



Top: Canterbury participants at the Women in Science Breakfast. Bottom: Canterbury Women in Science participants enjoying their breakfast

sustainability and agriculture.

- Invited to be a regional judge for the Sir Paul Callaghan Eureka Awards (2018)
- Featured in the Ministry of Education's Women in Stem Campaign (2016)
- Full scholarship to attend the 2016 Nuclear Research School in Sydney, Australia
- NZ Treasury Gold Award (2015) Awarded for essay titled "Chemistry and the Synthesis of a New, New Zealand".
- 200 level New Zealand Institute of Chemistry Award (2014) Awarded for first place Lab and Research Experience
- Research school of Chemistry, Australian National University (February 2017- November 2017) Towards the synthesis of the selaginellin and selaginpulvilin natural products
- Steve Davies Group, Chemistry Department, Oxford University (December 2016-February 2017) Asymmetric synthesis of (R,R)- $\beta$ -hydroxyornithine and its epimer
- Gareth Rowlands Research Group, Institute of Fundamental Sciences, Massey University (2015-2016) Synthesized new phosphine ligands for the use in BuchwaldHartwig amination and Suzuki coupling
- Undergraduate Research Paper, Institute of Fundamental Sciences, Massey University (2014) Attempted enantio-specific synthesis of the ABCE rings of the tetracyclic ring core of strychnine
- Organic synthesis lab, Institute of Fundamental Sciences, Massey University (summer 2014) Synthesis of caffeine from theobromine in an attempt to design a new undergraduate laboratory experiment Read more about Lilly
- <https://www.curiousminds.nz/profiles/lilly-taylor/>
- <https://chuffed.org/project/empower-woman-in-stemm-lillys-homeward-bound-journey>
- <https://nxtstep.co.nz/blog/life-as-a-science-leader-with-lilly-taylor/>

## MANAWATU

In December 2018, members of the **Telfer** group joined together in organising MOF2018 – The 6<sup>th</sup> International Conference on Metal-Organic Frameworks and Open Framework Materials. The location was the University of Auckland with **Shane Telfer** as the conference chair. 630 delegates from around the world attended the conference, which included scientists, engineers, students and industry representatives.

Adil Alkas, John Clements, Subo Lee and Omid Taheri gave presentations at MOF2018. Omid Taheri's talk won

the Best Presentation prize.

**David Perl**, **Ben Yin** and **Shane Telfer** attended AMN9, the biannual MacDiarmid Institute conference in Wellington on 10-14 February. David Perl won the Best Poster Prize for his poster entitled, *Rational design and synthesis of MOFs with different interpenetrated lattices*.

**Catherine Whitby** gave a presentation at the 9<sup>th</sup> Australasian Colloid and Interface Symposium (ACIS 2019) held in Hobart, Tasmania. She also attended and presented her work at AMN9.



Subo Lee demonstrates X-ray diffraction to high school students of the MacDiarmid Discovery Camp



Pat Edwards (left) teaching NMR spectroscopy to the students



Attendees of the NZIC breakfast celebrating Women in Chemistry

Jack Francois joined the Surface Chemistry lab of **Catherine Whitby** as a summer student.

The chemistry staff were delighted to welcome five high school students as part of the MacDiarmid Discovery Camp at Massey University. The students spent time in various labs in the university doing experiments and learning techniques as part of the camp, spread across one week. They were assisted by **Catherine Whitby** and Jack Francois (Microscopy), Brett Gartrell and Nimisha Mohandas (Veterinary Science), Sam Brooke and Sam Powick (Nanoscience), Ben Westberry (Physics), Ebubekir Avcı and Kate Andrew (Nanomachines), Emilia Nowak and Chris Hall (Ice cream making), **Joel Cornelio** and Subo Lee (Spectroscopy and X-ray diffraction), Matthew Barnes (Human performance studies), Pat Edwards (NMR spectroscopy). **Catherine Whitby** and **Justin Bendall** gave talks on pursuing careers in science.

On 16 November, **Paul Plieger** attended the ACES business meeting in Kyoto, Japan as an NZIC delegate.

On 27 November, the **Plieger** Group hosted Horst Puschmann, the co-founder of Olex2, software for crystallography. Puschmann gave a hands-on workshop on solving crystal structures using Olex2, which was held throughout the day.

David Nixon successfully submitted his PhD thesis and Sidney Woodhouse submitted her Masters thesis.

Congratulations to Sidney Woodhouse for being awarded the prestigious Massey University Vice-Chancellor's Doctoral Scholarship.

The NZIC Manawatu Branch organised a breakfast to celebrate Women in Chemistry on 12 Feb. Over 20 people attended this breakfast held at Café Cuba, Palmerston North. Anita Derks (Head of Quality, NZ Pharmaceuticals Limited) and Kathryn Stowell, ONZM (Professor of Biochemistry, Massey University) gave speeches and organised discussions on achieving equity in workplaces. Shelley Grace and Ruby Roach received sponsored breakfasts as part of winning the 100 words or less writing competition on *Challenges*

*in achieving diversity and equity in workplaces in New Zealand.*

## OTAGO

The Branch sponsored a local breakfast as part of the international series, "*Empowering women in chemistry: a global networking event*". This brought together 19 scientists, who discussed career options over breakfast with three guest speakers: Katie Baer Jones, Rebecca Stringer and Dorothy Page. The group of **Christina McGraw** is thanked for organising the event.

## University of Otago, Department of Chemistry

There was a great turn out of Otago Chemistry at the international Advanced Materials and Nanotechnology conference in Wellington (AMN-9, <http://www.cmnzl.co.nz/amn9-conference/>), a conference with 400 attendees from almost 30 countries. Otago Chemistry had 28 attendees including academic staff (**Anna Garden**, **Sally Brooker**, **Carla Meledandri**, **Keith Gordon**, **Nigel Lucas**, **James Crowley** and **Courtney Ennis**), postdocs (Jonathon Falconer and Santiago Rodríguez-Jiménez) and students (James Findlay, Roan Vasdev, Daniel Ross, Kenneth Ortega, Lachlan Gaudin, Natalie Lagesse, Lynn Lisboa, Joshua Sutton, Calum Gordon, Joseph Mapley, Charlie Ruffman, Geoffrey Weal, Luca Bondi, Jordan Smith, Sri Ram Sundaresan and Caitlin Casey-Stevens). Anna helped organise the conference, Jordan helped out with the Otago exhibition booth, Caitlin,

Charlie and Luca helped out as an "Ask Me" person and Carla was involved in the Tech Tasters evening highlighting her work with Silventum (<http://silventum.com/>).

Congratulations to **Dave McMorran**, who won an Otago Teaching Excellence award. The award is well-deserved recognition of Dave's huge contribution to teaching at Otago. Well done! Dave was also featured on *Nights with Bryan Crump* on RNZ National, discussing the element helium for the *Element of the week* series.

In news from **Christina McGraw's** lab, Christina and PhD student Wayne Dillon recently travelled to Vanuatu to help deploy the country's first ocean acidification monitoring system. About 30 University of the South Pacific (USP) students, technicians and members of the community contributed to the project.

**Carla Meledandri** hosted Dr Andreas Kiesow (Fraunhofer Institute, <https://www.imws.fraunhofer.de/de/mitarbeiter/andreas-kiesow.html>) as a sabbatical visitor between January and March. Lachlan Gaudin, a summer research student in Carla's group, won a poster prize at AMN9 for his poster on nanoscale MOFs.

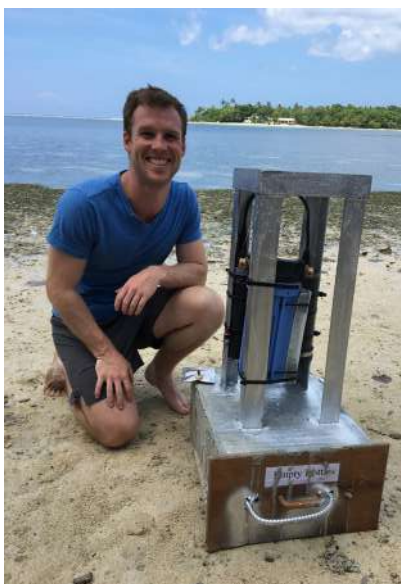
The group of **Anna Garden** attended the Quantum and Computational Chemistry Student Conference (Quaccs3.0) in Kioloa, Australia in December. Anna taught a workshop on global optimisation using genetic algorithms and Stephanie Lambie, Luca Bondi, Caitlin Casey-Stevens, Geoffrey



Otago scientists at the local *Empowering women in chemistry* event

Weal and Charlie Ruffman all gave excellent (PowerPoint-free!) presentations in the *Chalk and talk* sessions. Charlie was chosen the winner of the coveted Quaccs duck for the most engaging presentation. He also won talk prizes at the Otago Future Fuels and AMN9 conferences. Well done, Charlie!

The **Garden** group thanks undergraduate students Sam McIntyre and Frank Mackenzie for their hard work as summer students on developing structural recognition algorithms and modelling hydrogen evolution, respectively. Sam and Frankie presented posters of their research at the Otago Future Fuels conference, along with PhD student Caitlin Casey-Stevens, who won a poster prize.



Wayne Dillon with the ocean acidification monitoring kit deployed in Vanuatu



Charlie Ruffman with his "Quaccs duck" for the most engaging presentation at Quaccs3.0

The group of **Keith Gordon** is pleased to welcome two PhD students. Faiza Arshad has joined the molecular electronics team, studying donor-acceptor systems, while Fatema Ahmmed has joined the analytical team to study fish oil in collaboration with Daniel Killeen (Plant and Food). The group welcomes Jacob Harrison who is doing his Honours studying donor-acceptor systems. We also welcome back Elliot Tay for a one year Masters looking at HNO release systems with Professor **Nicola Brasch** (AUT). Many thanks to William Jessep and Henry Dunne who have recently completed summer studentships, collecting impressive datasets to help Chima Roberts and Samanali Garagoda Arachige in their ongoing research.

In addition, the group has been busy with several conferences. In late January Sara Miller, Ruth Sales, Kārlis Bērziņš, Chima, and Samanali attended the Dodd Walls Symposium in Dunedin. Chima presented the talk, *Discrimination of red meat using Raman spectroscopy*, while Sara, Ruth, Samanali and Kārlis presented posters with Ruth winning a prize for the best poster presentation at the symposium poster session. In mid-February, **Keith Gordon**, Joshua Sutton, and Joe Mapley attended AMN9 in Wellington. Keith presented a talk while Joshua and Joe presented posters.

Congratulations to Sara Miller for being accepted as an AI in the Dodd Walls Centre.

Joshua Sutton had his paper (*Variable-temperature resonance Raman studies to probe interchain ordering for semiconducting conjugated polymers with different chain curvature*) published as VIP in *Chemistry – An Asian Journal*. Jeremy Rooney and collaborator Matt Tarling (Geology) had their article, *Distinguishing the Raman spectrum of polygonal serpentine* accepted for the front cover of the December edition of the *Journal of Raman Spectroscopy*.

Georgina Shillito, Jeremy Rooney and Ruth Sales have been busy working on their theses, with Georgina submitting her thesis at the end of February.

Fola Akogun, a PhD student in **Sally Brooker's** research group, returned from nine weeks testing our designer complexes as photocatalysts for solar fuel production in Professor Garry Hanan's lab in Montreal.

Sally Brooker organised the first Otago Future Fuels (OFF) workshop at the University of Otago, 7-8 February, sponsored by the Catalyst fund, MacDiarmid Institute, Otago Energy Research Centre and the University. Interest in this meeting was high, resulting in a full house. We were treated to 10 fabulous keynote tutorials, ranging from the big picture to molecular catalysts to industrial implications and drivers. The tone was beautifully set by the opening keynote, Professor Tom Meyer (UNC Chapel Hill), and maintained by both local and international keynotes: Professors



Fola in Montreal as winter encroaches

Julio Lloret Fillol (ICIQ), Aaron Marshall (Canterbury), Ivan Daiz-Rainey (Otago, Finance), **Anna Garden** (Otago), Toni Llobet (ICIQ), Ed Constable (Basel), Linda Wright (NZ H<sub>2</sub> Association), Richard Blakie (Otago, Physics) and Garry Hanan (Montreal). The student talks were outstanding, with our international judges facing a tough challenge to decide the winners; they awarded the prizes to Charlie Ruffman and Fola Akogun (Otago). The poster panel judges awarded prizes to Shailendra Sharma (Canterbury), Sriram Sundaresan, Caitlin Casey-Stevens and Fabrice Karabulut (Otago).



Student prize winners (L to R): Shailendra Sharma, Sriram Sundaresan, Fola Akogun, Caitlin Casey-Stevens, Charlie Ruffman, Fabrice Karabulut

Thanks to Brookers Bunch for their stirring efforts behind the scenes!

**Sally Brooker** and three of her team then travelled to participate in AMN9. Her PhD student, Luca Bondi, (co-tutelle with Florence) gave a talk, whilst Sriram Sundaresan and Dr Santi Rodríguez Jiménez presented posters.

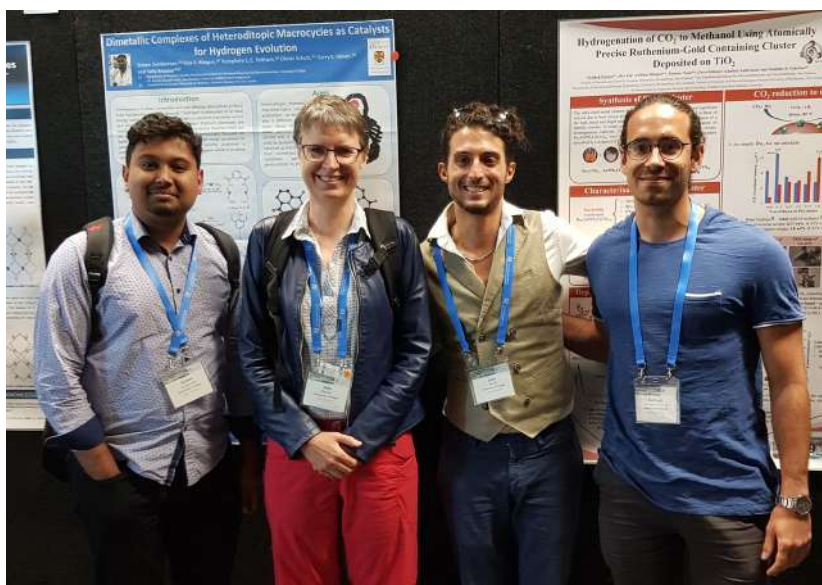
**Sally Brooker** hosted Professor Garry Hanan and two of his PhD students, Thomas Auvray and Olivier Schott, from the University of Montreal, as part of their joint Catalyst Grant.

## WAIKATO

A group of Waikato women chemists recently enjoyed participating in the IUPAC Global Women's Breakfast event, which saw over 200 individual breakfast events in over 50 countries. All agreed it was an extremely enjoyable and valuable networking event and thank IUPAC for the initiative.

## University of Waikato

A number of new PhD and MSc students have recently begun. Doctoral students include Greer Tanner-Dempsey, looking at breath volatiles and saliva of lung cancer patients as candidates for dog detection and Yanan Li, investigating an alternative method for determination of vitamin B12 in milk and infant formulas (both with Meryllyn Manley-Harris). Masters students include Taylor Farr and Claire Voogt who are working on different aspects of the chemistry of marine algae (both with **Michèle Prinsep**), **Ingrid Lindeman**, studying the influence of organic ligands over copper incorporation into speleothems (with Adam Hartland), Mat-



Brookers Bunch members at the AMN9 conference with left to right: Sriram, Sally, Luca and Santi (Sriram's poster is in the background)



Prof Garry Hanan, Sriram, Fabrice, Thomas, Olivier, Fola and Prof Julio Lloret Fillol at Emersons

thew Risi, investigating aspects of the coordination chemistry of substituted thioureas (with **Bill Henderson**), Rose Swears, investigating prebiotics in honey (with Marilyn Manley-Harris), Sukhjeet Singh researching new ICP-MS methodologies (with **Michael Mucalo** and **Megan Grainger**), Kaitlin Button, investigating the rapid maturation of spirits and **Nyssa Hewitt**, studying isolation and characterisation of a compound from a fermentation broth (the latter two with **Megan Grainger**).

**Nyssa Hewitt** also worked for **Megan Grainger** on a summer research scholarship, related to her current Masters research. Her poster was awarded in the top three from the School of Science at the end of summer function. Rolland Lin also worked with Megan on a summer research scholarship, developing a method for gold and silver nanoparticle analysis using Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS).

Dr Sebastian Breitenbach from the Institute of Geology, Mineralogy & Geophysics, Ruhr-Universität Bochum, Germany was a visiting scholar over December and January (with Adam Hartland).

Congratulations to the following students who won prizes at the School of Science Postgraduate Conference:

- NZIC (Waikato) Award for best chemistry-related oral presentation: Daniel Bernstein (\$150 + book prize)
- Waikato Regional Council Award for best PhD presentation: Geoff Tait (\$500)
- Waikato Science Club Prize for best SCIE501 Speech: **Ingrid Lindeman** \$50 voucher

Martina Pietsch-Brown and **Megan Grainger** had an enjoyable visit to Whitiara Primary School recently where they talked to the students about forensic chemistry and did a lab experiment with them.

Former colleagues and students were greatly saddened to learn of the death of Dr Ralph Thomson, who passed away after a short illness in December 2018, aged 73. Ralph oversaw the NMR capability at the University of Waikato for many years. He

completed both his MSc (*Studies of some germanium polycobalt species*) and PhD (*Some applications of multinuclear NMR*) at Waikato with Ken Mackay. Ralph's skill and passion was the introduction that many Waikato students had to theory and practical knowledge of NMR spectroscopy. He was always available to help staff and students with the collection and interpretation of data. Ralph moved to Wellington in later years to be near his family and is survived by his two sons and four grandchildren.

### Scion

On 14 February Scion hosted the conference, *Bioplastics and biocomposites – innovative building blocks of the emerging bioeconomy*. Around 100 delegates from Germany and New Zealand attended event. The conference covered topics on the sustainability of the growing biopolymer market and the ways that the European Union and New Zealand were integrating these fossil-based plastic replacements. Scion contributed five speakers: Drs Florian Graichen, Marie Joo Le Guen, Kate Parker, Dawn Smith, and Elspeth MacRae, along with Lou Sherman and Jeremy Warnes. They covered areas ranging from the economics of biopolymers in NZ to chemically designed biopolymers for specific purposes.

### WELLINGTON

Congratulations to Dr Jonathan Tailby for obtaining his PhD in 2018. He was jointly supervised by Professor **Ian Brown** (at Callaghan Innovation) and Professor **John Spencer** (VUW). The title of his thesis is *Hydrogen from ammonia by catalytic spillover*.

The 2018 Curtis Lecture was delivered by Professor Paul Bernhardt from the University of Queensland. He gave an excellent talk on the applications of electrochemistry towards understanding inorganic reactions, titled, "*Understanding catalysis using electrochemistry*". The following day, he displayed his diverse research as he also gave a talk to the VUW Centre for Biodiscovery on the use of electrochemistry in the understanding of metalloenzymes.

On September 26, Sara Quilter gave

a presentation on *Tailor Skincare: blending science with business*. She discussed how she turned a hand-made garage project using a cake mixer into a successful business. The moisturiser samples were a great hit with the audience!

The 2018 NIWA Wellington Science and Technology Fair was held 5–8 September. **Ralf Schwoerer** represented NZIC as a judge. **J. Robin Fulton**, Matthew Brett and Fraser Hughson entertained the audience with a *Chemistry of light* display at the prize giving ceremony.

During 2018, NZIC student travel grants were provided to six postgraduates: Tao Xu and Deanna Ayupova to attend a computational course on cancer biology; Chriselle Braganza to travel to Dr Shibata's laboratory in Japan; Tao Xu and Jordan McCone to attend the International Convention on Organic Synthesis in Florence; Loc Tran to attend the ACS National Meeting in Boston; and Joe Bracegirdle to attend a course on tropical seaweed biodiscovery and clean processing technology.

The 2018 NZIC Wellington Branch Chemistry and Biochemistry Scholarships were awarded to Brooke Nicholls, Andrew Paton, Matthew Brett and Anna Tribe for excellence in first-, second- and third-year chemistry and third-year biochemistry-related courses respectively.

The IUPAC Global Women's Breakfast was on 12 February. NZIC teamed up with the MacDiarmid Institute at their AMN9 conference at Te Papa. The breakfast was organised by AMN9 representative **Catherine Whitby**, with **Joanne Harvey** spearheading the NZIC group. An excellent talk on achieving equity, diversity and inclusivity in our workplace was given by Associate Professor **Nicola Gaston**, co-director of the MacDiarmid Institute. Professor Juliet Gerard, the PM's chief science advisor, and Julie Maxton, CEO of the Royal Society of London, gave video presentations. There were ~100 participants at the Te Papa breakfast, with Skype calls to the NZIC Manawatu and Otago branches, as well as to the event organiser, Professor Mary Garson at the University of Queensland in Australia.

# Transforming silica into silicate - pilot scale removal of problematic silica from geothermal brine

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## Abstract

The condensation of dissolved silica species to form a hard silica scale is a major issue in the generation of electrical energy and heat recovery from geothermal hot water and wet steam resources. In previous publications we have shown that nano-structured calcium silicate hydrate (NCaSiH) provides an attractive solution to the global problem of the formation of silica scale. NCaSiH is placed into context with silica species and other calcium silicate hydrates to demonstrate why the controlled formation and uses of this material are of interest in geothermal resource operation and management and in various end user applications. The formation and removal of this novel precipitated silicate from the brine is discussed in the early stages of pilot scale trials. A pilot scale test rig for such trials was constructed on site at MB Century, Taupo, New Zealand, and commissioned in September 2017. The test rig uses lamellar separation technology for recovery of NCaSiH and other species from brine. The development and implementation of this technology in the test rig is outlined. Early results showed that the source of silica is quite variable and comparatively low in silica and high in carbonate content. However, it served to show that our NCaSiH approach to removing problematic supersaturated dissolved silica species from a geothermal brine works. Removal efficiencies for various species were between 95% and 99%, slightly lower than laboratory results due to low silica levels. The test rig demonstrates that the technology is very robust in operation and offers a novel disruptive approach to facilitate the reduction in silica scale-forming species by removing most or all of the problematic dissolved silica species from such geothermal brines, along with calcium carbonate and some other species.

## Geothermal energy and the formation of silica scale

Geothermal energy is an attractive natural renewable energy resource, as it can produce large quantities of heat and electrical energy continuously and also on demand. The potential for harvesting geothermal energy presents itself when underground water reservoirs a few hundred metres to several kilometres below the surface, are located close to geothermal heat sources (e.g. magma). Water reservoirs can be natural or artificially generated. The hot geothermal water is piped to the surface and flashed to produce saturated steam which is used to drive a turbine and generate electricity. The flashing simultaneously creates a separated geothermal water or brine flow, which is usually supersaturated in dissolved silica species. The hot

brine is used for further binary cycle electricity generation, direct heating, discharge or re-injection. Re-injecting the separated brine and condensed steam from the turbines into a geothermal reservoir replenishes the reservoir and subsequently increases its life time, prevents subsidence and places this method of energy generation firmly into the realm of both benign and renewable energy resources.<sup>1</sup>

Due to microbial and chemical processes, the subsurface rock containing and surrounding geothermal water reservoirs is partially dissolved, resulting in a cocktail of cationic and anionic species and suspended particles within the sub surface hot geothermal water. During utilisation of this hot geothermal water resource, these dissolved species, notably silica and carbonate entities, can precipitate out to form an intractable scale which blocks pipes, valves, heat exchangers and other process equipment. They can also be carried over with saturated steam during the flashing process to scale and damage turbine blades. Therefore, saturated steam is scrubbed and treated to reduce the amount of carry-over, which leads to a loss of energy. Issues surrounding dissolved and suspended species become further problematic in the separated brine. The species are concentrated due to the flashing, which converts about 30% of the water flow into steam. Downstream extraction of further heat energy results in a lowering of the brine temperature. All these processes increase the issue of silica deposition. This is a major problem in the recovery of heat energy in the heat exchangers in a binary cycle electricity producing plant as well as for the general operation.<sup>1</sup>

The composition of the separated brine is somewhat production well and process specific, and various levels of toxic species, such as arsenic or selenium, valuable species, such as lithium, zinc, boron or gold, and environmentally harmless but problematic species, such as dissolved silica and calcium carbonate, are invariably present at different levels. The dissolved supersaturated silica species in the separated brine are particularly problematic as they can precipitate out and form a hard, amorphous silica scale that needs to be removed either using considerable mechanical force and effort or by the use of corrosive hydrogen fluoride, or both. These dissolved silica species become concentrated to supersaturation levels after the generation of steam in the flashing process and/or after reduction in the brine temperature in a binary plant. For example, sub surface geothermal water at 260°C can contain up to 600 mg/kg of dissolved silica.<sup>2</sup> Upon flashing at the surface about 30% of this

water is transformed into steam and the concentration of dissolved silica in the residual separated brine representing about 70% of the mass flow increases to approximately 800-900 mg/kg. The temperature of the brine correspondingly decreases to about 120-160°C as heat energy is removed. At 120°C only approximately 350 mg/kg of silica is soluble in water. The separated brine therefore becomes supersaturated with dissolved silica, which can condense (polymerise) and precipitate to form a hard, amorphous silica scale blocking pipes, heat exchangers and re-injection wells.

Costs associated with the re-drilling of re-injection wells and cleaning of pipes and equipment are significant and present one of the major challenges and impediments facing geothermal energy generation. Several methods have been investigated to address the issue of silica scale formation. Examples of these are the addition of acid to partially delay the condensation of the dissolved silica species,<sup>1</sup> the addition of silica seeds to capture such dissolved silica onto a pre-existing silica material,<sup>3,4</sup> and the addition of aluminum species, EDTA and other compounds to form silica and silicate species that do not precipitate.<sup>3,5</sup> Gill presents a good overview regarding this problematic issue of silica scale formation and the effect of pH and other ionic species on it.<sup>6</sup> In a parallel development, we and a group from Japan realized that the use of calcium ions (dissolved lime) allowed removal of silica from geothermal brine.<sup>3,4,7</sup> We focused on the silica-derived products, building a pilot plant to precipitate a silica product with a network structure from geothermal brine for use as a filler to enhance the optical and print quality of paper. Meanwhile Sugita et al. carried out successful trials in the reduction of dissolved silica species in geothermal systems in New Zealand (Mokai) and Japan but they appeared not to be aware of the nature and potential of the silica and silicate species they generated.<sup>3</sup>

In 2008 we shifted our focus away from the production of fine chemicals towards the geothermal energy sector as we realised that one of the materials we produced, notably nano-structured calcium silicate hydrate, NCaSiIH, offers a disruptive and attractive potential solution to preventing the occurrence of silica scale. The technology works by transforming the reactive silica species which is present at supersaturated levels in separated geothermal brine, into NCaSiIH which forms readily, does not polymerise further and does not bind to metal surfaces. Instead the NCaSiIH particles remain suspended in the geothermal brine flow and can be separated out as a useful product. The level of dissolved silica species remaining in the brine can be controlled to below the equilibrium solubility level at the brine temperature down to the essentially zero, depending on the amount of calcium ions used in relation to the dissolved silica species in the water.

Through laboratory scale and field trials, we have successfully developed the NCaSiIH geothermal technology and have since constructed a small-scale pilot plant test rig to address the following research questions, process chemistry issues and product characteristics:

1. Can our NCaSiIH technology, which has been success-

fully demonstrated in laboratory and field scale work, prevent silica scale formation in an operational geothermal field?

2. What are the preferred process chemistry and operating conditions to effectively prevent scale formation in an operational geothermal environment?

3. Individual geothermal wells essentially have different brine compositions in terms of their ionic and particulate content and undergo comparatively rapid cyclic changes in terms of their flow and chemistry. Is the NCaSiIH technology robust enough to work under these conditions? Which dissolved and particulate species are captured along with NCaSiIH material in its formation?

4. The NCaSiIH product needs to be recovered from the cooled brine prior to reinjection. What is the best process chemistry technology available for this and how will it be interfaced and implemented? The important issue here is dealing with the high flow rates of the brine stream which contains the suspended NCaSiIH particulates.

There are likely further issues to be addressed which will become apparent during the program, which we will investigate in future studies.

In this paper, we describe the design and operation of our pilot scale test rig and some of the considerations leading to its development.

### Recovery of NCaSiIH from geothermal brine: from laboratory chemistry to pilot plant development

In parallel developments, Harper and Johnston in New Zealand and a group from Japan discovered that the use of calcium ions (dissolved lime) allowed removal of silica from geothermal brine.<sup>3,4,7</sup> Our more detailed work has shown that if the dissolved silica is reacted with small doses of lime ( $\text{Ca/Si} < 0.4$ ), a silica material, with a type I network structure, precipitates (Fig. 1a).<sup>2,4,7</sup> The use of larger amounts of lime ( $\text{Ca/Si} > 1.3$ ) results in the formation of calcium silicate hydrate species (C-S-H) like tobermorite and jennite.<sup>8</sup> In our detailed studies of the reaction of sodium silicate solution and also geothermal brine with different quantities of lime under controlled pH conditions, we found that when using a calcium to silicon ratio of 0.8 a novel nano-structured calcium silicate hydrate, NCaSiIH, material (Fig. 1b, Equation 1) is produced very rapidly from either synthetic or natural sources of dissolved silica.<sup>9-11</sup>

NCaSiIH is distinct from other forms of precipitated silica in that the base unit present is related to the calcium silicate wollastonite  $\text{CaSiO}_3$  structure, shown by Borrmann et al. in a study of the material using nuclear magnetic resonance, ion bombardment and X-ray photoelectron spectroscopy.<sup>12,13</sup> In contrast to other C-S-H phases and silicates, NCaSiIH it is not crystalline or has the long-range order prevalent in these other structures.<sup>12,13</sup> Fundamental silicate units do, however, link together to form the backbone of the NCaSiIH structure and provide an open framework similar to a gypsum rosette, also known as

desert rose, where the calcium ions are accommodated on the surface of the particles. This gives NCaSiH a slightly positive surface charge and hence the ability to bind other silica or ionic species to such surfaces.<sup>9,11,14,15</sup> In the presence of anions such as carbonate or phosphate, the surface calcium ions can form insoluble calcium carbonate species (aragonite; Fig. 2a), or calcium phosphate in the NCaSiH particle matrix. The large available surface area resulting from the open framework nature of the NCaSiH structure is important here. Also, cations react with surface silanol groups or exchange with calcium and bind to the silicate surface.<sup>15</sup> Additionally, NCaSiH has a variety of pores from nano- to meso- in size, which allow it to act as a sponge and filter material and trap other solid particles on its surface (for example calcite crystals as shown in Fig. 2b).

The particles observable in the scanning electron microscope images (Fig. 2) are about 1 to 15 microns in diameter. The open framework structure is observable. Number weighted particle size measurements using the dynamic light scattering measurement method, also show that about 99 % of the particles fall within this size

range. However, our laboratory work has shown that the small particles have a tendency to agglomerate and form clusters of several microns to millimeters in diameter. This is partially verified by volume weighted particle size measurements, where particles with a diameter of 10 to 50 micron, being agglomerates of about one thousand particles are observable.<sup>16</sup> Although it is possible that the individual 1 to 15 micron NCaSiH particles could likely be reinjected with the cooled brine, the larger particle agglomerates would probably block the pores in an underground geothermal reservoir rock formation. Hence, it is most likely that the NCaSiH material needs to be removed from the geothermal brine before reinjection. A positive side effect of these larger agglomerates is that two sources of scale forming species, silica and calcium carbonate are removed from the brine at the same time by our NCaSiH technology. This is useful, since in current geothermal resource field operation and management while calcium carbonate scales tend to be soft and brittle compared to the silica scale, the carbonate occurrence is still problematic and the consequent need for its removal also entails operational down times and expenditures, as does the silica scale removal.

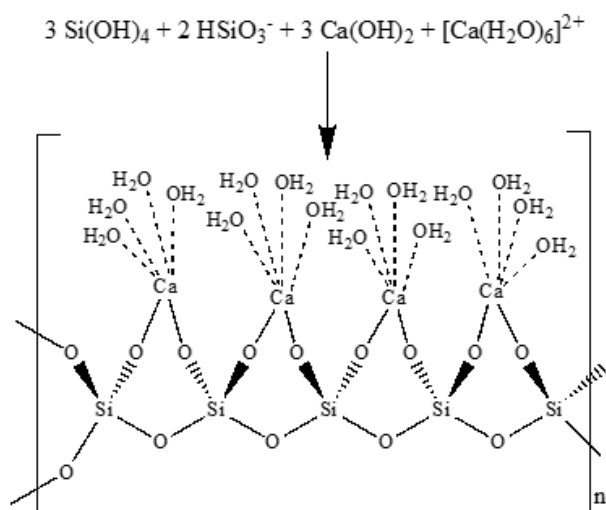
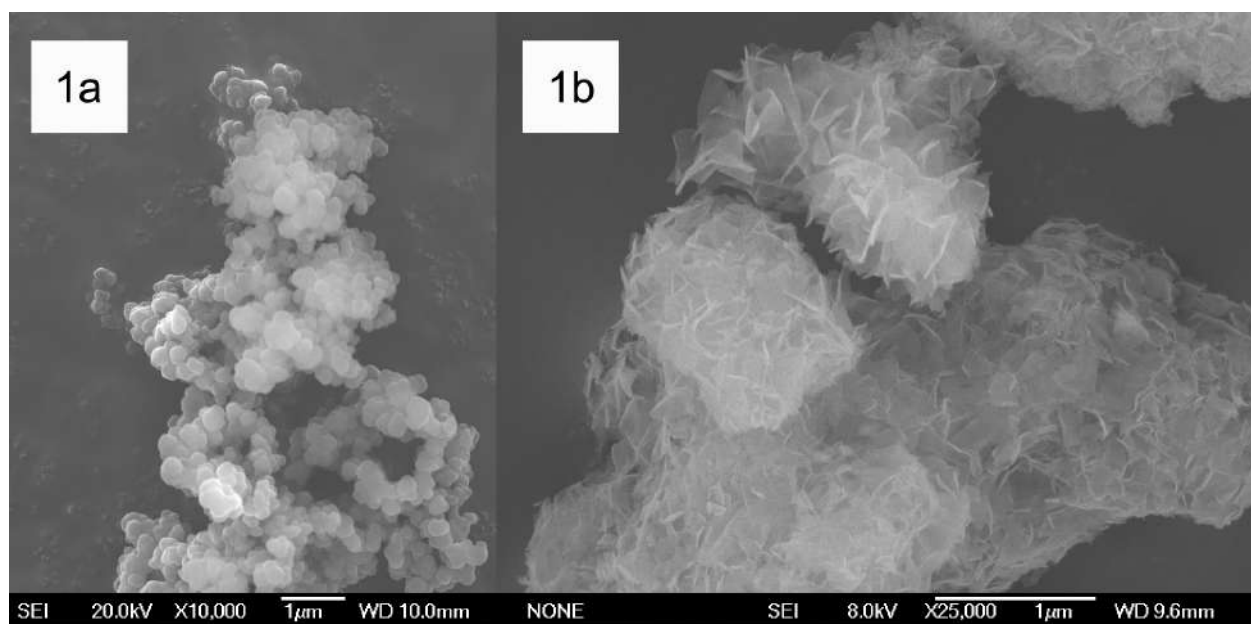


Fig. 1. Top: Scanning electron microscope images of (a) silica with a type I network structure and (b) nano-structured calcium silicate. Bottom: Representation of the formation of nano-structured calcium silicate.

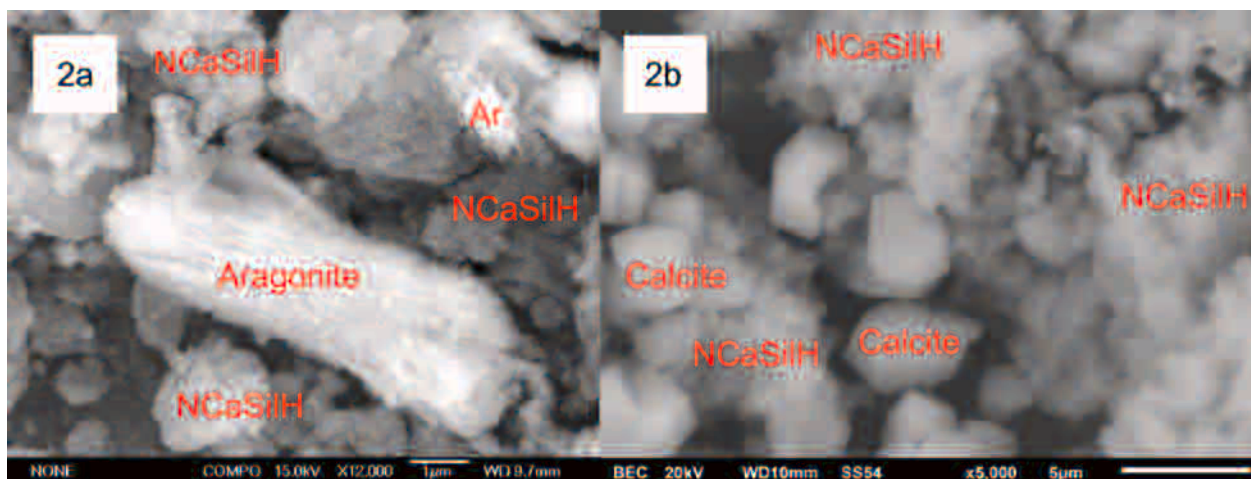


Fig. 2. Scanning electron microscope images of calcium carbonate trapped in NCaSiH: (a) aragonite and (b) calcite

Our laboratory and field results present a further strong argument as to why the NCaSiH material should be removed from the brine. The surface chemistry of NCaSiH changes over time depending on the pH of the environment. As a result, the calcium is very slowly leached from the platelet surfaces starting within minutes of the NCaSiH formation. This is particularly evident as the pH is lowered. The vacant sites then react with water to release hydroxide ions into solution. The calcium and hydroxide ions remain closely associated with the silicate particles and tend to facilitate reactions on the particle surface, so this is not an immediate issue. However, after several hours or days the NCaSiH does begin to dissolve noticeably releasing monomeric silica and silicate species back into solution, depending on the pH, ionic content and temperature.<sup>17</sup> This means that although NCaSiH acts to capture the reactive silica species and hence prevent the formation of the unwanted hard silica scale, if the NCaSiH material is not removed from the brine in a reasonable timeframe, this slow dissolution characteristic may result in silica precipitation. However, in reality this is not an issue as the water flow rates in geothermal pipework are fast and hence the residence time for a particular volume of brine and the associated precipitated NCaSiH material in the system before removal is very short. In contrast to several other treatment technologies, NCaSiH can be removed from the brine thereby irreversibly lowering the risk of silica scale formation. Other researchers, like Sugita et al.,<sup>4</sup> have also realised that removal of the solids offers this opportunity. While some other research groups have investigated the generation and removal of silica materials from geothermal brines,<sup>18</sup> our NCaSiH technology offers several opportunities and competitive advantages based on its process chemistry and the particulate structure and nature of the surface morphology of the material, which are not provided by such other approaches.<sup>9-11,15</sup>

The removal of nano-structured calcium silicate hydrate (NCaSiH) from geothermal brine is non-trivial due to the high surface area and pore volume of NCaSiH, low difference in the respective bulk densities of NCaSiH (1.6 g/cm<sup>3</sup>) and water (0.998 g/cm<sup>3</sup>), and the low mass concentration of NCaSiH in geothermal brine at about 0.1 wt%.

This is aggravated by the comparatively high brine flow rates found in geothermal power plants.

### Settling behaviour and settling tank sizes

Despite the aggregation of particles and formation of larger (up to millimeter scale) agglomerates, the sedimentation of NCaSiH is comparatively slow. The aggregates of NCaSiH are very porous. BET surface area measurements delivered results in the range of 100 to 500 m<sup>2</sup>/g of material. Oil absorption measurements showed that a typical sample of NCaSiH could absorb up to 1 to 7 times its weight in oil (or water), which indicated that the pores were quite accessible. The openness of the structure in combination with the mass concentration lead to hindered settling behavior, which meant all particles, regardless of their size, settled with the same sedimentation velocity. Therefore, the settling rate of the particles had to be determined empirically. Most of the sedimentation was completed after approximately 4 minutes (the compression point was reached), after which only a very slow compression of particles occurred. This means that the settling process could be terminated after the compression point, as further sedimentation is not economically viable. Prior to the compression point settling velocities were constant. All NCaSiH samples studied displayed hindered settling behavior. The rate of the settling process was determined to be about 65 mm/min at 70°C. Based on this settling rate the minimal theoretical size of a settling tank could be calculated. It needs to be noted that no safety factor was included in the calculation; for a real-life example a safety factor of about 50% of the settling area would have to be included, which is equal to a 22% increase in the diameter of a settling tank. Furthermore, the settling rate is strongly dependent on the salt content of the brine, the pH and mass concentration of silica. Increasing the salt content of the brine reduces the solubility and miscibility of silica and related species. Impurities, like silica, zinc or iron, can bind to NCaSiH raising its density and hence lead to an increased settling rate. Additionally, at higher temperatures, the viscosity of the fluid is lower and consequently the settling rate is elevated. Taking into account the settling rate for samples investigated here a tank diameter of 30 m for a flow rate of 3000 m<sup>3</sup>/h would be necessary; if a safety factor

is included that diameter would need to be about 37 m, which is comparatively large. For redundancy and maintenance multiple settling tanks would be required, which increases the overall footprint of the separation facility even further.

### Lamella separator

Several separation technologies were considered in the approach for separating NCaSiH from geothermal brine. While rotary drum filters, band filters, continuous centrifuges and filter presses could deal with the challenges presented by NCaSiH, they all have moving parts, require large amounts of electricity and are comparatively expensive. At the volume and flow rates and low concentrations of NCaSiH particles present they were considered uneconomical. Filter cartridges and membranes were tested successfully in the separation of NCaSiH and geothermal brine but experienced fouling, making them economically unviable. The pressures and temperatures prevalent in geothermal energy producing environments put considerable stress on the filters and membranes, which implied that their service life might be prohibitively short. Hydrocyclones are very efficient at solid-liquid separations and have a comparatively low footprint. Additionally, their principle use is familiar to the geothermal industry in the form of cyclone separators used in flash plants to separate steam from brine. However, the turbulence and fluid velocities present in hydrocyclones would very likely break up agglomerates of NCaSiH. Consequently hydrocyclones would need to handle 1 to 10 micrometer particles, which makes them inefficient for this process, as thousands of hydrocyclones would be required to handle the flow through even a small geothermal plant. After receiving advice, we started to investigate lamella separators. Lamella separators are also referred to as lamella clarifiers or inclined plate settlers. These separators are characterised by an array of inclined parallel plates providing a large settling surface. Because the plates are stacked, a lamella separator has a comparatively small footprint (20 to 35% of the size of a comparable settling tank). A schematic showing the main flows and settling along the plates is shown in Fig. 3.

A lamella separator can operate on the principle of a counter-current separator. Water rises up in the separator. Due to their higher density and related settling velocity particles progress at a slightly flatter angle than water and impact on the surface of the lamella, where they aggregate and slide down to a collection chamber and outlet at the bottom of the separator. Generally low flow velocities (and therefore low Reynolds numbers) mean that a lamella separator works very efficiently. Low flow velocities are desirable as it is less likely that turbulence occurs, which disturbs the settling process. Instead a laminar flow system is present. In the geothermal context, there is the possibility of the occurrence of temperature gradients, which introduces convection currents. Hence, steps need to be taken to avoid these, like insulating the surfaces of a lamella separator. The occurrence of convection currents was confirmed in laboratory tests.

The dimensions and arrangement of lamellae in each lamella separator is specific to the solid and liquid that

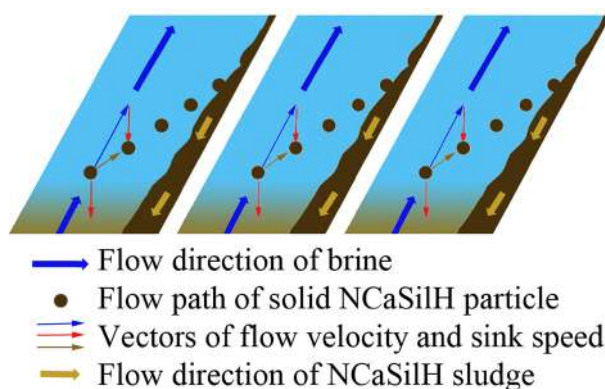


Fig. 3. Schematic showing particle flows along the plates of a lamella separator

require to be separated as well as to the ambient conditions present. Due to having no prior experience in the construction of a lamella separator, a rapid prototyping, empirical approach was chosen for developing a suitable separator. For dimensioning of the lamella area, a numerical model was developed to calculate the required settling surface for a given volume flow. Next, a laboratory model was constructed that allowed observation of the flows in the model and then refinement based on the observations. The refinement process took two iterations until a model was constructed that had a separation efficiency above 99% (Fig. 4). The first model developed an unwanted turbulence, where particles rapidly moved along the outside wall of the separator (Fig. 4: top image, white arrow), hence creating a circular current within the separator. This was thought to be due to the vertical entry of fluid and the wall angles in the separator. Baffles added to the front of the separator intended to break the fast inflow resulted in some solid-liquid separation (Fig. 4: top image, black arrow) but managed to only attenuate the circular current.

To prevent the occurrence of the circular current found in the first model, the entry into the second model was flattened to reduce fluid velocities. Tests showed that a laminar flow transported the fluid directly towards the first lamella (Fig. 4: middle image). Initially this was thought to be due to a thermal current, but addition of insulation did not resolve this matter. Once past the first lamella a comparatively high current directed towards the outlet meant that only the first lamella was contacted by the suspension. Most of the fluid in the rest of the separator was still and did not participate in any settling process as shown in dye experiments. Due to the flat angle of the intake area particles agglomerated and settled in the middle of the separator (black circle).

For the third model (Fig. 4: bottom image) the lamellae were turned by 90 degrees to ensure that all lamellae were active, and the outflow area was widened to reduce flow velocities towards the outlet. A laminar flow was observed as in model 2 (Fig. 4: bottom image, white arrow). Most particles settled directly into the compression area (Fig. 4: bottom image, black circle). The rest of the particles entered the lamella area. Due to the turning of the lamellae and perpendicular inflow into the lamellae the flow went past every lamella, making use of their

full surface area for settling. A flow breaker was added at the inlet (Fig. 4: bottom image, black arrow) to distribute the flow over the whole width of the inlet. A separation efficiency of 99.4 % was achieved. The residual NCaSiH particles that were transported into the supernatant were very small (not visible).

Based on the laboratory model, a larger separator (for a flow rate of 8 L/min) to be used in our pilot plant test rig was constructed. Results from the use of the larger scale separator in a pilot plant will be presented in future publications. To confirm our laboratory results, a computational fluid dynamics (CFD) model of the flows in this larger separator was simulated. The CFD simulation was produced using ANSYS R17.0 software and is shown in Fig. 5. Velocities and stream lines in the CFD simulation were the same as those observed for model 3 (Fig. 4: bottom image).

### Pilot scale test rig

In January 2017 plans were developed for a pilot scale test rig. While the test rig was being built, the settling characteristics and particle size distribution of NCaSiH were studied. As it became apparent that NCaSiH need-

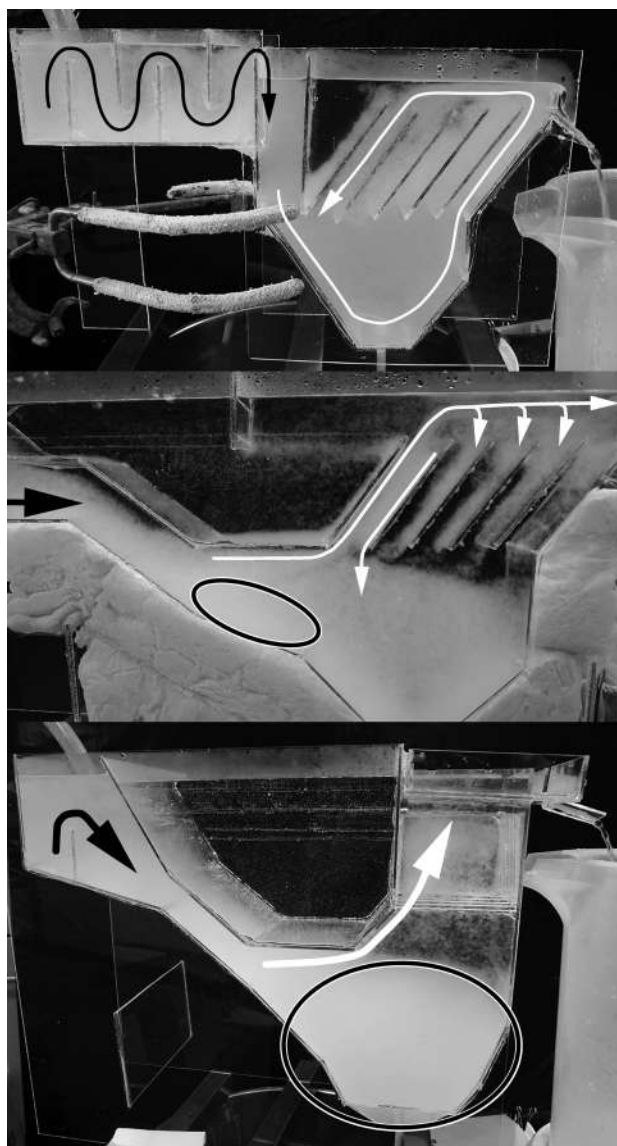


Fig. 4. Perspex lamella separators tested in the laboratory: top = model 1, middle = model 2, bottom = model 3

ed to be recovered from the brine, a lamella separator addition to the test rig was designed and built in July 2017 (Fig. 6).

A site was located for the test rig with access to brine from the Wairakei Power Plant located about 500 m away downhill.

In August 2017 the test rig was assembled on site and commissioned at the beginning of September (Fig. 7). Operation of the test rig started in September 2017.

Early results showed that the flow rate, silica and carbonate content of the brine received by the test rig changed widely and comparatively rapidly (Fig. 8).

Despite those variations, the technology worked very successfully with separation efficiencies for the separator ranging from above 95% to 99% (Fig. 9). Furthermore, the separator proved to be effective in recovering all sorts of particles not just NCaSiH (see calcite and NCaSiH recovered in Fig. 2b).

### Concluding remarks

The formation of silica scale can be prevented by transforming the silica into nano-structured calcium silicate (NCaSiH). Lamella separators were successfully tested for the removal of NCaSiH from geothermal brine, reaching a solid-liquid separation efficiency in the laboratory of 99.6 % and in the field of above 95%. The lower efficiency in the field was due to the silica concentrations present in the brine, 400 ppm on average, which meant that agglomerates were less likely to form, which in turn meant that separation by gravity became less likely. However, the residual supernatant was free of visible particles and silica levels in the supernatant were below saturation levels.

The shape and configuration of the lamella separator were determined empirically using a rapid prototyping approach. Transparent models were built that allowed observation of the flows within them. Based on the findings a pilot scale lamella separator was constructed and commissioned. The validity of the up-scaled model was confirmed in a computational fluid dynamics simulation. The fluid velocities and stream lines in the model were the same as in laboratory model 3. Lamella separators were chosen for the recovery of NCaSiH from brine due to their comparatively small footprint compared to settling tanks and as they don't contain any movable parts easing maintenance. Other solid-liquid separation techniques were not explored at this stage in the project. NCaSiH is only going to be concentrated to a solid content of about 0.25 % in the lamella separator. Therefore, it is necessary that a secondary solid liquid separation technique will be employed. This along with uses for the recovered NCaSiH will be considered in future projects. It appears important to collect sufficient amounts of samples of NCaSiH for analysis and to provide material for end user testing and evaluation purposes. Initial samples of NCaSiH have been collected but due to low levels of silica in the brine and comparatively low flow rates the test rig will produce these comparatively slowly. Therefore, a larger separator and test rig is in development.

Overall, NCaSiIH technology offers the opportunity to reduce the levels of not only the problematic dissolved silica species, but also calcium carbonate trapped in the silicate hydrate, to below levels where scale formation of either occurs. The separator removed particulate matter independent of its nature. Gravel and plant matter were found in the collected product. Consequently, the residual brine could be used to harvest valuable compounds from it, which were so far inaccessible due to destructive species, such as silica. This opens up possibilities for geothermal mining and access to new revenue streams. Future research projects will investigate this possibility more closely. Looking at some projects aimed at gaining access to supercritical geothermal resources, the need

to solve the silica scale issue becomes even more pressing. Under supercritical conditions it is likely that the dissolution of the subsurface reservoir rock, the saturation of geothermal water and oversaturation of separated brines becomes a much more significant issue and problem to address. This is an interesting possibility in the medium and long term. However, our current focus is on the successful implementation and demonstration of the NCaSiIH technology and the removal of the NCaSiIH on large scale, and also on establishing potential uses for the material. The possible issue of contamination of the NCaSiIH material with a variety of other species will also be explored in future studies.

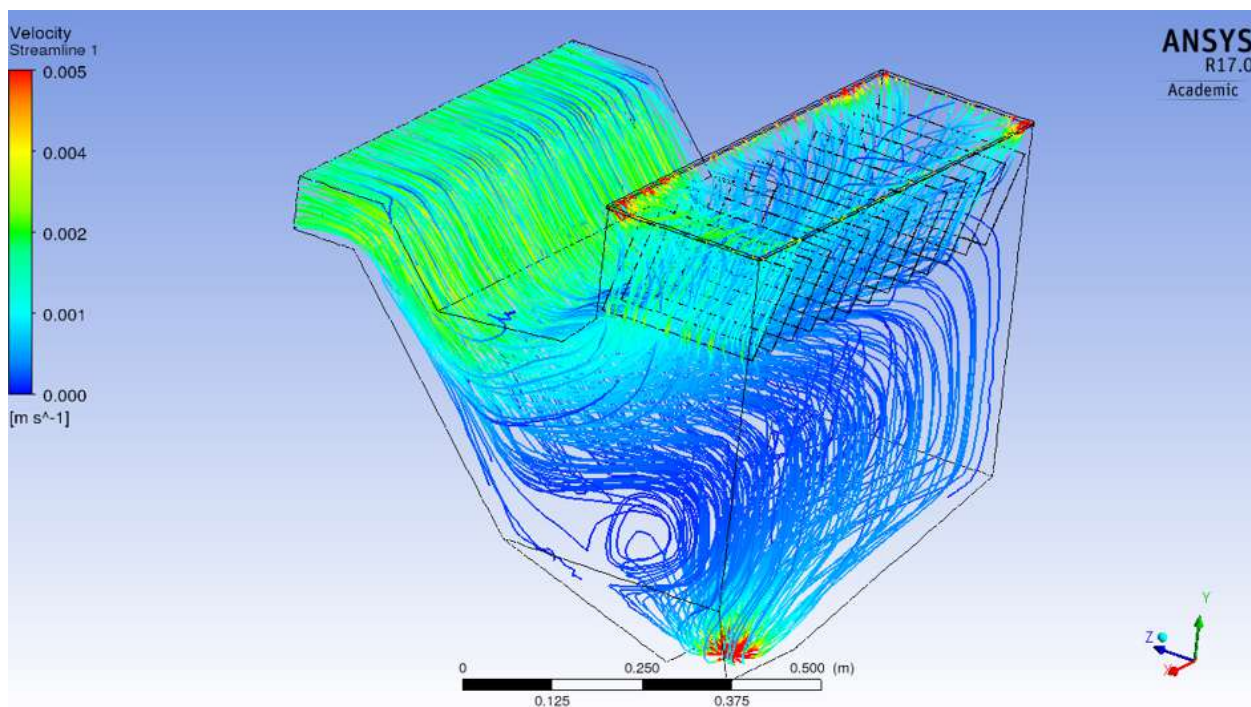


Fig. 5. CFD model showing the velocities and stream lines in a large-scale lamella separator based on laboratory model 3

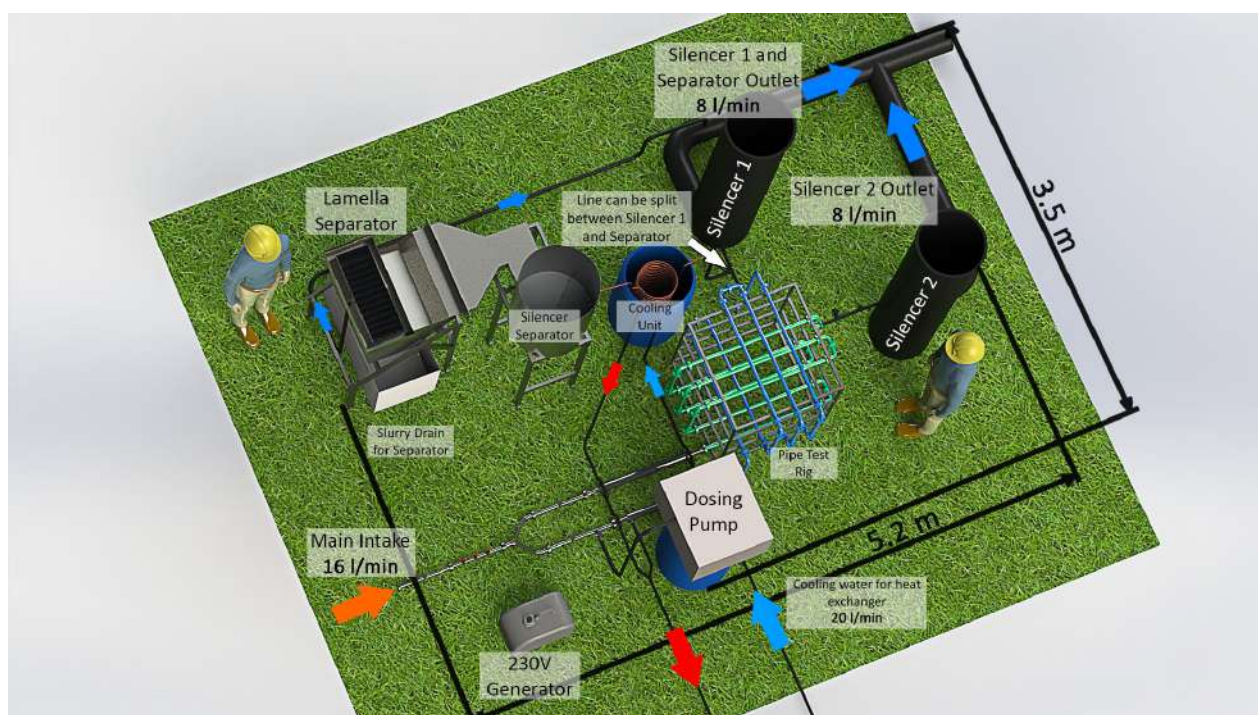


Fig. 6. Design sketch of pilot scale test rig



Fig. 7. Photographs of test rig

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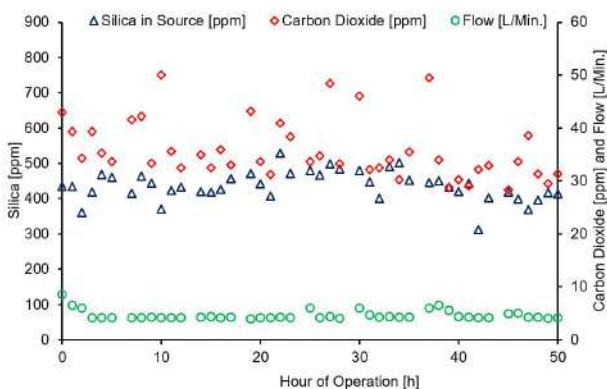


Fig. 8. Variations in measured parameters for the test rig

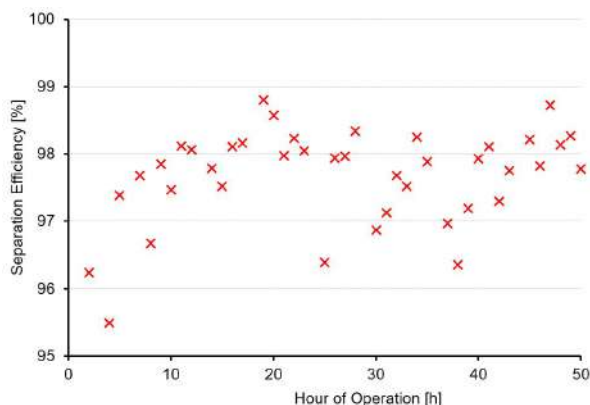


Fig. 9. Separation efficiency of lamella separator used in test rig

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# Modern techniques for the discovery of marine natural products

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## Introduction

The medicinal properties of naturally occurring compounds from living organisms have been exploited for thousands of years to treat a huge range of ailments and diseases. The marine world is one of the richest sources of biodiversity on our planet, relatively untouched and unexplored, and represents a unique wealth of unknown chemistry.<sup>1</sup> Marine natural products (MNPs) chemistry is the field which examines the chemical structures and bioactivities of metabolites derived from organisms of the sea. The sea is home to a huge range of chemically interesting organisms, all frequently used for the isolation of MNPs, with the most successful sources being algae (seaweeds), microorganisms (bacteria, fungi, cyanobacteria) and invertebrates such as sponges, tunicates, echinoderms and molluscs, each of which produce a variety of different classes of compound.<sup>2</sup> These desired bioactive molecules are colloquially known as secondary metabolites, which are typically restricted to individual taxonomic groups, and provide a selective advantage to the organism that is not strictly essential, but increases survival fitness relative to competing organisms. Marine organisms encounter substantially different ecological and physiological challenges compared to their land-dwelling counterparts, which results in the acquisition of bioactive molecules produced by unique pathways with intriguing structures and variations e.g. halogenation patterns.

The chemical space occupied by approved drugs mirrors that of natural products,<sup>3</sup> with over half of approved drugs being natural products or derived/influenced from them.<sup>4</sup> Indeed this was shown to be particularly true for MNPs through a recent statistical study using principle component analysis (PCA) comparing the physico-chemical descriptors such as clog *P*, molecular weight, ring structures and number of stereogenic centres, of 28,609 MNPs to 2908 approved drugs.<sup>2</sup> Although the number of drugs used in the clinic derived from MNPs represents a small, but significant portion, there are many promising leads in clinical/preclinical trials and more being tested every year. Currently there are seven FDA (US Food and Drug Administration) approved drugs that are derived directly from MNPs, and nineteen different compounds in various phase I-III trials. The clinical pipeline of marine pharmaceuticals is regularly updated online.<sup>5</sup>

The first FDA approved MNPs were vidarabine (Ara-A; approved 1976) and Cytarabine (Ara-C; approved 1969), for the treatment of herpes simplex virus infection and acute non-lymphocytic leukaemia, respectively.<sup>6</sup> These drugs were synthesised from lead molecules isolated from the sponge *Tectitethya crypta* (formerly *Cryptotethya crypta*),

collected from the Bimini Islands, Bahamas.<sup>7</sup> In 2010 eribulin mesylate (Halaven®) was approved, based on the sponge-derived macrolide halichondrin B,<sup>8</sup> which targets microtubules for the treatment of metastatic breast cancer. Sufficient quantities of halichondrin B could be isolated from natural sources for preclinical studies, but this was not viable for long term use and synthetic efforts proved costly and complex. However, a synthetic intermediate to the macrolide core was equipotent and far more simple to produce in quantity (although still hugely complicated, with 19 chiral centres and a mass of 731 gmol<sup>-1</sup>), which ultimately gave rise to the drug eribulin, the pharmacophore of halichondrin B.<sup>9</sup> The most recent clinically approved drug from the sea to date, is trabectedin or ET-743 (Yondelis®, approved 2015), which represents a rare example of a natural product moving to the market unaltered from its isolated form. Trabectedin is the most potent and abundant of the six ecteinascidins isolated from the colonial Caribbean ascidian *Ecteinascida turbinata*.<sup>10</sup> The ecteinascidins are tetrahydroisoquinoline alkaloids produced in very small quantities, with trabectedin only present at 0.0001% yield of animal biomass. In order to support clinical development, PharmaMar developed extensive (and successful) aquaculture farms throughout the Mediterranean, resulting in the harvest of 250 tonnes of biomass with a yield of ~ 1 µg g<sup>-1</sup>.<sup>11</sup> Commercialisation, however, required a much more consistent and economical approach. Total synthesis was achieved but was not applicable to industrial scale,<sup>12</sup> with semi-synthesis from cyanosafraicin B (obtained from the cultured bacterium *Pseudomonas fluorescens* on a kg scale) finally resolving the supply issue.<sup>11</sup> Trabectedin alkylates guanine residues on DNA, bending the helix towards the major groove, and this causes cell death through disruption of replication events. Trabectedin was therefore approved as a treatment for soft tissue sarcoma and ovarian cancer.<sup>13</sup>

The source of all of these clinically approved drugs are marine invertebrates, which are sessile organisms and typically void of any physical protection mechanisms. Sponges, tunicates, bryozoans and echinoderms have been particularly fruitful animals for MNP studies, found throughout the world with a range of predators, particularly grazing fish and crabs. Invertebrates therefore often acquire toxic secondary metabolites that act as anti-feedants for survival, and it is these molecules that are of particular interest for the discovery of new drugs. Secondary metabolites also have a host of other functions, such as reducing neighbour growth in the competition for resources, and even protecting the organism from UV radiation in tropical environments, which allows shallow

water habitation that may otherwise be too hazardous.<sup>14</sup> Therefore further investigation of a range of unexplored invertebrate species should result in the discovery of new molecules that can be used in the development of new drugs.

### Dereplication

By far one of the largest challenges in natural products drug discovery is dereplication, the identification of previously reported metabolites. The probability of re-isolating known compounds is very high,<sup>15</sup> which can become extremely costly in terms of both time and money. The faster chemical novelty can be established within an extract, the more optimal the procedure becomes, in terms of maximising the use of resources. With this comes the concept of screening, an assessment of an organism (or extract) for target molecules of interest, which is completed at the beginning of any NP program. Assays can be used to probe a desired biological activity within an extract, while spectroscopic techniques profile the types of molecules within. These include 1D <sup>1</sup>H NMR spectroscopy or more advanced 2D NMR (COSY, TOCSY, HSQC) experiments which help to increase resolution of chemical shifts by spreading the data over two dimensions, but take longer to acquire.<sup>16</sup> Many spectroscopic and spectrometric tools are utilised for dereplication, and in combination with biological data of the organism (taxonomy, bioactivity etc.), databases such as the Dictionary of Natural Products,<sup>17</sup> DEREPI-<sup>18</sup> or MarinLit<sup>19</sup> can be searched. These databases are not extensive, however, and do not contain every molecule described in the literature but can give clues as to the structural classes of some 'hits'. They also often rely on precise spectroscopic/metric inputs which may vary according to the solvent or concentration used (e.g. <sup>1</sup>H NMR chemical shift), and are very difficult to use when mixtures of compounds are present, such as early in the purification procedure. The sharing of raw data between research groups has the power to rapidly speed up the process of dereplication, including studies of organisms that do not result in the isolation of novel chemistry and are therefore not published. A recent communication expressed the need for more data sharing in metabolomics, which faces a similar problem analogous to that of natural products.<sup>20</sup> Therefore, although tools exist, dereplication is still a substantial problem today.

Clearly, the earlier dereplication is achieved the better. This is the main reason to use a spectroscopic-guided isolation procedure as opposed to the more common bioassay-guided method. Although the molecules isolated through such guidance do not have guaranteed bioactivity, producing secondary metabolites is very energetically demanding for the organism and inactive/pointless molecules are removed by evolution, therefore the vast majority are active. Experiments such as 1D (<sup>1</sup>H and <sup>13</sup>C) and 2D (COSY, HSQC and HMBC) NMR and LCMS use very little of the material to provide a wealth of data. In contrast, bioassays not only use up the sample and can take a long time, but they may give a negative result on a bioactive sample if the wrong assay is used. Bioassay-guided isolation procedures also frequently result in the

isolation of known compounds, as dereplication is very difficult to couple to this technique.

### Molecular networking and GNPS

Mass spectrometry (MS) is well suited as a screening tool, as it is easy to run, very sensitive and can be used in a high-throughput manner for rapid analysis of large datasets. Tandem mass spectrometry (MS/MS) introduces another dimension to data acquisition, providing information on how the molecule dissociates or fragments upon collision with an inert gas. With mixtures of compounds, untargeted LCMS/MS selects and fragments the most intense ions above a certain ion intensity threshold, which are then ignored in subsequent scans in favour of other ions. This generates a large dataset for each sample with information on many molecules within an extract, including those of low abundance. This is in contrast to classic <sup>1</sup>H NMR screening where peaks of minor metabolites may be masked by more concentrated compounds, particularly minor analogues present that can easily be missed, and the deuterated solvents required to run NMR make high-throughput processes costly.

Global Natural Products Social Molecular Networking (GNPS) is an online tool used for the sharing and processing of MS/MS data.<sup>21</sup> Users upload both annotated and unknown raw data to contribute to the crowd-sourced library. The annotated spectra can then be used to label previous unknowns, and as "deposited" data is continuously reanalysed, connections can be made in the future if an annotated spectrum is uploaded later. Therefore this tool is extremely powerful for dereplication in the screening process. Molecular networks are generated on the basis that similarly structured molecules will fragment through analogous pathways to provide spectra with similar patterns. Therefore, the MS/MS spectra of each precursor ion (node) represents a 'fingerprint' for a molecule, and through spectral alignment these nodes are connected to each other. A proxy for the degree of similarity of the molecules is the cosine score, which is often labelled on the edge (connecting line) or represented by the edge line thickness. This then generates a visual network representing the structural chemical space occupied by the metabolites in the sample. Within networks, clusters of nodes form when analogues with slightly different structures are detected. This is particularly useful when looking at minor derivatives of major metabolites, as structural information can also be ascertained from the difference in precursor ion  $m/z$ , which is unlikely to be determined from a <sup>1</sup>H NMR screen. For example, two nodes with a high cosine score and a difference of  $m/z = 2$  is possibly indicative of a double bond, whereas differences of 14, 28 or 42 suggest differences of methylene groups, possibly as part of an alkyl chain. There are various common functional group changes that can occur between related molecules, all resulting in diagnostic mass shifts, many of which are detailed by Meta-Mass Shift Chemical (MeMSChem) profiling.<sup>22</sup> This is a tool initially developed for comparing the metabolomes of coral reefs, showing that, although genetically similar, the MeMSChem profiles were unique and thus the metabolites are modified differently depending on

the environment the reef inhabits. Therefore GNPS has two key applications in screening; dereplication of known metabolites present in the database, and molecular networking of similarly structured molecules.

Often in natural products research, a large number of samples are generated either from the collection/library used or as a result of extract fractionation. Molecular networking through the GNPS platform allows more information to be displayed by labelling the nodes with metadata, which can be represented by its size or colour(s) within the networks, such as the location/origin of a fraction or its relative bioactivity. Because many invertebrate natural products are produced by symbiotic microbes, it is not uncommon for the same neighbouring species to contain different secondary metabolites, exemplified by two samples of the *Didemnum molle* tunicate, both collected on a single coral reef in the Eastern Fields of Papua New Guinea, where one colony produced the anti-HIV divamide A, whereas its neighbour only produced the far less active divamides B and C.<sup>23</sup> This technique allows the prioritisation of organism samples which most likely contain novel chemistry.

Although only recently introduced in 2012,<sup>24</sup> through its development GNPS has gathered a lot of traction in the natural products community, growing rapidly in user numbers and therefore database size. The majority of current publications utilising this tool has focused on plants and microorganisms, including those collected from the sea. A plethora of new MNPs have been isolated from these studies, such as samoamide A,<sup>25</sup> laucysteinamide A<sup>26</sup> and samholides A-I<sup>27</sup> all from marine cyanobacterial species, and a new rhamnolipid from an Arctic marine *Pseudomonas* sp.<sup>28</sup> In terms of reported investigations on invertebrates, all are on sponges or their associated symbionts thus far. *Latrunculia* species collected in the cold waters of Antarctica, South Africa and New Zealand have been the source of a range of pyrroloiminoquinone alkaloids, such as the potent antitumour discorhabdin A first isolated from a New Zealand species.<sup>29</sup> The molecular network of an Antarctic *L. biformis* sponge extract showed clusters dereplicated as discorhabdins and epinaridins, with a separate cluster containing the structurally related tsitsikamamine A ( $m/z$  304.125) manually annotated based on its fragmentation pattern. In this cluster, a node at  $m/z$  302.111 was linked with a high cosine score, and therefore has a similar chemical structure. Following targeted purification and spectroscopic structural elucidation, the compound was determined to be the previously unknown 16,17-dehydrotsitsikammamine A.<sup>30</sup>

A molecular networking based approach was used for the comparison of the secondary metabolites of the Mediterranean sponge *Spongia officinalis*, collected over three years at two different sites.<sup>31</sup> Nodes were coloured based on the year of collection, shaped according to the collection site and annotation status visualised through the node outline. Although previously extensively studied, this method annotated the major cluster as furanoterpenes by dereplicating several known metabolites of the sponge, and resulted in the isolation of three new compounds, furofficin and spongalactams A and B. The

production of spongonucleosides by the associated bacteria of sponge *T. crypta* was also investigated, identifying a producing strain of *Vibrio harveyi*.<sup>32</sup> Molecular networking was used to link the presence of spongosine and two derivatives to both sponge and bacterial prefractionated extracts, and also identified other structurally related molecules present.

If a specific type of molecules is desired, the generated networks can be probed for molecules of interest by doping extracts with a molecule of similar structure and known mass. By adding a semisynthetic probe derived from ilimaquinone, an extract from the sponge *Dactylospongia metachromia* was mined for zwitterionic quinonoids, resulting in the isolation of the bright-blue coloured dactylocyanines A-H.<sup>33</sup> The cluster around the probe provided the  $m/z$  of the derivatives present in the sample, which are then targeted through an LCMS-guided fractionation.

Natural product chemists have observed that, even though an extract is bioactive, the compounds isolated may not show corresponding activity, as the active constituent may break down during purification, may be present in too low a concentration, or may be the result of synergistic effects of multiple compounds.<sup>34</sup> By integrating bioassay results into the molecular network, the bioactive constituent(s) in a sample can be more readily visualised and identified. Recently, a bioinformatic workflow to more accurately pin down the source of bioactivity present in the molecular network of an extract was developed.<sup>34</sup> Termed “*bioactive molecular networking*”, the procedure takes into account the intensity of a feature in a fraction and how this correlates with the bioactivity using a Pearson correlation, thus nodes can be annotated (e.g. size) with a bioactivity prediction score. This method was applied to an anti-chikungunya virus (CHIKV) *Euphorbia densroides* extract, where previous bioactivity-guided isolation resulted in the isolation of many new compounds, however none showed the representative bioactivity of the crude.<sup>35</sup> The network showed a cluster of undescribed nodes, three showing a large predicted bioactivity score which were isolated, along with a positional isomer in the cluster with a low score for comparison. These molecules were all previously undescribed 4 $\beta$ -deoxyphorbol esters, and showed potent anti-CHIKV activity. Although there are no reports to date of use of this method with marine samples, there is a large potential for application towards the isolation of new bioactive MNPs.

To demonstrate how molecular networking can be used, Fig. 1 shows an analysis of a collection of Pacific sponge extracts. The nodes are annotated with pie-charts, where the colours represent the different samples and the relative quantity of the metabolite, with the thickness of the edges reflecting the cosine score magnitude. The number on the node is the precursor mass and on the edge is the difference between the two nodes. Primary metabolites are present in all samples and are of less interest for the discovery of new drugs. These form clusters from a large number of different species (*cluster A*). Secondary metabolites, however, are restricted to a taxonomic spe-

cies, and are therefore usually only derived from one or two species (*cluster B*). These molecules can then be targeted through further purification procedures using MS of the precursor ions.

### Symbiotic natural products and metagenomics towards drug discovery

In many cases, the secondary metabolites derived from invertebrates are believed to be produced by symbiotic microorganisms living in association with the organism. This is particularly true for polyketide and non-ribosomal peptide compounds, where the biosynthetic enzymes for these types of molecules are very rare in animal genomes.<sup>36</sup> Aside from the benefits of providing secondary metabolites to the animal, a symbiotic relationship gives reward to both parties involved. Cyanobacteria are common symbionts for tunicates, where the animal tissue provides a habitat with nutrition to the microbes. The mutualistic benefits go further with some forms of organic nitrogen and carbon from cyanobacterial photosynthesis provided to the tunicate for nutrition, in addition to that obtained by filter feeding.<sup>37</sup> In NP research, it is common to culture microorganisms to harvest their metabolites produced, however these symbionts are most often unculturable outside of the host organism, therefore the main method for chemical profiling is full invertebrate extraction. This is well evidenced by the cyanobacteria genus *Prochloron*, a common symbiont of tunicates, which produces a huge range of natural products yet since their initial discovery some 40 years ago,<sup>38</sup> have not yet been cultured.<sup>23</sup> The bryostatins are a well-known class of cyclic polyketides, originally isolated from the *Burgula neritina* bryozoan, but believed to be produced by the symbiotic *Candidatus Endobugula sertula* bacterium.<sup>39</sup> Although it is challenging to confirm microbial origin without direct cultivation, there are many suggestive pieces of evidence, such as reduced metabolite content on antibiotic-treated larvae, lack of metabolite production in a sibling species void of the symbiont, and

finally expression of mRNA from the *bry* gene cluster was detected by *in situ* hybridisation studies in the symbiont cells but not the host.<sup>40</sup> The cyclic depsipeptide didemnin B, was the first marine drug to be clinically tested on humans, and was initially isolated from *Trididemnin solidum*, a colonial ascidian that hosts a range of symbiotic cyanobacteria.<sup>41</sup> The metabolite's symbiont origin was initially suggested based on the hybrid non-ribosomal peptide-polyketide chemical structure, with more evidence coming from the isolation and discovery of the biosynthetic gene cluster (BGC) from a completely independent culturable marine derived  $\alpha$ -proteobacterium.

In his review of the highlights of MNP chemistry prior to the turn of the millennium,<sup>42</sup> Faulkner predicted that while elucidating the structures of compounds will still be a major focus of MNP chemistry in 2025, a considerable focus will be on genetically engineered microbes as a source of new compounds. This statements refers to the BGCs contained within the genomic DNA of the source organism(s), and how they can be inserted into the genome of a host organism such as *E. coli*. to produce the compound that may often be hard to come by naturally. Indeed in 2019, metagenomics, the study of genetic information obtained from an environmental sample such as soil or a holobiont (host organism and all of its symbionts),<sup>43</sup> is a field attracting considerable attention. After DNA isolation and sequencing, bioinformatic methods are used to probe for new and interesting BGCs, which can then be expressed in a heterologous host to produce the natural product. It is believed that 99% of soil bacteria are uncultivable in the laboratory via contemporary techniques.<sup>43</sup> This, coupled with the fact that BGCs are often silent, i.e. not expressed, without exposure to specific promoters or ecological triggers, severely restricts the discovery of potentially therapeutic molecules from these sources.

The supply issue is one of the greatest challenges for MNP derived drugs and is often cited as being the main

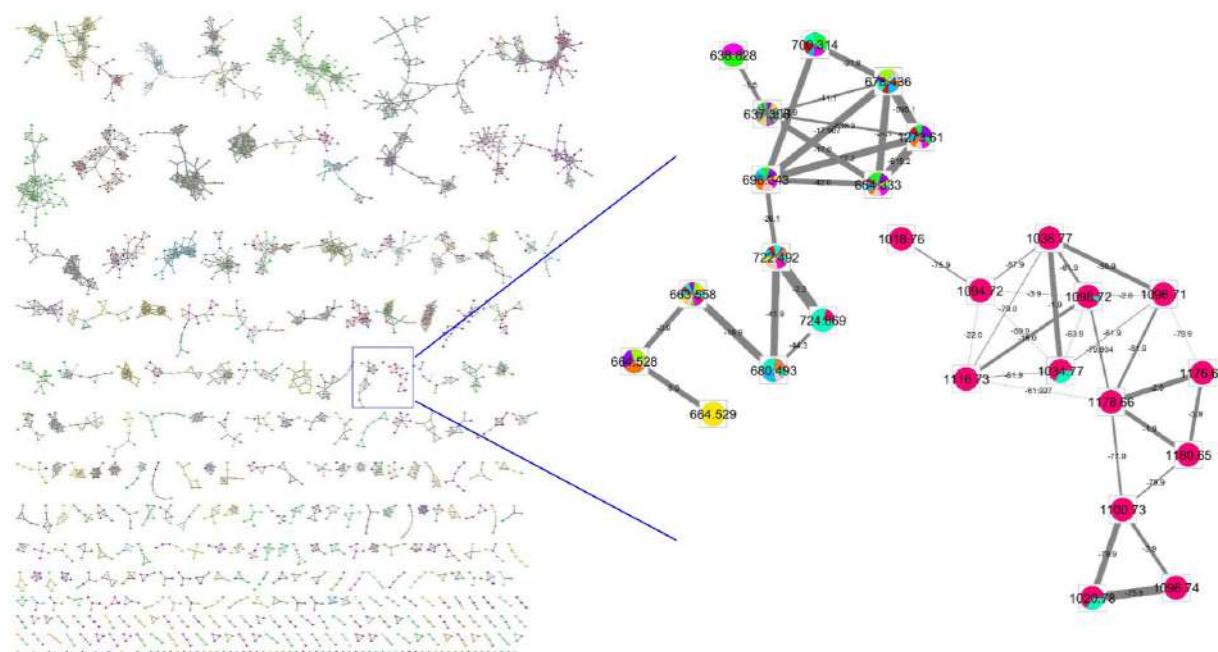


Fig. 1. Molecular networking analysis of a collection of Pacific sponges, zoomed in on clusters A and B

reason why there are relatively few that have been clinically approved. Often only a small amount of the source organism is collected due to low biomass or environmental issues and may only contain a very minor amount of the target compound, too little for structural elucidation, let alone supplying clinical trials. Synthesis (or semi-synthesis) is an ideal solution, however, it is only economically and environmentally feasible for relatively simple products. Aquaculture/cultivation can also be used, but this is not applicable for the majority of pharmaceutically relevant marine organisms.<sup>44</sup> Culturing symbiotic microbes in laboratory conditions has had very limited success outside of the natural habitat or host animal. Therefore, gene expression through metagenomics represents an ideal solution for this problem. This method not only gives access to some molecules not expressed in the source, corresponding to 'silent' genes, but provides a theoretically unlimited supply of microbes for production once structural elucidation and bioactivity evaluation have been completed.

As the most widely studied in terms of MNPs, it comes as little surprise that the field of sponge metagenomics is the most established of the marine invertebrates. Methods on the procedures and how to overcome shortcomings have been thoroughly reviewed,<sup>45</sup> with limitations typically arising from the amount and quality of isolated DNA and then the difficulty in deducing novel candidate BGCs aside from all the others sequenced. Metagenomic sequencing of the Japanese sponge *Discoderma calyx*, revealed the BGC for calyculin A, a potent cytotoxin commonly used as a chemical tool to evaluate intracellular signal transduction as it selectively inhibits phosphatases 1 and 2A.<sup>46</sup> The metagenomic library produced was mined for a *trans*-acyl transferase type I polyketide synthase-containing gene cluster, and analysis-matched homologues predicted for the metabolite. Three phosphotransferases were encoded in the BGC, and functional analysis by heterologous expression predicted the real end product to be the pyrophosphate containing, yet much less bioactive, phosphocalyculin A. Indeed this was the major metabolite in the extract of a flash frozen sponge sample, therefore dephosphorylation occurs on sample wounding, referred to as activated chemical defence, so as to avoid self-toxicity. Through traditional NP methods, this would not have been observed.

This method relies on homology of the unknown genes in a cluster with previously annotated genes present in databases. Another method, functional-based screening, uses a phenotype to screen all of the different clones generated from insertion of a small sequence of metagenomic DNA into a host such as *E. coli*. Through this method, different traits of the clones can be targeted, such as antibacterial or cytotoxic activity, or even production of pigments, by selecting those that are coloured and clearly produce the molecules.<sup>47</sup> A metagenomic library of the same Japanese sponge, *D. calyx*, was assayed for antibacterial activity, resulting in the isolation of turbo-mycin A and 2,2-di(3-indolyl)-3-indolone from the most antibacterial pDC112 clone.<sup>48</sup> The DNA insert was then subcloned to reveal the open reading frame (ORF) re-

quired to produce the latter metabolite, revealing insight into its biosynthesis for the first time. Aside from the positive clone successfully expressing functional enzymes and an active metabolite, the key benefit for novel drug discovery is that no prior knowledge of the biosynthetic enzymes is required, leading to the potential discovery of new biosynthetic machinery.

Significant progress has been made in metagenomic studies concerning tunicates, led by the Schmidt group's research on cyanobactins.<sup>49</sup> Cyanobactins are a group of ribosomally synthesised and post-translationally modified peptides (RiPPs) with potent cytotoxic activity and produced by a range of cyanobacteria, including the tunicate symbionts *Prochloron* spp.<sup>50</sup> The first examples, ulicyclamide and ulithiacyclamide, were initially isolated from a Palauan didemnid tunicate *Lissoclinum patella*,<sup>51</sup> and further tropical collections around the world led to the discovery of the patellamides,<sup>52</sup> lissoclinamides,<sup>53</sup> trunkamide<sup>54</sup> and patellins,<sup>54</sup> all of which are bioactive. The symbiont source was proven in 2005, with the sequencing and heterologous expression of the pateallamide A and C biosynthetic gene clusters from *L. patella* derived *Prochloron*.<sup>55</sup> The cluster consists of seven genes (*patA-G*), where *patE* encodes the precursor peptide that is recognised and modified by enzymes catalysing heterocyclisation of cysteine and threonine residues to form thiazoline and oxazoline rings, and also N to C terminal cyclisation. Polymerase chain reaction (PCR) primers for *patE* were used to probe the BGCs of 46 *Prochloron*-containing Pacific tunicates, which led to the discovery of six gene variants that are able to successfully produce the cyanobactins present.<sup>56</sup> With this library of data, the authors were able to engineer a new cyclic cyanobactin by simply changing the ribosomally coded sequence, showing the utility of this method for the generation of new, "non-natural" natural products.

Through metagenomic studies of the tunicate *D. molle*, the anti-HIV divamides A and B were discovered and characterised.<sup>23</sup> DNA from the whole tunicate holobiont was extracted, sequenced and assembled, and although several key features predicted by the isolated BGC, such as lanthionine residues, were detected by NMR of the tunicate extract, too little of the major product divamide A was isolated to solve the full structure. Whole-pathway expression in *E. coli* led to production of a product with identical NMR spectra to the natural product, which confirmed its proposed structure. The minor metabolite divamide B was also expressed heterologously. This represented the first example of a direct discovery-supply system for symbiont natural products.<sup>23</sup>

In terms of its impact on human health to date, trabectedin (Yondelis®) is one of the most significant tunicate natural products discovered, and is actually produced by the major symbiont in *E. turbinata*, the uncultivable  $\gamma$ -proteobacterium *Candidatus Endoecteinascida frumentensis*.<sup>57</sup> After identification of trabectedin in a tunicate sample, the hologenomic DNA was extracted, sequenced and filtered for sequences related to the previously deduced saframycin and safracin nonribosomal peptide synthetases. This resulted in a 35 kb contig of 25

genes, which represented part of the BCG for the product.<sup>58</sup> On assembling the full genome,<sup>59</sup> it was discovered that *Ca. E. frumentensis* has lost the ability to biosynthesise many primary metabolites such as amino acids, CoA and glucose. This helps explain the struggle in cultivating these obligate symbionts under standard conditions, and the genome reduction whilst maintaining secondary metabolite production gives evidence towards trabectedin being essential for survival of the holobiont.<sup>60</sup>

## Conclusions

The traditional methods used in the discovery of marine natural products are still very useful today, however the field continues to evolve to maximise the chances of finding novel chemistry and thus the discovery of new drugs. Dereplication of known structures is still a major issue; however, the use of molecular networking through the recently developed GNPS platform can help minimise this, and rapidly signal if chemical novelty is present in a sample. Metagenomic analyses are also providing a route and source to new molecules encoded by uncultivable microorganisms living in a holobiont, which may not even be present in the sample collected from the sea. There is no doubt that marine natural products will continue to play a major role in the discovery of new drugs, and the field will only continue to expand with the development of new tools and techniques.

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## Elementary history

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2019 has been designated by UNESCO as the *International Year of the Periodic Table* in recognition that that pervasive device of chemical knowledge, thought and memory has a history; one form of which was laid out by Mendeleev 150 years ago.

However, the individual members of that table, the elements, have a complex history because none of the four ancient elements – air, fire, water, earth – appear anywhere on the modern periodic table and many of the early members of the table (hydrogen, oxygen, nitrogen) were not identified as elements until the late eighteenth century.

In his masterful *Elements of Chemistry*, first published in Paris in 1789 (the same year of the revolution that would claim his life five years later), Antoine Lavoisier drew up a *Table of Simple Substances* that contains only 33 entries. We would recognise some of these as elements belonging in the modern periodic table, namely 17 metals from antimony to zinc, 6 non-metals from sulfur to the boracic radical and the gases oxygen, azote and hydrogen, but others we would not recognise, such as light and caloric and five earths from lime to silex.<sup>1</sup>

This may seem strange to us now - how could light or lime be elements? But Lavoisier cannot be accused of deliberate blunders or a lack of intelligence, so how did this come to pass? Lavoisier himself had little time for the history of his science in a work such as his noting acerbically in the preface that if “I had allowed myself to enter into long dissertations on the history of the science ... I must have lost sight of the true object I had in mind.”<sup>2</sup>

Nonetheless, he acknowledged that even he floated within the stream of history and any elementary treatise would require constant revision, noting of his table that “these things we at present suppose simple may soon be

found quite otherwise” because as “chemistry advances towards perfection, by dividing and subdividing, it is impossible to say where it is to end.”<sup>3</sup>

Lavoisier himself derided the use of the word “element” if it meant “the simple and indivisible atoms of which matter is composed ... [of which] we know nothing at all.” Instead, he adopted a functional definition of an element being a substance that was not capable of being further reduced by chemical operations.<sup>4</sup>

It is to chemical operations we must turn because without chemical procedures or instruments, elements could not be brought into being. In particular, while chemists had, prior to Lavoisier, routinely handled, transformed and analysed the products of the three kingdoms (animal, vegetable and mineral) these products were either liquid or solid and the associated apparatus (for calcining, distilling, extracting, reducing) were not able to contain or analyse any associated airs that might be produced. The containment and analysis of gases and the consequent demonstration that air and water are not elementary because they can be broken down, are central to the *Elements* and to the history of elements and will be dealt with next time.

## References and notes

1. Antoine-Laurent Lavoisier, *Elements of Chemistry*, translated by Robert Kerr, Edinburgh, 1790, pp 175-176 (hereafter *Elements*). The boracic radical (hypothesised to exist by Lavoisier, but not yet isolated), azote, caloric, and silex would now correspond to boron, nitrogen, heat or energy, and a silicon oxide respectively.
2. *Elements*, pp xxxii-xxxiii.
3. *Elements*, p 177.
4. The converse of this would be that an element was that substance which could never become lighter after any chemical analysis or procedure.

# Biodegradable magnesium in temporary medical implants

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**Keywords:** *magnesium, biodegradable, temporary implants, orthopaedics*

## Introduction

The field of orthopaedics has been very active in the integration of new technologies, developing new and superior approaches for the replacement of missing joints or bones and the support of damaged components of the musculoskeletal system.

Due to the composition of the human body, implants are required to withstand a complex environment, while simultaneously promoting the regrowth and repair of the body. Implants are constructed from materials which are selected for their high mechanical strength and fracture resistance; typical materials are metals, ceramics, or plastics.<sup>1</sup> Permanent implants, such as hip replacements, are designed for long life (10 years and beyond), and thus use materials such as stainless steel, titanium, and cobalt-chromium-based alloys which have excellent corrosion resistance in the body.

A different approach to material selection is required for implants which are designed to be temporary. These implants are most commonly used as fixtures for fractures in arms or legs, where an external support, such as a cast, may not be satisfactory. The traditional materials used in permanent implants may actually hinder the regrowth of damaged tissue when compared to more novel alternative materials. A main concern relating to the use of permanent implant materials for temporary implants is the mismatch between the mechanical properties exhibited by metallic materials and natural bone which can result in stress shielding effects.<sup>2,3</sup> Wolff's Law states that the strength of a bone is proportional to the loads it is placed under; therefore, if a bone is supported by a mechanically stable implant, it will become weaker.<sup>4</sup>

Another drawback of using permanent implant materials for temporary implants is that the implant will eventually need to be removed, either after the healing process is complete, or due to complications. Removal requires supplementary operations that increase healthcare costs and unwanted complications and trauma, and may

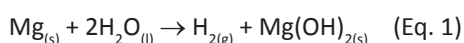
even result in refracturing of the healed bone.<sup>5</sup> In a randomised study of adult patients with distal radius fractures, 91% of the patients considered removal surgeries to be the largest drawback of temporary implants.<sup>3</sup>

These limitations have led to the recent explosion in the interest of biodegradable materials, which Zheng *et al.*<sup>6</sup> define as materials which are expected to corrode gradually *in vivo*, with an appropriate host response elicited by the release of corrosion products, before dissolving completely, matching the recovery process of tissue healing. Biodegradable materials would completely eliminate the need for additional operations and if the degradation is controlled successfully, stress shielding can be limited.

## Magnesium as a biodegradable implant material

Magnesium is of considerable interest as the primary base metal in many biomaterials. Not only is it one of the lightest engineerable metals, it has very similar mechanical properties to natural bone (Table 1). Further, magnesium has one of the highest no-observable-adverse-effect levels when compared to other biodegradable metals (6.7 mg/kg/day for magnesium and 0.28 mg/kg/day for iron, another possible implant metal<sup>7</sup>). Because of this, Mg is at the forefront of biodegradable metal research and development.

Although magnesium appears to be an ideal biodegradable implant candidate, it readily reacts with water, which makes up approximately 70 % of the human body. Magnesium has the lowest reduction potential out of all engineerable metals, with  $E^\circ_{(\text{Mg}^{2+}/\text{Mg})} = -2.37 \text{ V}$  vs. standard hydrogen electrode.<sup>12</sup> The reaction of magnesium with water is given by Eq. 1:



When pure magnesium is exposed to moist air, a natural oxide coating comprising MgO and Mg(OH)<sub>2</sub> forms rapidly and acts as a corrosion protective layer in water.<sup>13</sup> However, when this layer is exposed to chloride ions

**Table 1.** Comparison of different biomaterials and their physical and mechanical properties<sup>8-11</sup>

Properties	Natural bone	Magnesium	Titanium	Co-Cr alloy	Stainless Steel	HA <sup>a</sup>	PLLA <sup>b</sup>
Density (gcm <sup>-3</sup> )	1.8–2.1	1.74–2.0	4.4–4.5	8.3–9.2	7.9–8.1	3.1	1.21–1.43
Elastic modulus (GPa)	3–20	41–45	110–117	230	189–205	73–117	2.7
Compressive yield strength (MPa)	130–180	65–100	758–1117	450–1000	170–310	600	-
Fracture toughness (Mpa m <sup>1/2</sup> )	3–6	15–40	55–115	-	50–200	<1	-

<sup>a</sup> hydroxyapatite <sup>b</sup> poly(L-lactic acid)

(which have a concentration of approximately 100 mM in a human body) the surface layer is converted to  $\text{MgCl}_2$  which is very soluble (Eq. 2). The next result is that the underlying magnesium is rapidly exposed.



The accelerated degradation of magnesium due to chloride also results in the rapid production of  $\text{H}_2$  gas (Eq. 1). If left unchecked this gas can build up around the implant leading to gas cavities under the skin. Lowering the rate of magnesium corrosion due to the presence of chloride is the major challenge limiting magnesium's implementation in medical implants.

### Historical use of magnesium in orthopaedics

For almost 150 years, surgeons and physicians have explored magnesium and its alloys for numerous clinical applications. In 1878, Edward C. Huse was the first to describe using magnesium wires as a ligature for bleeding vessels of three human patients.<sup>14</sup> The relationship between the thickness of the wire and time taken to degrade fully in vivo was already understood by Huse, who used this to his advantage, selecting different gauge wire for different applications.<sup>14</sup> Erwin Payr was one of the most significant pioneers of the use of magnesium as a biodegradable material and was able to propose that tissue oxygen and water content, carbon dioxide, dissolved salts in blood and cell physiology all contributed to the corrosion of magnesium.<sup>15,16</sup> From 1902-1932, Albin Lambotte extensively investigated the use of magnesium in orthopaedic clinical studies, with his work being continued by his assistant Jean Verbrugge in animal studies.<sup>17,18</sup> A comprehensive summary of clinical and animal studies of magnesium and its biomedical applications from this period can be found in the 2010 review by Witte.<sup>16</sup>

Many medical applications for magnesium were evaluated in this early work, including ligatures,<sup>14</sup> vessel connectors,<sup>15</sup> plates and sheets,<sup>18</sup> and pins and screws.<sup>18</sup> However, the high degradation rate and hydrogen evolution were significant problems and led to the decreased interest in the use of magnesium as a biomaterial,<sup>7</sup> with more corrosion-resistant steel appealing to many surgeons.<sup>16</sup>

### Recent advances

Within the past 20 years, interest in magnesium from material scientists, engineers, and physicians has dramatically increased due to the potential applications of the material.<sup>7</sup> An increased understanding of corrosion characteristics, human physiological responses and biomaterial design has led to significant strides in the development of magnesium-based biomaterials. Knowledge of alloying technology led to the in vitro studies completed by Kuwahara et al.,<sup>19</sup> one of the first "modern" magnesium studies. Kuwahara et al. investigated the corrosion properties of pure magnesium and two alloys (AZ91 and AZ31) in Hank's solution (a cell culture medium) and concluded, much like the physicians of the past, magnesium could be a possible biomaterial. Since then, hundreds of publications have appeared describing physical properties, and cytotoxicity and haemocompatibility evaluation of magnesium alloys, the pure metal, and composites, both in vi-

tro and in vivo.<sup>7,16</sup> Over 30 magnesium-based biomaterials have been evaluated within bones of small animal models (rats, guinea pigs, and rabbits) as well as larger models (sheep). A comprehensive list of recent in vivo studies can be found in a 2014 review by Zheng et al.<sup>6</sup>

One major result from these studies is that magnesium has a positive effect on the formation of new bone in the vicinity of the metal implant.<sup>16,20</sup> Witte *et al.*<sup>20</sup> showed that a greater regrowth of periosteal and endosteal bone formation could be achieved using a magnesium biodegradable implant when compared to another biodegradable material, polylactic acid. Promoting the regrowth of bone is a valuable property of magnesium and could widen the possible applications of the metal.

### Future prospects

Pure magnesium exhibits corrosion behaviour which is typically too fast for many applications and results in the formation of gas cavities. To be useful, magnesium corrosion must be slowed, either by alloying or by coating the surface. Alloying can result in the improvement of strength and creep resistance but consideration of the pathophysiology and toxicology of degradation products must be taken into account.<sup>6,8</sup> Not only does the alloying material have to slow the corrosion rate, but it should remain biocompatible within the vicinity of implantation. The alloys of most interest include elements which are biologically essential ( $> 50$  mg/kg: Fe, Ca, Zn, and Mn), potentially essential ( $< 50$  mg/kg: Sr, Si, and Sn), or have proven characteristics which may be advantageous for alloying (Li, Al, Zr, Bi, and Y and lanthanides). A potential problem with alloy use is that the phase boundaries of individual grains of the alloy can form anodic and cathodic regions on the surface, and result in accelerated degradation due to galvanic corrosion.<sup>6</sup>

Surface modification with a deliberately added coating has been shown to decrease the rate of corrosion, anywhere from 20-90 %.<sup>6</sup> However, obtaining uniform corrosion remains a significant problem, as microcracks and defects in the surface coating can result in the acceleration of local degradation.<sup>5,6,21</sup> Many different surface protection methods have been reported in the literature, including chemical methods such as fluoride<sup>22</sup> and alkali treatment<sup>23</sup> electrochemical treatment,<sup>24</sup> bone-like mineral deposition,<sup>25</sup> sol-gel treatment,<sup>26</sup> and organic (polydopamine,<sup>27</sup> chitosan,<sup>28</sup> cellulose,<sup>29</sup> collagen,<sup>30</sup> and gelatin<sup>31</sup>) and polymer (polylactic acid,<sup>32</sup> polycaprolactone,<sup>33</sup> and poly(lactic-co-glycolic acid)<sup>34</sup>) coatings.

### Concluding remarks

The future of biomedical materials is wide open. The use of biodegradable metals seems inevitable, but significant challenges need to be overcome before widespread adoption can occur. Controlled gradual corrosion would alleviate the cost, time and trauma of additional removal and adjustment operations and reduce stress on the healing bone. However, magnesium will never be fully accepted as a biomedical material until its degradation is slowed to a more practical rate. Alloying has had some success in reducing the corrosion rate, but the major

drawback comes from the choice of alloying material and its effect on the viability of cells and tissues. The biocompatibility of the alloy should be fully understood before clinical trials can begin. Surface modifications have led to significant reductions in corrosion rate, but inhomogeneous coatings can result in local accelerated degradation. Overcoming these problems can be achieved by smart design using a combination of chemical, physical, and mechanical techniques and within a relatively short period, magnesium-based biomaterials could become a reality.

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## The fading of acetylene's bright light

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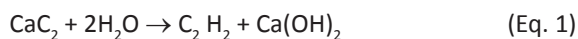
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In the late nineteenth century as the larger cities and towns of New Zealand used coal gas to light their streets and businesses,<sup>1</sup> a competitor – acetylene – was emerging. Particularly in the smaller towns and in houses and farms distant from a reticulated coal gas supply, acetylene was potentially an attractive fuel, its burning providing a far brighter light than coal gas at much lower cost.<sup>2</sup> In a comparison experiment held in Nelson, a box was placed half-way between a burner fueled by acetylene and one fueled by coal gas: “the small jet of acetylene gave so brilliant a light that a strong shadow was thrown by it from the box in the direction of the common gas flame. A test of the diffusive power of the two lights was distinctly in favour of the acetylene, which also gave a much purer light.”<sup>3</sup> The experiment was performed by William Tyree, an enthusiast for lighting up with acetylene gas<sup>4</sup> and a notable colonial photographer in Nelson.<sup>5</sup>

Acetylene is generated by the action of water on calcium carbide (Eq. 1), the calcium carbide having been made by heating lime and coke at temperatures greater than 2000°C (Eq. 2):



As one of the authors recalls from a school-friend's home laboratory experiment decades ago, acetylene produced by this means has a characteristic smell – actually hydrogen sulfide and phosphine from impurities in the calcium carbide.

The governing councils of New Zealand's colonial towns and cities were generally keen to be perceived as “the location and embodiment of Western modernity”.<sup>6</sup> Thus, resident George Wilks' letter to the Feilding Borough Council suggesting that the borough should follow the example of Paris in investigating the use of acetylene for gas lighting was probably well received,<sup>7</sup> and the prospect of the Nelson city gas works being an agent for the Sydney-based Australasian Incandescent Gaslight Company warranted consideration.<sup>8</sup> It is, therefore, unsurprising that New Zealand's colonial newspapers reported interest being shown in the use of acetylene by the councils of towns and cities,<sup>9</sup> and gave examples of buildings in which it had been installed.<sup>10</sup>

In 1902, Kaiapoi's well-known local store Blackwell's, which had already relocated from its original site to take advantage of the commercial opportunities of being close to the railway once it had arrived in the town,<sup>11</sup> “installed improved shop lighting replacing kerosene lamps with acetylene gas. This proved very successful, [although] it caused some anxious moments occasionally

on late nights when flickering lights caused a rush to replace carbide stocks.”<sup>12</sup> This small-town commercial success may have assisted in the subsequent decision by the Kaiapoi borough to adopt acetylene for street lighting.<sup>9</sup>

Picton was the first New Zealand town to introduce street lights using acetylene gas, in 1906, followed by Kaiapoi, Geraldine and Opatiki. The commercial entity behind this activity was the Acetylene Gas Lighting Company, which was established in Dunedin in 1902 and had branches in Christchurch and Wellington. Although re-purposed, the firm's original buildings survive in Dunedin (Fig. 1) and Wellington (Fig. 2). As Blackwell's experience suggested, acetylene lighting was not without its risks, although insurance companies seemed comfortable about insuring premises where it had been installed:

“That acetylene is a safe light is attested by the fact that the apparatus is installed with the consent of the insurance company and no increase is made in the rate. On the contrary, insurance authorities acknowledge that wherever acetylene supplants oil or gasoline the fire risk is reduced materially.”<sup>13</sup>

Explosions or fires attributed to acetylene's use in buildings appear to have been rare. A fire in Upper Hutt in 1914 which caused eight deaths which originally was attributed to acetylene was eventually attributed to the



**Fig. 1.** NZ Acetylene Gas Lighting Coy Ltd's building, Stuart Street, Dunedin in 1910. After several re-brandings and re-orientations of its business, the firm eventually ceased trading in 1956. Since then the building has been used for many purposes, including – recalling William Tyree – a photographic studio from 1962-1993. [Image: Toitu - Otago Settlers Museum]

ignition of gelignite stored on the premises.<sup>14</sup> In 1914 a miner's acetylene powered helmet lamp triggered an explosion when the miner entered a disused part of Ralph's Mine near Huntly that contained high levels of methane gas – miners' "firedamp".<sup>15</sup> Despite this incident, exploration of most of the limestone caves in the nearby Waitomo district was undertaken with acetylene light.<sup>16</sup>

Lighthouses were another remote location in which acetylene lighting was used, the earliest being at a 'cottage lighthouse' at Bean Rock near Thames in 1912.<sup>17</sup> A probably better-known lighthouse, that on Tiritiri Matangi, was converted to acetylene in 1925, illuminating the Hauraki Gulf until converted to electric operation in 1954.<sup>18</sup>

Although the NZ Acetylene Gas Lighting Company had showrooms in Christchurch, Dunedin and Wellington and advertised extensively throughout the country (Fig. 3), the New Zealand International Exhibition held in Christchurch in 1906-1907 provided a great opportunity for the company to promote 'home-made gaslight for country houses'. The Exhibition Programme crowed:

"Takes about 20 minutes labour per week and after that you only have to turn a tap and apply a match when you want LIGHT. Yes, a brilliant beautiful white light, too. A light that spreads all round the room like Sunlight. A light that gives sparkle to every polished article that it falls on, gleam and glisten to white table linen, and a genial, cheery glow to everything it illuminates.

"Wouldn't you like to get rid of the everlasting smell of kerosene in your home?

"Wouldn't you like to know that never again would you have filthy Kerosene Lamps to clean and fill, wicks to trim, chimneys to clean, and the permanent dread of fire.

"Wouldn't you like to know that in every room you had a nest, pretty fixture, firmly attached to ceiling or wall, where it couldn't be tipped over by the children, where it was never in the way, and was always ready to touch a match to when you wanted a light?

"Wouldn't you like your visitors to find in your home that smart 'city style' which Gas Lighting gives, with that soft radiance shining down from the ceilings, where it does not get in your eyes like the glaring light of smelly kerosene table lamps?

"A GOOD ACETYLENE PLANT will be good for the use of a lifetime and the light is a luxury and a comfort, both time-saving and eye-sight saving, and after the initial cost at a cheaper rate per candle power than kerosene.

"Now, just drop us a line, stating how many rooms you have got, and we will tell you how much it would cost to light them properly with this beautiful white light, which is similar to Sunlight."<sup>19</sup>

In addition, the NZ Acetylene Gas Lighting Company exhibited its equipment and wares at Agricultural and Pastoral Shows, such as that in the Manawatu (Fig. 4). This particular display included what must have surely been for the time a totally unexpected innovation: the automatic 'Advance' burner.

"The so-called automatic burner is one which not only lights the gas by electricity but also automatically extinguishes it. It is operated from a push, having a white and black button; pressing the white button ignites the gas, while the black one extinguishes it. Any number of these push buttons can be connected to one burner, so it is possible to ignite and extinguish the light from any number of different locations. By its use a system may be so arranged that a person can visit any part of the house and light the gas ahead by means of a push button conveniently located, extinguishing it in the rear by means of the same push button."<sup>20</sup>

On-site acetylene generation systems "do away with the necessity for laying mains and building works on the present system. Every householder will have his own gas-works on the premises. He has but to turn the water tap on the retort when he wants gas... every country house and every house above the rank of cabin could be lighted by this gas."<sup>21</sup> A typical installation, schematic diagrams of which are shown in Fig. 5,<sup>22</sup> is described below.



Fig. 2. Warehouse and offices of NZ Acetylene Lighting Co., 5 Tory Street, Wellington, 1917. Architect: Crichton & McKay. The floor plans indicate a show room, office and store on the ground floor with an internal lift connecting the store to two upper floors. The use of the upper floors is not indicated on the drawings. The parapet was removed in 1936, as a response to the 1931 Hawkes Bay earthquake. (Image: Bulleymont Fortune Architects Archive, used with permission). An architecturally unsympathetic two-storey addition made to the building around 2000 attracted the comment "they have reinvented cool", when the building was recently for sale.

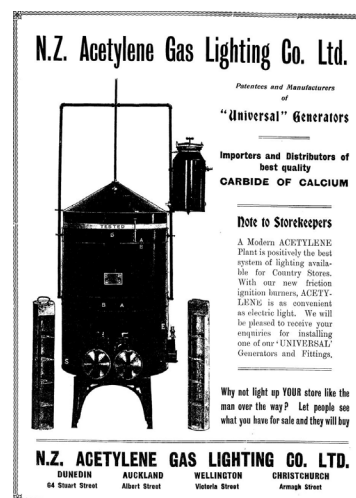


Fig. 3. The NZ Acetylene Gas Lighting Company advertised its equipment throughout the country. (Image: *Progress* 1915, 1 May, p.33)

“Mr John Ramage, of this town [Clutha] has just completed arrangements for the installation of an acetylene gas lighting plant into the handsome brick residence recently erected by Mr John Gibson of Ashley Downs. The generator to be used is one of Mr Ramage’s own manufacture – the Patent Sunlight Generator – and is capable of supplying between 20 and 30 burners. The installation is to be completed in the course of

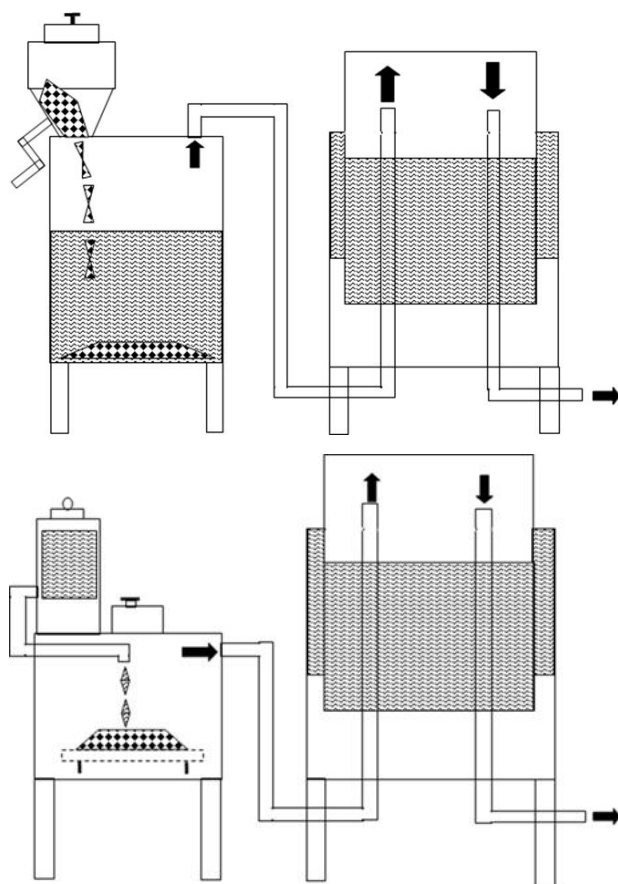
a week or 10 days... Arrangements are being made for a continuous local supply of carbide from Sydney landed here at considerably less price than it could be from Dunedin.”<sup>23</sup>

Rarely commented on was the requirement for calcium carbide and acetylene (whether liquid or gas) to be stored in a separate building from that where it was used, and that there were appropriate arrangements for releasing over-pressurised gas safely.<sup>24</sup>

Brancepeth Station near Masterton generated acetylene gas from 1905 (see Fig. 6A), and the fittings are still all through the house,<sup>25</sup> and remnants of the system may still be in the attic.<sup>26</sup> A notable feature of Brancepeth Station was its library, which “acted as a social space for men working on the farm, who could sit by the fire in the evening or on Sundays reading the papers; it is likely, too, that women from the homestead, family members and the governesses, browsed the shelves peacefully during



**Fig. 4.** “The large and varied display of generators, gasoliers, brackets, lamps, etc., [which] were manufactured at the works of the [New Zealand Acetylene Gas Lighting] company in New Zealand” at the A&P show in Palmerston North during 1-3 November 1905 [Image: Sir George Grey Special Collections, Auckland Libraries, AWNS-19051116-12-4]



**Fig. 5.** Schematic diagrams of the operation of an acetylene generating apparatus. **A. Top:** Adding calcium carbide to water (the technique shown for Brancepeth Station in Fig. 6A). **B. Bottom:** Adding water to calcium carbide. In both variants of the process, the acetylene is collected in a telescopic reservoir, similar in function to the much larger gasometers that were a feature in New Zealand towns before natural gas replaced coal gas in the 1960s.



**Fig. 6.** Brancepeth Station, near Masterton. **A Top:** Hugh Beetham, owner of the station, refilling the carbide reservoir of the station’s acetylene gas system in 1956 (see Fig. 5A). (Image: Alexander Turnbull Library: EP/1956/0397a-F). **B. Bottom:** Interior of the Brancepeth Station Library in 1966. The glass-fronted book cases and their contents were later relocated to the library at Victoria University of Wellington. The pull-cord for the suspended electric light is just to the right of the chimney. (Image: VUW100183; used with permission of Victoria University of Wellington).

the day.”<sup>27</sup> On a September day in 1894, “a fire, a Rochester [a notoriously smoky three-wick kerosene lamp<sup>28</sup>] and four men smoking” made the library uninhabitable.”<sup>29</sup> A 1966 photograph of the library shows it was eventually lit by electricity (Fig. 6B), but it is just possible that it was formerly lit by acetylene.

Supplies of calcium carbide were not always reliable, prompting a suggestion in 1897 that carbide could be manufactured in disused watermills in Ireland!<sup>30</sup> A year later Tyree noted, “The business of the company in New Zealand has developed so rapidly that we have decided to erect works for the production of carbide of calcium in the colony – on the West Coast...”<sup>31</sup> Nothing seems to have come of this proposal since by the time of the First World War most carbide was imported via Australia from sources in Switzerland, Austria-Hungary, Norway and Sweden. The carbide production from these countries was controlled by a British-German ‘combine’, which was even then potentially vulnerable during the conflict.<sup>32</sup> However, security of supply of carbide was not the death-knell of acetylene gas lighting; rather it succumbed to electricity as supplies became increasingly available and accessible.<sup>33</sup>

Had electricity not supplanted acetylene, the professional lives of scientists and academics might have been a little different: views through microscopes and projection of images for lectures to students would have benefited from the ‘sunlight’ characteristics of acetylene (Fig. 7).

As a footnote to acetylene’s use for lighting, a provincial newspaper reported that the compound could be:

“... transformed by a simple chemical process into alcohol of such purity as to require no rectification, so that every person may become his own distiller and produce a good spirit at about three centimes (three pence) a quart. Questioned

upon the subject, M. Berthelot, the most renowned chemist in France has said, ‘I affirm that, with a really scientific apparatus, of small dimensions, every intelligent operator may obtain, without difficulty and without danger, a spirit which no verifier will be able to distinguish from that which bears the Government stamp.’”<sup>34</sup>

The ‘M. Berthelot’ referred to in the above quotation was Marcellin Berthelot, who in 1855 had demonstrated that ethylene and propylene could be hydrated using sulfuric acid to form ethyl and propyl alcohol respectively,<sup>35</sup> although a later critique of this work suggested Berthelot’s efforts were of little commercial value.<sup>36</sup> A recent history of French chemistry considered these efforts were a modest initial contribution to “a concerted synthetic program” of organic compounds.<sup>37</sup>

Eq. 3 shows acetylene being reduced with hydrogen to form ethene; the reaction is catalyzed by palladium and calcium carbonate. The resulting ethene can then be hydrated – *comme Berthelot l’aurait faite* – to form ethanol, as shown in Eq. 4.



The commercial prospects in New Zealand for the production of ethyl alcohol from acetylene and its social consequences were described in 1896:

“The *Popular Science News* says, ‘The recent discovery by Mr Wilson of the production of acetylene gas from lime and coal dust treated with electricity from carbon electrodes has made it possible to produce ethyl alcohol so cheap that all other processes should be abandoned. Should this discovery prove to be what is expected, alcohol will be made for 2c to 3c a gallon or even less. Its use in the arts will be largely increased, and as a beverage it

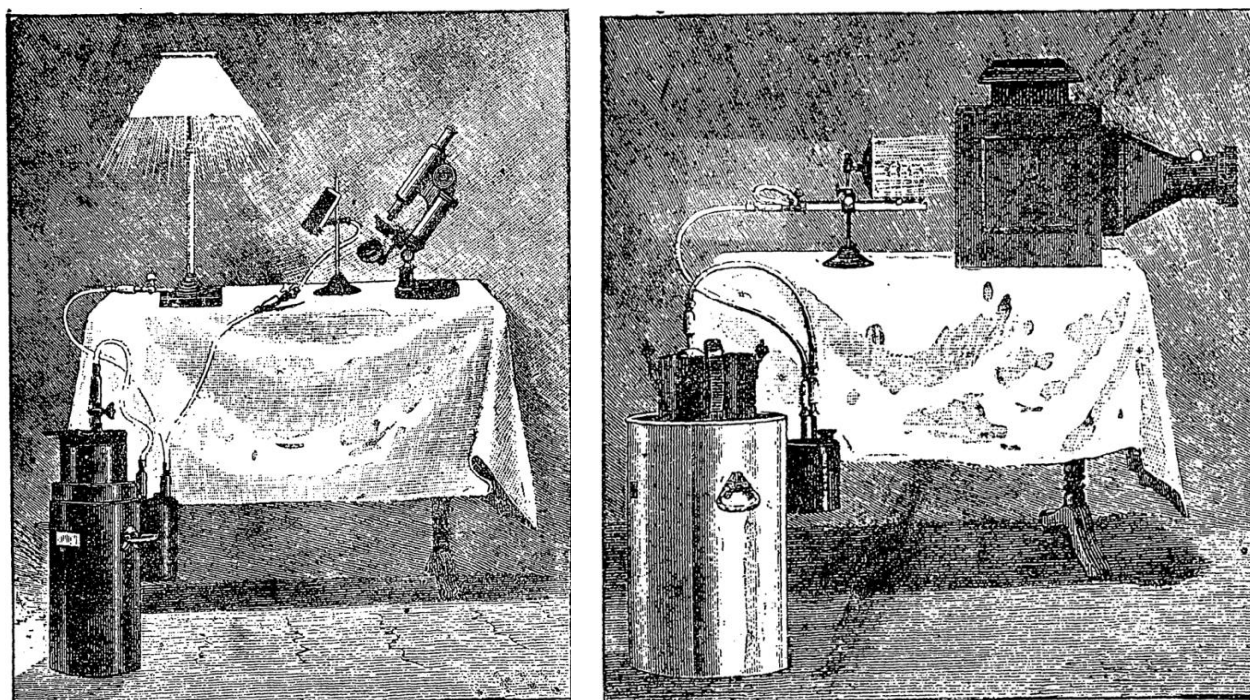


Fig. 7. ‘Academic’ applications of acetylene lighting. A. Left: As a light source for microscopy. B. Right: As a light source for ‘magic lantern’ image projection (Images: *Star* 1896, 20 October)

could be cheapened to an enormous extent. The occupation of distilling will be superseded, and the manufacture of whiskey and other alcoholic beverages will change, and the great problems which centre around them commercially, scientifically, and socially will have new features.”<sup>38</sup>

Just as the brightness of the acetylene light did not last, so the cheap acetylene-derived booze was also not to be.

## References and Note

1. “The four main cities [of New Zealand] had been making gas for lighting purposes from the 1860s... By 1891 there were 27 gasworks in New Zealand”; by 1911 this had increased to 48 “and gas prices were competitive with those of coal”. From: Leach, H. *Kitchens: The New Zealand Kitchen in the 20<sup>th</sup> Century*. Otago University Press: Dunedin, 2014, p. 33 and p.49.
2. An advertisement ‘Sunlight at Night – Acetylene Gas – Safer, cheaper and more brilliant than coal gas’ (*Nelson Evening Mail* **1897**, 10 April, p. 3) noted that coal gas cost seven shillings and sixpence per 1000 cubic feet, while an “equal light of acetylene” cost three shillings and six pence, i.e., about half the cost of coal gas.
3. Acetylene Gas A Local Trial. *Colonist* **1897**, 7 April, p. 2
4. A measure of Tyree’s enthusiasm is his presentation, entitled ‘Further experience with acetylene gas’ to the Engineering Association of New South Wales, 10 May 1900; recorded in the Association’s Annual Report, 30 September, 1900.
5. William Tyree. In *Early New Zealand Photographers and their successors*: <http://canterburyphotography.blogspot.com/2009/08/william-tyree.html> (accessed 20/09/2018).
6. Schrader, B. *The Big Smoke – New Zealand Cities 1840-1920*. Bridget Williams Books: Wellington, 2016, p. 23.
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# Ruby gold glass: early nanotechnology in art and science

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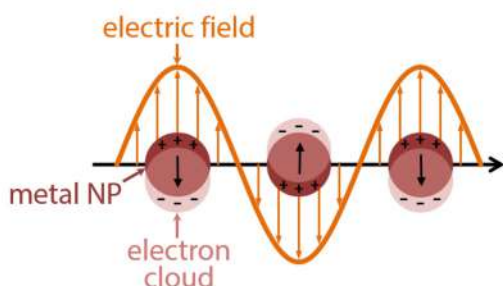


Emma Wrigglesworth is in the final year of her PhD in chemistry at Victoria University of Wellington. Her research is focused on developing nano- and micro-particles with unique optical properties, and their incorporation into polymer composites.

Since the Roman Empire the attractive colours displayed by gold nanoparticles have been utilised by their incorporation into glass to produce pink, red and purple shades. At this time the theory behind the colours was not understood. In fact it is unlikely that these glassmakers knew that the colours they were making resulted from very small gold particles, and it is unclear if they had controlled methods to reproduce colours. However their skills as some of the world's first nanotechnologists were admirable and the examples that survive today continue to impress and inspire.

## The colour of gold

Whereas bulk gold displays the golden yellow colour we know from jewellery and old coins, gold nanoparticles display a range of attractive colours due to the localised surface plasmon resonance (LSPR) effect. LSPR results from the interaction of electromagnetic radiation with a particle of a size comparable to the wavelength of light, i.e. a nanoparticle.<sup>1,2</sup> The incoming light induces a displacement of the particle's negatively charged conduction electrons away from the positively charged metal core. The resulting net charge difference acts as a restoring force resulting in oscillation of the electron cloud (Fig. 1). When the frequency of the electromagnetic radiation is resonant with the electron oscillation then the light absorption and scattering at this frequency is greatly enhanced, dictating the colour of the nanoparticles.<sup>2</sup> The size and shape of the particles determine the frequency at which the electron oscillation and incoming light are resonant. For example, spherical gold nanoparticles with diameters of 20 nm undergo LSPR resonance at approximately 520 nm which gives a red colour.<sup>3</sup> Increasing the size of the particles results in a red-shift in the LSPR absorption and a change in colour from red to purple to grey. Changing the shape to a nanorod introduces a new size dimension and so a new LSPR absorption, giving rise to a whole new range of colours.<sup>4</sup>



**Fig. 1.** Schematic illustration of LSPR. Upon interaction with an electric field the nanoparticle conduction electrons are made to oscillate in resonance with the radiation.

## Ancient gold nanoparticles

One of the oldest examples of the use of gold nanoparticles as a colourant remains one of the most famous and impressive. The Roman Lycurgus cup, dated to the fourth century and currently on display in the British Museum in London, displays unique optical properties due to the presence of metallic nanoparticles embedded in the glass.<sup>5</sup> When the cup is on display the curators have placed a small white light inside of it, and where the light shines through the glass it appears red in colour (Fig. 2).<sup>6</sup> However where the light does not reach and when the cup is lit from external light sources it instead appears green.

In the 1950s the base of the cup was removed and some small coloured glass fragments were found and conserved. At the time it was necessary to study these fragments by indirect means, as the particles in the glass



**Fig. 2.** Photograph of the Lycurgus cup showing how it appears red when lit from within (bottom of cup, where the light inserted inside is shining through) and green when lit from outside (top of cup, where the light does not reach). Reproduced from Wikimedia Commons under license CC BY-SA 2.0.<sup>6</sup>

were too small to be observed by available techniques. A number of chemical analyses were performed,<sup>7-9</sup> and from these studies it was inferred that the red and green colours observed resulted from finely dispersed particles of gold, probably alloyed with silver.<sup>9</sup> The evolution of transmission electron microscopy enabled the 1990 study of the particles present in a 2 mm<sup>3</sup> sample of remaining glass, conducted by Barber and Freestone.<sup>10</sup> They observed alloyed nanoparticles 50-100 nm in diameter, with a composition of 66.2 (±2.5) at.% silver, 31.2 (±1.5) at.% gold and 2.6 (±0.3) at.% copper. However, because of the small number of particles able to be examined and the precious nature of the cup precluding any further studies, the exact nature of the relationship between the size, shape and composition of the particles and the two colours observed is still poorly understood.

There are very few other examples of gold coloured glass from this era, and none as impressive as the Lycurgus cup. These examples are generally considered to be the result of happenstance as there is no evidence that their producers could control or reproduce the colouration process.<sup>5</sup> However a 2010 study has examined several pink tesserae (small pieces of glass used in mosaics) from five Roman churches dated between the fourth and ninth centuries, and found that all investigated samples contained gold or gold-silver nanoparticles as the colourant.<sup>11</sup> It is believed that the flesh-coloured pieces, used for faces, hands and feet, were prepared by mixing an opaque white glass with a transparent ruby gold glass. The authors concluded that because such coloured glass tesserae were used in a considerable number of Roman churches, the colour was most likely obtained routinely and that glassmakers of this era were able to achieve control of this colouration technique.

Following the decline of the Roman empire there are no significant examples of the use of gold nanoparticles as a glass colourant for some time. It is often stated in research articles that gold nanoparticles are responsible for the red colour of stained glass windows in churches dated to the Middle Ages. Yet there is no evidence of this as all analyses of these glasses have shown the presence of copper as the colourant.<sup>5,12</sup>

### Purple of Cassius

The production of coloured gold nanoparticle glass was rediscovered in the 17<sup>th</sup> century when Purple of Cassius was used to make red and purple shades. The recipe for Purple of Cassius, which involves the precipitation of gold by a mixture of stannous and stannic chlorides, has been largely attributed to Andreas Cassius.<sup>13</sup> This is confused by the fact that there were two people by the name Andreas Cassius, father and son, both of whom were physicians and interested in gold. The son published the book *De Auro* in 1685 in which he gave his father's recipe for Purple of Cassius. The metallurgist Johann Christian Orschall reported the anecdote that the son "*succeeded in making a very fine ruby flux and sold the secret of this in various places for a certain sum so that it can be seen here and there, and even today some of it is still made at Freysing although it is kept very secret.*"<sup>13</sup>

However it is now widely believed that Andreas Cassius (the father) was influenced by Johan Rudolf Glauber, who wrote an account of the purple precipitate in his book *Prosperitatis Germaniae* published in 1659 some 25 years before *De Auro*.<sup>13</sup> This is now considered the first report of the precipitation of gold with a tin compound solution, but there is no evidence that Glauber used the precipitate to colour glass. Glauber was an influential and important man in his time. An argument can be made that he was one of the first chemical engineers as he developed processes for the manufacture of medicinal preparations which he then sold, which was unusual at the time. However it is important to remember that this was the era of alchemy. Glauber believed that the red colour of precipitated gold was the gold's "soul", and he also worked extensively on the attempted transformation of base metals to gold and on finding the elixir of life.<sup>14</sup>

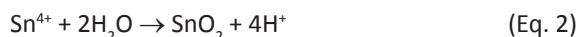
### Chemistry of Purple of Cassius

Purple of Cassius is prepared by the addition of a mixture of stannic and stannous chloride (prepared by dissolving tin in aqua regia) to gold chloride (prepared by dissolving gold in aqua regia). There are two important steps that then occur.<sup>15</sup>

First is the redox reaction between the gold and stannous ions to form metallic gold, described by Eq. 1:



The second step is the hydrolysis of stannic ions to form a tin oxide precipitate according to Eq. 2:



The gold is stabilised by adsorption onto the precipitated tin oxide. Without this step the gold would agglomerate and the colour would be lost. The precipitate is then recovered by filtration and dried for later incorporation into glass.<sup>16</sup>

### Commercial ruby gold glass

The commercial production of ruby gold glass was first achieved using Purple of Cassius by Johann Kunckel in the 17<sup>th</sup> century (Fig. 3).<sup>17</sup> Exactly how he produced the coloured glass on such a large scale remains a mystery, as Kunckel was very secretive about the recipe and his factory was located on an isolated site on the island of Pfaueninsel between Berlin and Potsdam.<sup>16</sup> Transmission electron microscopy and elemental analysis in 2002 of a piece of coloured glass found in the remains of the factory revealed cubo-octahedral gold nanoparticles with an average diameter of  $39 \pm 1$  nm, as well as a number of iron particles ( $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ).<sup>18</sup> The authors of this study conclude that gold nanoparticles may have formed by the reduction of gold ions by  $\text{Fe}^{2+}$ . They also state that the larger  $\alpha\text{-Fe}_2\text{O}_3$  particles observed will have contributed to the red colour of the glass.

Kunckel said of his ruby gold glass that "*only I know what trouble I had to find the composition, to get it right and to obtain a durable red.*"<sup>19</sup> It becomes obvious why this production was so difficult when considering how gold glass is made.

## Chemistry of ruby gold glass

The formation of ruby gold glass is divided into three steps.<sup>16</sup>

Gold is added (as gold chloride or Purple of Cassius) to melt glass at around 1400 °C. The glass is colourless at this point.

The glass is rapidly cooled to room temperature in a quenching step. An oversaturation of atomic gold results in the formation of nuclei. The presence of lead, tin or bismuth ions in the glass enhances the solubility of the gold and facilitates this step, ensuring a portion of the gold remains as atomic gold to grow the nuclei in the next step. In contrast, sodium silicate or borax glass with steep solubility curves lead to the formation of large gold crystals and a spoiled brown-coloured glass.

The glass is annealed by reheating to 500-650 °C. This causes the nuclei to grow into gold nanoparticles between 5 and 100 nm in size, resulting in a red or purple colour.

The size of the resulting nanoparticles and colour of the glass depends on a number of factors, including the duration and temperature of each step (particularly the annealing step), the composition of the base glass, the form in which gold is added in step one. These are factors that would have been difficult for early producers of ruby gold glass to understand and control, making Kunckel's large-scale production in the 17<sup>th</sup> century especially impressive.



**Fig. 3.** Ruby gold glass displayed in the Munich Residenz. The glass with the lid is attributed to Kunckel. Reproduced from Wikimedia Commons under license CC BY-SA 3.0.<sup>17</sup>



**Fig. 4.** A cranberry glass cruet set dated to the Victorian era. Reproduced from Wikimedia Commons under license CC BY 2.0.<sup>21</sup>

## Modern gold nanoparticle glass

Ruby gold glass, and in particular a pale, almost transparent shade called cranberry glass, became very popular in the Victorian age when "almost every household item that could be made in glass was produced in cranberry colours."<sup>20</sup> Many examples from this era, such as that shown in Fig. 4, can be purchased from antique shops and dealers.<sup>21</sup> Depending on the rarity, the visual appeal, and the intricacy of the design, these pieces can range in worth from several hundred to several thousand dollars.<sup>22</sup>

Today, ruby gold glass has gone somewhat out of style. However, despite the availability of other materials such as cadmium sulfoselenide to colour glass red, modern commercial glassmakers still often choose gold when red glass is needed.<sup>23</sup> This reflects the desirability of gold nanoparticles as a colourant. What the Romans knew 1500 years ago is still true: gold nanoparticles impart clean, stable and beautiful colours to glass.

## Acknowledgements

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## Brian Halton PhD (Southampton), DSc (VUW), Hon. FNZIC, FRSNZ, 1941 - 2019

On Saturday 23 February 2019, the New Zealand and international chemical communities lost a brilliant, highly respected scientist, colleague, mentor and friend to many. Brian Halton's chemical journey began at the University of Southampton, UK, from where he graduated with a BSc(Hons) in 1963 and a PhD in 1966, with studies for the latter being under Richard Cookson's guidance. He then moved to Florida as a postdoctoral fellow with Merle Battiste, before being engaged as an assistant professor. In the latter role, Brian found it necessary to feign/acquire an American accent when the students in his first lecture complained they couldn't understand his (British) accent that he rapidly regained when he left for New Zealand. The move to Wellington in 1968 ended up being a permanent one, starting with a lecturership at Victoria University of Wellington (VUW) and evolving through the promotion levels to appointment as professor in 1991. His later years were illustrative of his sheer determination, as he suffered multiple heart failures between 1983 and 2018, yet continued with his research, teaching and writing as well as enjoying life through those years. He is survived by his wife, Margaret, also a chemist, and sons Mark and Paul, and their families.

A major focus of Professor Halton's research was the chemistry of cycloproparenes – pungent smelling, strained organic molecules containing a cyclopropane ring fused to various aromatic rings. He published over 120 peer-reviewed original research articles on this subject, thus contributing in the most incisive and fundamental of ways to knowledge in this field. The regard in which Brian was held can be seen in his decade-long editorship of the book series *Advances in Strain in Organic Chemistry*. Brian supervised 11 PhD students and 36 Honours/Masters students as well as several postdoctoral and other research employees. His strong research ethos and enquiring mind have enabled these people to achieve greatly on the NZ and international science scenes. With Jim Coxon (Canterbury), Brian co-wrote the 1974 textbook *Organic Photochemistry*, which was so successful it enjoyed an expanded second edition (published in 1987) and is still found on researchers' bookshelves the world over.

Brian taught many generations of chemists at VUW, who delighted in his lucid expositions, interesting anecdotes and exacting standards. Who can forget the moment in first year when a student, foolish enough to think that he can eat chippies during a Halton lecture, was invited to either share them with the class (all 100+ students) or desist?! The rigours of second year organic chemistry were dealt with thoroughly, third year was conformational analysis and mechanism, and in fourth year we were thrilled by the amazing advances in supramolecular chemistry, a topic of intense fascination to Brian.

New Zealand chemistry has Brian Halton to thank for our involvement in the huge Pacificchem conferences that are



held every five years in Hawaii. Originally, only the larger Pacific rim countries were on the organising committee of Pacificchem, viz. the chemical societies of America, Canada and Japan. It was Brian's friendships, networks and persistent efforts that persuaded these organisations to include the NZIC and the Royal Australian Chemistry Institute (RACI) as contributing organisations from 1990. Brian served as the first NZ representative to Pacificchem for over a decade, and Pacificchem profits continue to provide a valuable income to the NZIC.

Brian Halton contributed enormously to the NZIC in many additional ways. He was the President during 1986–7, and the Editor of *Chemistry in New Zealand* for a decade (2001–2011), and then the Consulting Editor until 2018. More locally, Brian was the Wellington Branch Editor for over 15 years and on the local committee for over a decade. Through his retirement, Brian continued to write for this publication, with a *Today in History* column that ran for several years, his *Unremembered Chemists* series (2013–2018), and a piece to mark the International Year of the Periodic Table in the first 2019 issue of *Chemistry in New Zealand*.

Brian's links with the international chemistry community are evident from the myriad of influential and important chemists who visited New Zealand during Brian's tenure, many of whom came to Wellington primarily because of their regard for him. Notable visits that immediately

spring to the mind of this writer were Nobel Laureate Bob Grubbs, who visited the same day as the announcement of his Nobel Prize in 2005, and IUPAC President Leiv Sydnes in 2005 (plus several other visits outside of his presidency). The Halton retirement symposium in 2005 also saw international chemists travel to Wellington to celebrate with Brian, including Jun Nishimura and Yoshito Tobe from Japan as well as Martin Banwell, David Officer and Andrew Grimsdale from Australia. In addition, senior New Zealand organic chemists Jim Coxon, Rob Smith and Margaret Brimble joined former students and colleagues in attending this symposium. Much of Brian's delight in these visits, as well as the joys of again meeting his collaborators and friends, was in the inspiration they brought to the young chemists (especially students) in the audience and post-VUW opportunities they highlighted. Brian also travelled widely, with sabbaticals in Reading (UK, 1974–5, including visits to Germany), Utah (USA, 1981–2), USA and Germany (1988), Japan and Germany (1993), Australia (1999), Norway (2002) and international conferences worldwide.

Throughout his retirement, Brian attended VUW most days and during these times he wrote articles and books, supported postgraduate students by proof-reading theses and presentations, and occasionally also contributed to teaching when staff were absent. When not at work, he was an avid bowler at the local club and resumed photography, which had been a hobby during his youth. Some of his stunning photos were featured on the slide show after his funeral and at other recent events. Brian also wrote several books. His accounts of his life and the history of chemistry at VUW, *From Coronation Street to a Consummate Chemist* and *Chemistry at Victoria: the Wellington University* are both highly informative, written with his astute sense of humour and available at <https://www.victoria.ac.nz/scps/about/history/history-of-chem->

istry as well as in print. He also published an ebook on his encounters with heart disease, intended as a resource for others with similar conditions, entitled *A Cat of Nine Lives – and the Beat Goes On: Living with heart disease*, available at [https://archive.org/details/ACatOfNineLives-AndTheBeatGoesOn\\_249](https://archive.org/details/ACatOfNineLives-AndTheBeatGoesOn_249)

Brian's contributions to chemistry through his research, teaching, writing and service have been recognised through numerous awards and fellowships. He was made an Honorary Fellow of the New Zealand Institute of Chemistry (2005) and a Fellow of the Royal Society of New Zealand (1992). Amongst other accolades, Brian was awarded the ICI Medal for Excellence in Chemical Research (1980), a Fulbright Award (1981), the New Zealand Association of Scientists' Shorland Medal (2001), and gave the 2003 NZIC Wellington Branch Mellor Lecture. The NZIC has instituted the triennial Wellington Branch Halton Lecture, for which the first two lecturers were Martin Banwell (ANU, 2014) and David Officer (Wollongong, 2017). On Friday 21 September 2018, the School of Chemical and Physical Sciences at VUW held a celebration marking 50 years (to the day) since Brian arrived in Wellington to begin working at the university. Many Wellington-based scientists, former students and colleagues attended this very special event.

So, as we farewell our colleague/mentor/collaborator/friend, please raise a glass (of red wine, ideally, as Brian theorised that this was medicine and should be available on prescription!) to toast an exceptional scientist and a true pillar of the NZIC.

**Contributed by Joanne Harvey**  
**School of Chemical and Physical Sciences**  
**Victoria University of Wellington**

## Robin Jon Hawes Clark PhD (Lond.), DSc (Lond.), Hon DSc (Cant.), Hon FRSNZ, FRS, CNZM, 1935 - 2018

Robin Clark, who passed away on 6 December 2018, was one of New Zealand's most internationally recognised chemists.

He studied chemistry at Canterbury University College from 1953-1957 obtaining a BSc and an NZU Senior Scholarship in 1955 and an MSc with 1<sup>st</sup> class honours in 1957. In 1958 he took up a research and teaching fellowship at the University of Otago with Professor W.S. Fyfe FRS, but when Professor Fyfe moved to Berkley soon after, Robin won a British Titan scholarship which took him to University College London (UCL) to commence a PhD in chemistry with Professor Ron Nyholm FRS. He remained at UCL for the rest of his life, having an illustrious academic career. He obtained his PhD in 1962 and was awarded a DSc in 1969. He became a member of the staff as an Assistant Lecturer in 1962, advancing to Lecturer 1963-71, Reader 1972-81, Professor 1982-87, Dean of Science 1988-89, Head of Chemistry Department 1989-99, Sir William Ramsay Professor 1989-2008 and on retirement in 2009 Sir William Ramsay Professor Emeritus.

In spite of his long association with UCL he remained very much a New Zealander at heart, making numerous visits home. In London he represented many NZ organisations. He took great interest in NZ High Commission matters (his first cousin being Sir Geoffrey Palmer), was chairman of the NZ Universities Graduates' Association in the UK for about seventeen years, chairman of the University of Canterbury NZ trust, and twice gave the address at the ANZAC Day Service at the Guildhall, London. His services to New Zealand were recognised by his being awarded an Honorary Fellowship of the Royal Society of New Zealand in 1989, an Honorary DSc by the University of Canterbury in 2001, and CNZM in 2004.

His achievements in the UK are far too numerous to list in detail. He was elected FRS in 1990, was made a member of the American Philosophical Society and was the first winner of the Franklin Lavoisier Medal and Prize of the *Maison de la Chimie* (Paris) and Chemical Heritage Foundation (Philadelphia). He held many positions on committees of the Royal Society of London, of the Royal Institution of Great Britain, (where he lectured several times, giving a Friday Evening Discourse in 1997 and becoming its Secretary from 1998-2004 and an Honorary Fellow in 2004), the Royal Society of Chemistry and the University of London. He held visiting professorships at thirteen universities in ten different countries, and published over 530 scientific papers, wrote or edited (with others) 36 books, and gave 350 lectures at other universities and research institutions worldwide. Many of these lectures were invited prestigious named lectureships including the Bakerian Lecture-ship, the premier annual "Prize Lecture" and Medal of the Royal Society of London in the Physical Sciences. The UCL Chemistry Department is historically one of the most famous in the UK. One of Robin's proudest achievements as Head of Department was to raise it back to the highest ranking (along with Oxford and Cambridge) after it had



slipped a few places, by persuading the Provost that to do this one must spend money to attract the highest quality staff.

Robin made major contributions to the field of inorganic chemistry with his synthesis and structural investigations of new classes of metal compounds, including those containing unusual metal-metal bonds. He made advances in the theory and practice of resonance Raman spectroscopy and was a pioneer in using this technique to study the composition of dyes and pigments of ancient manuscripts and works of art in a non-destructive way. He was able to separate forgeries from genuine works of arts by showing that in these, the materials used were not available until long after the supposed work was created. He studied the Vinland map, Lindisfarne Gospels, Egyptian papyrus, Renaissance art, ancient maps and items in royal collections. This technique is now widely used by museums and art galleries to separate valuable works from counterfeits.

Growing up in New Zealand, Robin developed a love for the outdoors. On a number of his many visits back home he was accompanied by his wife and children and showed them much of New Zealand. Robin is survived by his wife Beatrice, whom he married in England in 1964, his daughter Victoria, his son Matthew and four grandchildren.

He was best man at the wedding of the contributor of this obituary.

Contributed by John Packer,  
Retired Associate Professor of Chemistry, University of  
Auckland

## Book review: *Clay Mineral Catalysis of Organic Reactions*

Benny K.G. Theng, *Clay Mineral Catalysis of Organic Reactions*. CRC Press: Boca Raton, 2018, 425 pp.

The contents of this book will be of interest to a wide range of researchers in academia and industry. Anyone who wishes to utilise sustainable, easily controlled, high yielding and highly specific processes for the synthesis and production of fine organic compounds, petrochemicals, polymers, pharmaceuticals, etc. will see that clay mineral catalysis can often provide solutions for many such problems. The absorptive properties of clay minerals, combined with their catalytic activity and low cost, can also be used to provide effective processes for removal and destruction of many organic and inorganic pollutants in the environment.

This book provides a comprehensive review of the many organic chemical reactions that can be catalysed very effectively by a wide variety of intact or acid activated clay minerals, or by reagents supported on clay minerals. The review builds upon and brings up-to-date several books and book chapters both by the author himself (e.g. Theng, 1974) and several others (e.g. Balogh and Laszlo, 1993; McCabe and Adams, 2013) and reviews this continually expanding field of knowledge up to early 2018.

The first three chapters of the book give a cogent and concise explanation of the background needed to understand the properties of clay minerals that make them good adsorbents and excellent catalysts for many useful organic reactions. These chapters may seem unnecessary for mineralogists or clay mineral chemists who will be very familiar with their content. However, these chapters do provide essential background understanding for those who might wish to begin utilising the many advantages of clay mineral structures and their modifications to influence the specificity, yield and sustainability of a wide range of catalytic processes. The following five chapters catalogue the wide range of organic reactions for which clay minerals can be very effective for influencing the outcome advantageously.

Chapter 1 outlines the compositions and the types of layered structures that are responsible for the useful properties of clay minerals. Chapter 2 describes the in-

herent surface acidity of cationic clay minerals and its relationship to the control of the catalytic activity. Chapter 3 describes how the catalytic activity and/or adsorption properties of the clay mineral may be enhanced by either surface activation prior to use (mainly by acid activation or calcination), or by use of microwave or ultrasound irradiation during use. In addition, modifications such as pillaring the clay interlayer, intercalating organic molecules or surface grafting of e.g. silyl groups have been used to make the clay mineral interlayer more receptive to a wider range of organic molecules so that catalysis can take place.

Chapter 4 describes the utility and enhanced activity of inorganic reagents and catalysts supported on clay mineral surfaces. Chapter 5 lists many (35+) of the named reactions that have been catalysed by clay mineral catalysts and explains the multitude of advantages conferred by the clay mineral structure. Chapter 6 describes the more traditional uses of clay mineral catalysis, mainly in the petrochemicals and polymer fields, but also brings more modern applications into perspective. Chapters 7 explains the novel uses of clay mineral catalysts for enhancing redox processes and for helping to control the asymmetric and enantioselective syntheses of molecules. Chapter 8 describes the possible involvement of clay minerals in geo-catalytic situations that may help to transform hydrocarbon deposits or even aid formation of biological precursor molecules such as amino acids, peptides and nucleotide in a non-biological environment.

Overall this book is very informative and provides an excellent, up-to-date view of what might be considered a mature, interdisciplinary field of knowledge, but which is still developing and manages to bring new and often unexpected advantages for, amongst others, synthetic chemists, industrial developers and those involved in remediation of pollution problems in the environment.

**Richard W. McCabe**

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