Chemistry IN NEW ZEALAND

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Laboratory recreations of Titan’s cyanide sky

Chemical speciation models: simplifying the complexity of the ocean

Determining the provenance of the water source by measuring strontium isotope abundance ratios in beer and cider made in Dunedin, New Zealand

From ugly duckling to real swan: transformation of the Science I chemistry laboratories into the new Mellor Laboratories at the University of Otago

Celmisia, New Zealand’s alpine daisies: assessing a sticky situation to “trichome” up with some answers

Happy 50th anniversary, Jim!

Davy and the voltaic pile

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The New Zealand Institute of Chemistry Incorporated

PO Box 13798
Johnsonville
Wellington 6440
Email: nzic.office@gmail.com

Editor

Dr Catherine Nicholson

C/- BRANZ, Private Bag 50 908
Porirua 5240
Phone: 04 238 1329
Mobile: 027 348 7528
Email: catherine.nicholson@branz.co.nz

Publisher

Rebecca Hurrell
Email: rebeccajhurrell@gmail.com

Advertising Sales

Email: rebeccajhurrell@gmail.com

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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

ISMSC 2020
15th International Symposium on Macrocyclic and Supramolecular Chemistry
12th -16th July 2020 Sydney

Chemistry in New Zealand

Volume 83, No.4, October 2019

Articles and features

Other columns

Comment from the President

Welcome to the October issue of Chemistry in New Zealand. 2019 is drawing to a close already (!) and we are coming towards the culmination of our **International Year of the Periodic Table** celebrations with our IYPT2019 competition for schools and school-age children now closed. The judges will shortly start deliberating with the outcomes announced at the **NZIC2019 National Conference**. Preparations for the conference are almost complete, and more details can be found on the website here: *https://nzic2019.co.nz* The provisional timetable is being compiled and the clock on the front page is counting down to the opening ceremony so get those last minute registrations in before they close completely. We have a fantastic line-up of plenary and keynote speakers including recent NZIC prize-winners and many Australasian representatives on the **IUPAC Periodic Table of Younger Chemists** who will be giving keynote presentations. Combined with the popular student oral presentation competition, poster session, conference dinner at the amazing Christchurch Town Hall and beer tasting event for all you craft beer lovers it is sure to be a great celebration of all things chemistry in New Zealand.

Council are currently working through the strong applications for the 2019 NZIC national prizes and we are delighted to welcome sciPAD on board as our new sponsor of the Denis Hogan Chemical Education Award. SciPAD is produced by Silverback Academic Media, a New Zealand company. sciPAD with augmented reality (AR) offers learners incredibly immersive visualisations and provides an extraordinary learning experience by bringing to light unseen perspectives of the learning content. We are excited to have them sponsor our premiere award for chemistry education in New Zealand. All the winners of the 2019 prizes and awards will be formally announced at the **NZIC AGM to be held on the afternoon of Wednesday 27th November at the NZIC2019 conference**.

We are definitely in Science and Technology Fair season, and the NZIC is proud to be associated with these as a sponsor. The Otago and Canterbury Fairs have taken place, with some excellent projects being acknowledged with prizes. It is essential to support our young budding scientists and chemists with advice and encouragement, perhaps providing access to facilities or key pieces of equipment in our workplaces that the students cannot access at school. Also important is to encourage the students to keep asking questions and not lose that scientific curiosity that is the hallmark of great researchers around the world.

I am excited to be heading to Taiwan in December to represent the NZIC at the **20th General Assembly of the Federation of Asian Chemical Societies** (FACS) immediately before the 18th Asian Chemical Congress (ACC). The Asian Chemical Congress is a biennial event organised by members of the FACS. It is important to maintain and build the relationships with our regional societies and I look forward to connecting with my fellow society presidents as well as participating in the ACC, giving a scientific research talk as well as sitting on an RSC discussion panel. The panel session is on women's progression in chemistry and specifically the topic of supporting women as early career researchers. I am looking forward to this opportunity to discuss career progression for early career researchers, the challenges that can be faced and strategies to overcome them.

Once the ACC conference is over it will definitely be time for a wee break but then the planning for NZIC events in 2020 will start in earnest. I am looking forward to being able to come to the branches to meet lots of members and interact with everyone throughout the year. We also have a new student prize that will be announced at the AGM and introduced at the start of 2020, so there will be plenty to do to promote that exciting opportunity.

Please do remember that we are part owners of several journals, namely **Physical Chemistry Chemical Physics** (PCCP) and those associated with the Asian Chemical Editorial Society (ACES) namely **Chemistry – An Asian Journal**, **Asian Journal of Organic Chemistry** and **ChemNanoMat**. As a society we receive royalties whenever a researcher based in New Zealand publishes an article in these journals. This income is valuable to us as it allows us to further support researchers in New Zealand through sponsorship, travel grants and other forms of recognition.

Finally, a reminder again that **NZIC is on social media**! We're on 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. It has been great to see this used by NZ and overseas researchers to highlight their fantastic research and outreach activities. Use #NZIC2019 for the upcoming NZIC2019 conference.

Sarah Masters

NZIC President

New Zealand Institute of Chemistry

supporting chemical sciences

October News

NOTICE OF NZIC AGM

Date: Wednesday 27 November 2019

Venue: C1, Central Lecture Theatre Block, University of Canterbury, Christchurch

Time: TBA (following the close of NZIC conference)

AUCKLAND

The University of Auckland

School of Chemical Sciences Research Showcase

In June the School of Chemical Sciences held the annual Research Showcase highlighting the research of PhD students within the school. All the speakers gave excellent presentations and the poster session was very professional – well done to everyone!

The day started with Jim Metson, Deputy Vice Chancellor – Research, talking about what the modern world demands of chemistry. He suggested that as well as exploring the unknown, we needed to consider our social license to operate. How could we contribute to a carbon neutral world? What would a world without concrete look like? He stated that chemical scientists will play a critical role in thinking differently and finding solutions to society's problems through "thoughtful chemistry".

Those themes of sustainability and thinking differently bookended the day, with viticulturist Mark Krasnow giving examples of how thinking outside the square could lead to decreased irrigation or reduced use of herbicides in the vineyard. He also reminded us that much of science today relies on strong collaborations with people you trust. He ended his talk with the thoughts, "Stay curious, stay hungry for knowledge, ask questions, and travel".

Thank you to Fan Zhu, Viji Sarojini, Rebecca Deed, Tasdeeq Mohammed, Katie Parish-Virtue and John Lau for organising the Showcase – well done! The generosity of our sponsors is also acknowledged, especially our Platinum sponsors ECP and the Energy Education Trust of New Zealand, and Gold Sponsors MicroAnalytix, Total Lab Systems, and Thermofisher Scientific, together with all our other sponsors. Events like this could not happen without their support.

Incredible Science

Incredible Science is a community outreach programme run by the Faculty of Science that shows students the diversity of science and attempts to capture their interest. It provides an opportunity to learn and see things that wouldn't normally be in their school science curriculum.

The School of Chemical Sciences had multiple activities to engage the students, including fingerprinting, UV-activated beads, Vitamin C testing, and polymer worms as well as a Chemistry Magic Show put on by Associate Professor Gordon Miskelly and Dr Nina Novikova. Thank you to Katrina Graaf and John Lau who organised the event beforehand and on the day as well as Bikimi Ayiya, Luis Camacho, Stephen Lo, Taniela Lolohea, Stuart Morrow, Mansa Nair, Sneh Patel, Joel Rindelaub, Rosanna Rov, Tasha Steel, Deanna Truong, Fearghal Walsh, Andy Wang, Pooja Yadav, Jeff Boyle, Selena Choi and Sandra Otty who assisted before and during the day.

Staff Successes

Dame Companion of the New Zealand Order of Merit

Distinguished Professor Margaret Brimble was made a Dame Companion of the New Zealand Order of Merit by the Governor-General, Dame Patsy Reddy, in an investiture ceremony in May.

Jean-Marie Lehn Award

Congratulations to Professor Ralph Cooney, who was awarded the Jean-Marie Lehn Award for his outstanding contribution in the field of materials science and engineering at the POLY-CHAR 2019 conference in Kathmandu in May. This IUPAC award carrying the name of Nobel

Distinguished Professor Dame Margaret Brimble with her husband Mark, daughter Rebecca and the Governor-General Dame Patsy Reddy at her investiture ceremony

Laureate Professor Jean-Marie Lehn is bestowed to a senior scientist to recognise significant contribution in the field of materials science and engineering.

ACS Medicinal Chemistry Division Hall of Fame

The Medicinal Chemistry Division of the American Chemical Society (ACS) inducted Distinguished Professor Dame Margaret Brimble, along with three other scientists, into the Medicinal Chemistry Hall of Fame at the August ACS National Meeting in San Diego. Margaret joins Bill Denny (2016) as a member of the Hall of Fame, and to our knowledge the only other Australasian inductee was Adrien Albert in 1981.

For 50 years the Medicinal Chemistry Division of the American Chemical Society has publicly recognised pioneers who have made impactful discoveries in the field of medicinal chemistry. Efforts especially considered include drug discovery, excellence in teaching and training future pioneers of medicinal chemistry, and outstanding service to the medicinal chemistry community at large. Past recipients are listed here: *https://www.acsmedchem.org/?nd=inductees*

KiwiNet Research Commercialisation Awards

Congratulations to Distinguished Professor Margaret Brimble, who won both the Entrepreneurial Researcher Award and the BNZ Supreme Award at the KiwiNet Research Commercialisation Awards. Margaret was recognised for her drug discovery and development research, including trofinetide and NNZ2591 being trialled for serious neurodevelopmental conditions by Neuren Pharmaceuticals, and her newer research on anticancer vaccines with SapVax. Margaret acknowledged the role and support of Auckland's UniServices during her acceptance speeches. Will Charles from UniServices was also successful, winning the MinterEllisonRuddWatts Commercialisation Professional Award.

School of Chemical Sciences seminars

The School of Chemical Sciences at the University of Auckland hosted several seminars between June and August 2019:

Emeritus Professor Laurie Melton (University of Auckland): F*rom pirate to professor: the garden of the forking paths*.

Professor Bernhard Kräutler (University of Innsbruck, Austria): *Vitamin B12 and the periodic system*.

Professor Buddy D. Ratner (University of Washington, USA): *RF-plasma deposition for tailoring polymer surfaces: control of biointeractions*.

Professor Federico Marini (University of Rome La Sapienza, Italy): *Coupling spectroscopy and chemometrics for the analysis of foodstuffs*.

Professor Jay S. Siegel (Tianjin University, China): *Silyl cation and novel aromatics*.

NZIC Auckland Branch seminars

The University of Auckland hosted the following NZIC Auckland Branch Seminar between June and August 2019:

Dr Renee Goreham (University of Newcastle, Australia): *Bio-inspired nanoclusters and bio-derived nanoparticles*.

Science for Technological Innovation (SfTI) Seed Funding

Congratulations to Dr Cameron Weber, who was awarded $200,000 for his project entitled, *New approach to microwave processing for the production of bio-based chemicals*. This is a Seed project within the SfTI National Science Challenge.

Manufacturing and Design NZ Conference (MaD2019)

Congratulations to Jeffrey Low, Control Systems Manager for the Photon Factory, who won the first place poster prize at the MaD2019 conference. His poster is titled, *Laser beam shaping for optimised industrial laser micro-machining and surface patterning*.

Publications

Congratulations to Dr Lisa Pilkington who has been highlighted in the

Professor Ralph Cooney receiving the Jean-Marie Lehn award

2019 Emerging Investigators Issue of Chemical Communications. For more details see: https://pubs.rsc.org/en/content/articlepdf/2019/cc/c9cc90270h?page=search

Lisa's invited article reports on a multidisciplinary project involving synthetic chemistry, yeast biochemistry and analytical chemistry. This project included key contributions from Dr Rebecca Deed, Dr Katie Parish-Virtue, Dr Max Huang and other researchers from the University of Adelaide, and was led by Associate Professor David Barker and Associate Professor Bruno Fedrizzi.

Outreach Activities

International Day of Light

16 May 2019 was the International Day of Light, and Professor Cather Simpson gave one of the keynote talks at the flagship event in Trieste, Italy, sponsored by UNESCO. Her talk was on how a greater understanding of light is changing the way we grow food.

Student successes

London Calling Conference

Congratulations to Rebecca Richards (PhD student), who won the short presentation (Spotlight) competition at the London Calling conference and was then invited to present her full talk on *Biological evidence of the future: the use of sequencing in forensic DNA analysis*.

23rd Annual Green Chemistry & Engineering Conference

Congratulations to PhD student Trang Pham, supervised by Associate Professor Jon Sperry, who won a prize for her poster, *Access to valuable bio-derived chemicals from the chitin-derived building block 3-acetamido-5-acetylfuran (3A5AF)* from the American Chemical Society Green Chemistry Institute at the 23rd Annual Green Chemistry & Engineering Conference / 9th International Conference on Green and Sustainable Chemistry in Reston, Virginia.

Trang Pham receives a poster prize from the ACS Green Chemistry Institute

Research Showcase Prizewinners

Congratulations to the prizewinners:

15 min talks

1st prize: Annabelle Collins

2nd prize: Taniela Lolohea

3rd Prize: Dona Gunawardana

Energy Education Trust of New Zealand Audience Choice

Taniela Lolohea

3 min talks

1st Prize: Andrew Earl

2nd Prize: Bethany Forsyth

3rd Prize: Martin Spasovski

ECP Audience Choices

1st Prize: Jin Wang

2nd Prize: Kapish Gobindlal

3rd Prize: Aljo Anand

2nd year Posters

1st Prize: Nabangshu Sharma

2nd Prize: Jessica Liyu

3rd Prize: Kelvin Tong

3rd year and above Posters

1st Prize: Martijn Wildervanck

2nd Prize: Dianna Truong

3rd Prize: Phillip Grant

Honourable Mentions

Rakesh Arul

Rosanna Rov

Bayer Postdoctoral Fellowships

Congratulations to Hans Choi, Danielle Paterson and Jared Freeman (PhD students with Margaret Brimble and Dan Furkert) who have all been offered prestigious postdoctoral fellowships with Bayer in Germany. The fellowships comprise a generous salary and a living allowance. They will take up the fellowships in December.

Publications

Congratulations to Xiaobo Ding (working with Margaret Brimble and Dan Furkert) who has recently had a first author paper accepted for publication in *Angewandte Chemie* (Highly diastereoselective synthesis of syn-1,3-dihydroxyketone motifs from propargylic alcohols via unusual spiroepoxide intermediates, X.Ding, D. P. Furkert and M. A. Brimble, *Angewandte Chemie International Edition*, **2019**, *58*, https://doi.org/10.1002/anie.201905736).

Congratulations to Emma Davison and Alan Cameron (working with Paul Harris and Margaret Brimble) who have had their recent paper feature as the front cover article in a Special Issue on Natural Products published in *MedChemComm* (Synthesis of endolides A and B; naturally occurring N-methylated cyclic tetrapeptides, E. K. Davison, A. J. Cameron, P. W. R. Harris and M. A. Brimble, *MedChemComm*, **2019**, *10*, 693-698).

Congratulations to BSc(Hons) student Chris Bainbridge, who has had a paper published in *Applied Polymeric Materials* (DOI: 10.1021/acsapm.9b00458). His paper is titled, Visible light-induced transformation of polymer networks, which aims to develop photo-expandable/transformable polymer networks (PET-PNs) *via* visible light-induced controlled radical polymerisation.

Rebecca Jelley (PhD student with David Barker and Bruno Fedrizzi) and Professor Allan Blackman (AUT) published a comment in *Nature Chemistry*, giving a tongue-in-cheek determination of The most boring chemical element. See: https://www.nature.com/articles/s41557-019-0307-9.epdf?author_access_token=646XyU4yw2-q-yA8MjeYZdRgN0jAjWel9jnR3ZoTv0Otj5zTdXNhZd1pnrymD79C9qs-QPa7wc3Let61STvf2QTZ50T-OxyE_rmPJmUqgAnvWSWm0Tpy7FKY7ErE3LXOBGbLtoDYSbJHcO8fCKB87A%3D%3D

PhD Completions

Congratulations to Alissa Hackett who was recently awarded her PhD for her thesis entitled, *Polymer brushes grafted from conducting polymer backbones for functional materials*. Alissa was supervised by Jadranka Travas-Sejdic and Duncan McGillivray.

Congratulations to Megan Quach for successfully defending her PhD thesis entitled, *Synthetic studies towards gombaspiroketals and a cobalt catalysed epoxide olefination*, supervised by Distinguished Professor Dame Margaret Brimble and Dr Daniel Furkert.

Congratulations to Dongxing Li! Dongxing successfully defended his PhD thesis on the properties and food uses of kiwifruit starch and was supervised by Dr Fan Zhu.

Massey University (Auckland Campus)

Distinguished Professor Peter Schwerdtfeger has returned from an extensive overseas trip giving keynote and plenary lectures at conferences in Spain, Norway, Columbia and Austria. He also visited Stuttgart University to collaborate with the local theoretical chemistry group on atoms in quantum confinements and on molecular parity violation. He is soon off again to Germany and Poland to participate at international conferences and to give lectures on the chemistry and physics of superheavy elements (watch this space: *Angewandte* hot paper on oganesson to be published soon).

Dr Debbie Jordan, Dr Marie-Anne Thelen and undergraduate helpers had over 300 Year 12 and 13 students come to our labs over two weeks in June to do one of two workshops. The first workshop was a synthetic lab exercise to make aspirin and assess its purity using IR spectroscopy. The second was a chemical cluedo using NMR and IR spectroscopy alongside mass spectrometry to establish the various chemicals in Professor White's lab, and therefore establish his murderer.

Auckland University of Technology

New Faces

We welcome new MSc students Winter Tolentino and Madhu Panjeta who will be working with Dr Marcus Jones and Dr Jack Chen respectively.

Events and Invited Talks

Dr Marcus Jones gave a public lecture in Wanaka at the event NZ Innovation for Sustainability as part of the MacDiarmid Institute's regional lecture series.

Dr Marcus Jones also gave an invited talk at Victoria University of Wellington entitled, *Exciton-plasmon coupling in nanoscale materials*.

Professor Nicola Brasch gave an invited lecture at the 19th International Conference on Biological Inorganic Chemistry (ICBIC-19) entitled, *Exploring the mechanism of HNO release from photoactive piloty's acid*

Left: Ruth Cink at her graduation with Professor Nicola Brasch. Right: Sabeena at her graduation with the Chen research group *derivatives incorporating the (hydroxynaphthalenyl)methyl phototrigger*. She also presented her photoactive HNO donors research at the Gordon Research conference in Photochemistry in Boston, USA. And she gave invited seminars at The University of Akron, Case Western Reserve University and her former institution, Kent State University in the US.

Dr Jack Chen's PhD students Pablo Solís Muñana and Chloe Zhijun Ren presented talks at the Perspectives in Supramolecular Chemistry meeting at the University of Padua, Italy. The talks were entitled, *Self-assembly of cooperative catalysts for synthetic organic chemistry* and *Dynamic formation of a light-responsive cooperative catalyst*, respectively.

Congratulations

Dr Ruth Cink graduated with her PhD and Sabeena graduated with an MPhil with 1st Class Honours.

Professor Allan Blackman's quest for the most boring chemical element has been published in *Nature Chemistry*. Professor Blackman's investigation into the 118 known chemical elements as part of a series of short podcasts (Elemental, Radio New Zealand) has highlighted the fact that every element, no matter how abundant or obscure, has its own story — but which is the most boring?

Dr Jack Chen successfully obtained funding for a SfTI, *Cellulose-based surfactants: enhancing manufacturing and product performance with minimal environmental impact* worth $199,543 as Principal Investigator.

Dr Jack Chen published an article in *Angewandte Chemie* entitled, Reversible formation of a light-responsive catalyst by utilising intermolecular cooperative effects, together with students Chloe Zhijun Ren and Pablo Solís Muñana. This work was supported by a Catalyst: Seed grant.

CANTERBURY

NZIC Canterbury's annual Mid-Winter Feast was held on 20 June and attracted a good turnout.

Dr Stephen Ashworth (University of East Anglia, UK) gave a well-attended NZIC sponsored talk on 3 July entitled, *Light powered therapeutics*. Stephen discussed what properties contribute to a good photodynamic therapy agent, how we measure these and outlined light powered therapeutic agents which are inactive in a biological system until activated by the absorption of light.

Although Stephen's research career has concentrated on high resolution spectroscopy and spectroscopy applied to atmospheric chemistry using a number of laser techniques, he is now much more involved in the communication of science. Over the years he has won a number of grants for his communication activities. In 2018 he was awarded an Inspirational Member Award by the Royal Society of Chemistry for his Kitchen Chemistry outreach work. In 2009 he was awarded a CUE East Individual Award for Engagement. He is a member of the Advisory Committee of Scifest Africa and Curator of the 2019 festival. For more about Stephen see: https://people.uea.ac.uk/s_ashworth. Some of his work on light powered therapeutics can be found at: https://pubs.rsc.org/en/content/articlelanding/2014/pp/c3pp50219h#!divAbstract and his Scifest Africa 2016 lecture Kitchen Chemistry at: https://www.youtube.com/watch?v=c1VJGUbp__k

MANAWATU

The Telfer group welcomed Lauren Macreadie who joined the group as a post-doctoral fellow along with Caitlin Setter of CSIRO, Melbourne as an intern. Another intern, Camille Navas of École Nationale Supérieure de Chimie et de Physique de Bordeaux, France joined in June 2019.

Adil Alkaş successfully defended his PhD thesis on *Synthesis of multicomponent metal-organic frameworks and investigations of their physical properies*. Adil was supervised by Professor Shane Telfer.

Aaron Whitehead joined the Rowlands group as a BSc Honours student.

Maulik Mungalpara of the Rowlands group attended and presented a poster at the 26th International Symposium: Synthesis in Organic Chemistry. The event was held between 15 – 18 July at the University of Cambridge, UK. Maulik was jointly funded by the School of Fundamental Sciences of Massey University and an NZIC Travel Grant.

Tim Usher of California State University gave a lecture on Metal-organic nanomaterials on the 12 June.

A public lecture titled, *Elementary! A celebration of 150 years of Mendeleev's Periodic Table* was organised by the NZIC on 1 July. Stephen Ashworth of the University of East Anglia spoke about the history and future of the periodic table. The event was held to mark the 150th anniversary of the development of the Mendeleev's periodic table.

On 17 July, Angela Grommet of the Weizmann Institute of Science, Israel gave a seminar on Coordination cages for the transportation of molecular cargo.

Three members of the Manawatu branch – Karen Lyons, Mark Waterland and Catherine Whitby served as part of the judging panel for the 45th Fonterra Manawatu Science and Technology Fairy 2019. The competition was strong among the 95 exhibits and it was a pleasure to meet and talk with the students about their projects. Congratulations to the following chemistry prize winners:

New Zealand Institute of Chemistry prize: Nathan Emeck from Amanaki STEM Academy/Palmerston North Boys High School for his project, Acid gelation in goat, sheep and cattle milks investigating the correlation between the pH and flow behaviour of milk during the acid gelation process.

Massey University School of Fundamental Sciences – Chemistry Prize

Highly Commended: Caitlin Langvad and Lillie Srey Keo from Hokowhitu School for their project, *Iron juice, measuring the iron content in fruit juices*

First Place: Charlotte Kirk from Carncot School for her project, *pH and nitrate - what do fish need to survive,* investigating the pH and nitrate content of different water supplies.

Congratulations also to the winner of the overall Best Exhibit in Fair for Science: Nicola Sutherland-Smith from Palmerston North Intermediate Normal School for her project, *Sunscreen in the water* testing how sunscreens affect freshwater aquatic life.

Several of our chemistry students took part in the School of Fundamental Sciences Student Research Symposium. The quality of the presentations was high, making it a highly rewarding day for all those involved. Sam Powick was awarded the NZIC Prize for the Best Chemistry Presentation for his talk, Evaluation of New Zealand ironsand as a catalyst for thermo-catalytic methane decomposition.

Sam Powick won the Masters Runner Up Prize at the 2019 Massey University Three Minute Thesis Finals with his presentation, T*owards emissions-free hydrogen: cracking methane with black sand*. Sam is supervised by Mark Waterland.

Ben Munro successfully defended his PhD thesis, *Structure and properties of tunable Pickering emulsions* and was awarded his PhD with just minor emendations. Ben was supervised by Simon Hall and Catherine Whitby.

Stephen Ashworth answers questions from the public after his talk on the periodic table

Vyacheslav Filichev (left) thanks Stephen Ashworth for his wonderful talk

Catherine Whitby was appointed to the Advisory Board of the Royal Society of Chemistry journal Soft Matter.

The recent work of the APOBEC3 team led by Associate Professor V.V. Filichev, Dr E. Harjes and Professor G.B. Jameson was published in *Biochemistry* and has been featured in the blog of Worldwide Cancer Research highlighting the importance of finding inhibitors of APOBEC3B to stop cancer evolution.

Bruce Chilton and Ruby Roach have both started their PhD studies in the team of Dr Tracy Hale, Associate Professor V.V. Filichev and Professor G.B. Jameson working on project that seeks to transform the current understanding of functional genome organisation by showing that non-Watson Crick (non-canonical) nucleic acid structures are essential for the formation and maintenance of heterochromatin.

OTAGO

The Otago branch of the NZIC held its annual quiz night in early August, in the School of Pharmacy. This event is in its third year and is getting bigger every year, with a record 12 teams entered, and several teams of enthusiastic first-years. It was a tough contest, with many teams neck-and-neck but the team Periodic Table Dancers were eventually proclaimed the winners. Congratulations! Second place went to The Product of a Misspent Tea Break (PMT), and in third place were the Solvent Squad. The Beta-Carrot-Team received the prize for best team name. Thanks to all those who helped organise and run the quiz this year, in particular, Andrea Vernall, Dave McMorran and Courtney Ennis.

The Aurora Otago Science and Technology Fair was held at the Otago Museum in early August. The Otago branch maintained its sponsorship of the event through student prizes. The branch chair, Nigel Lucas, awarded prizes to ten students, a difficult job considering the high standard across the 268 entries from 28 local schools. The projects awarded prizes all had an underlying chemistry theme, and were: Iron content in vegetables (Sophie Restall), What is the best way to remove oil from water? (Callum Attwell, William Leslie), Does an orange per day keep a cold away? (Cormac de la Harpe), Ice ice baby (Cody Labes, Joseph Combe), Making paints out of natural resources (Danika Billington), Bad apples (Becca More), The battle of bleach vs fabric (Emily Wright), Withered away (Phoebe Jaquiery), To freeze or not to freeze (Zoe McElrea), and Fantastic is not having plastic (Kate AC, Mikayla Alter).

The Otago branch held a student essay competition for students to write on a chemistry-related topic of their choice. As always, these were really interesting to read and it is great to see the enthusiasm and passion that our students have for chemistry. First place was awarded to David Rubin for *Celmisia, New Zealand's alpine daisies: assessing a sticky situation to "trichome" up with some answers*, second place went to Anna Lunde Hermansson for *Chemical speciation models: simplifying the complexity of the ocean* and third place went to Tayla Hill for D*etermining the provenance of the water source by measuring strontium isotope abundance ratios in beer and cider made in Dunedin, New Zealand*. Well done, to all of the winners!

The Otago NZIC branch awarded PhD student Daniel Ross a travel award to attend the 14th International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC) held in Lecce, Italy from 2 - 6 June 2019. Daniel thought the conference was an amazing experience, which brought him into contact with some of the world's leading chemists. He attended talks from Nobel Prize winners Sir Fraser Stoddart and Professor Ben Feringa and also engaged in stimulating conversations with prominent researchers such as Professor Michael Schmittel, Professor Neil Champness and Assistant Professor Johnathan Barnes.

The Otago NZIC branch also awarded Alistair Richardson a travel award to attend The American Society of Pharmacognosy Annual Meeting in Madison, Wisconsin. The ASP meeting always attracts high calibre researchers and this year was no exception. While there were many noteworthy oral presentations, two that stood out were the plenary lecture by Pieter Dorrestein (University of San Diego, Scripps Institution of Oceanography) and a presentation by Joseph M. Egan (Simon Fraser University) as part of the young members symposium. Alistair's poster, *The discovery of a stable vitamin C glycoside at high concentrations in apples (*Malus *spp)*, was recognised as the winner of the poster competition at the final banquet. Alistair is grateful for the support of the NZIC and would encourage others to attend similar meetings in their own area of research.

Nigel Lucas (NZIC Otago Branch chair, left) with the Periodic Table Dancers, winners of the 2019 Chemistry Quiz

NZIC Quiz participants during the "Movies" round

University of Otago, Department of Chemistry

The department farewells long-serving administrators Kristine Faed and Pip Jack as they move on to new adventures. However, we are really happy to welcome our new Client Administrator, Shae MacMillan, pictured here looking far more glamorous than the rest of us at the Otago 150th anniversary ball.

Elaine Burgess and Alistair Richardson (Plant & Food Otago) were part of a team across many science disciplines judging entries at the annual Aurora Otago Regional Science & Technology Fair (Hutton Theatre, Otago Museum, 6 August 2019). The entries were from schools across Otago from Years 7- 11, and were of a very high standard. Other judges from the Chemistry Department were Lyall Hanton, Nigel Lucas (on behalf of the NZIC) and Anna Garden (on behalf of the Otago Institute for the Arts and Sciences).

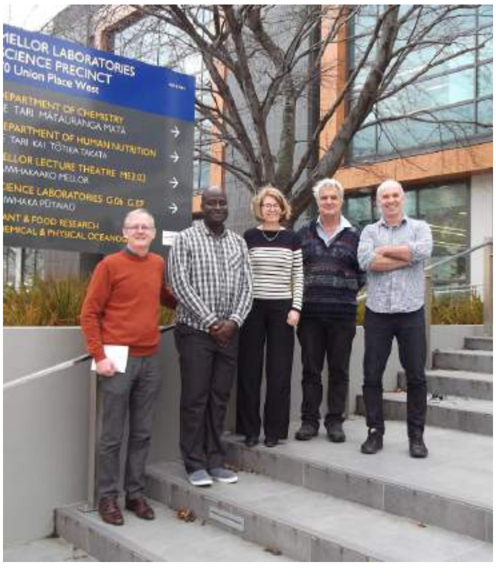
Chemistry celebrated another group of graduates in August, with six students and their families gathering for a celebratory morning tea before the main event. Well done to all of the graduates and we wish you well as you go on to bright futures!

Congratulations to Olu Babaranti (supervised by Russell Frew and Cliff Law), who has successfully defended his PhD! Joining the Frew group is Emma Hodgson, from Durham University, who is visiting as a summer intern for six weeks.

Carla Meledandri and postdoctoral fellow Jonathan Falconer attended the 9th International Colloid Conference in Sitges, Spain in June (Jonathan presented a poster, Carla gave a keynote), and Carla also attended the 10th International Nanomedicine Conference in Sydney in June (invited lecture). Ombéline Marone-Hitz, from France, joined the Meledandri group as a PhD student.

Plant & Food Research's Bioactives people based in the Chemistry Department (Elaine Burgess and Nigel Perry on this project) are working with Victoria University Wellington and Māori partners in the MBIE Smart Ideas project, Mātauranga Māori guided discovery of anti-microbials targeting kauri dieback caused by Phytophthora agathidicida. Mātauranga Māori (traditional knowledge) was used to select native plants that were considered most likely to produce anti-Phytophthora compounds. Plants collected by Ngāpuhi collaborators in the Hokianga rohe were sent to Plant & Food Research Dunedin, botanically identified, extracted and tested in vitro for anti-Phytophthora activity in the Microbiology Dept of the University of Otago by Scott Lawrence. Two out of five Hokianga rongoā plants showing strong anti-Phytophthora activity, a much higher hit rate than has been found in other Plant & Food Research screening projects (dating back to 1991) using NZ native plants collected at random. Bioassay-directed isolation work on a kānuka plant (also called mānuka in the Hokianga) led to three flavanones, previously unreported from New Zealand Kunzea, as the main bioactives. These compounds have not previously been reported as anti-Phytophthora. This work is documented in the Journal of the Royal Society of New Zealand as a multi-disciplinary paper entitled, *Mātauranga-guided screening of New Zealand native plants reveals flavonoids from kānuka (Kunzea robusta) with anti-Phytophthora activity* (https://doi.org/10.1080/03036758.2019.1648303). One simple rapid application of this discovery

Left: Shae MacMillan (right) with friend at the University of Otago 150th anniversary ball. Right: Alistair Richardson judging an entry: How does pollution affect plants?



Left: University of Otago Chemistry graduates for August. L-R: Sage Robinson, Alex Craig, China Payne, Georgina Shillito, James Findlay, Lee Glasier. Right: Olu Babaranti after his successful PhD defence. L-R: Russell Frew, Olu, Karyne Rogers, Stephen Moratti, Cliff Law.

could be use of extracts of this widespread plant in footwear baths/sprays, to protect kauri areas from *Phytophthora agathidicida* transport. Media coverage of the work can also be found here: https://www.stuff.co.nz/auckland/115144514/knuka-could-halt-kauri-dieback-disease-study-finds?fbclid=IwAR32lNPa5wS9CieA6JOdpxHFniL7YofOA_l9aiE02-Ezbquqrd6C-3dCQsI

The group of Anna Garden are sad to farewell long-serving group member Stephanie Lambie who, after graduating with an MSc in the group and completing several research assistant positions is moving to Auckland to undertake a PhD in physics with Nicola Gaston. All the best for the new position, Steph! Ingrid Lindeman from the University of Waikato visited the Garden group for a week in August to work on modelling phonon vibrations in calcite crystals. Anna Garden and Geoffrey Weal attended the Energy Landscapes 2019 conference in Belgrade where Anna presented a talk and Geoff a poster. Anna and Geoff have also been visiting the University of Iceland for ongoing collaborative projects.

In news from Christina McGraw's lab, students Denise Chen, Wayne Dillon and Habibeh Hashemi presented their latest sensors at the 2019 NZ Marine Sciences Society Conference in Dunedin in July. Wayne Dillon was awarded the MPI Prize for the student poster making the best use of quantitative methodology. In June, Christina attended the Integrated Marine Biosphere Research (IMBeR) Future Oceans 2 conference in Brest, France, where she co-led a pre-conference workshop (Setting priorities for research into changing ocean biological systems) and co-chaired a session on Multiple drivers and their role in ocean global change biology. After IMBeR, she travelled to Monaco, where she led a 5-day International Atomic Energy Association (IAEA) workshop on Best practices for ocean acidification experiments in multi-stressor scenarios.

Sally Brooker presented an invited plenary lecture at the 12th European School on Molecular Nanoscience (EsMolNa) in Elche (Spain). Afterwards Eugenio Coronado and his partner Ma'belle hosted her and Selly Demir (Michigan State Uni) for the weekend, at his holiday house (which includes a commercial avocado grove).

New PhD student in the Meledandri group, Ombéline Marone-Hitz

Top: Sally Brooker, Selly Demir (Michigan State), Ma'belle and Eugenio Coronado at a beach restaurant in Cullera near Valencia Bottom: Photo taken at the dinner for invited speakers (including a plenary by Sally) after the session celebrating Professor Barry Lever's (York Uni, Canada; 4th from right) contributions as founder and 50 years editor of Coordination Chemistry Reviews

Supported by a Catalyst Seed grant, Sally's PhD student Abdullah Abudayyeh has just returned from working for 6 weeks in Garry Hanan's lab (Montreal), testing the group's molecular catalysts for photocatalytic production of hydrogen from protons, and also testing for photocatalytic reduction of carbon dioxide on their new setup. Sally also visited during that period, and whilst there they participated in two conferences; the 6th Crystal Engineering and Emerging Materials Workshop of Ontario and Quebec (CEMWOQ-6) at Concordia University, and the 102nd Canadian Chemistry Conference and Exhibition at Quebec City, with Sally presenting invited keynotes at both meetings, and Abdullah a poster.

Brookers Bunch has just welcomed Sjoerd Verbeek, a five-month research intern from Professor Elisabeth Bouwman's group (Leiden).

From the group of Keith Gordon, Georgina Shillito has graduated with her PhD at the University of Otago in August, for her work on the "Interaction of charge transfer states in transition metal complexes. She was placed on the Sciences Division List of Exceptional Theses as her research was assessed as being amongst the top 10% of theses examined. She has completed a three-month MacDiarmid internship, working at the Office of the Prime Minister's Chief Science Advisor, examining photovoltaic technologies. In November she will begin a postdoctoral research position at the University of Bordeaux in France.

Stephan Kupfer and Martin Richter (Friedrich Schiller University, Germany) spent a week visiting the Gordon group from the University of Jena to discuss the expansion of ongoing collaborations.

Keith Gordon chaired the International Conference on Advanced Vibrational Spectroscopy (ICAVS) 2019 and most of the members of his group attended the conference in Auckland in early July. Joshua Sutton, Joe Mapley, Kārlis Bērziņš and Elliot Tay presented posters and Kārlis won the best poster prize for his poster, *Low frequency Raman spectroscopic study on compression-induced destabilization in amorphous Celecoxib*. Sara Miller, Chima Robert, Fatema Ahhmed and Samanali Garagoda Arachchige gave talks on *Ex vivo detection of coeliac disease: a multi-spectroscopic approach to disease diagnosis*, *Isothermal dehydration of crystalline hydrates using low frequency Raman spectroscopy, FT-Raman and FT-IR of tuna oil coacervates* and *Probing consolidant penetration into harakeke fibres using Raman microscopy and chemometrics*, respectively. After ICAVS 2019, Joshua and Joe also attended the International Symposium of Photochemistry and Photophysics of Coordination Compounds (ISPPCC) in Hong-Kong, where they presented posters.

Jacob Harrison is doing his Honours with the group and Elliot and Jacob are busy with writing their theses.

Kārlis had papers published in Molecular Pharmaceutics (Low-frequency Raman spectroscopic study on compression-induced destabilization in amorphous Celecoxib) and Journal of Raman Spectroscopy (Application of low-wavenumber Raman spectroscopy to the analysis of human teeth).

Chima and Samanali are preparing to attend the 16th Annual Witec Symposium, Germany at the end of September, where Chima and Samanali are presenting posters. Kārlis is attending the 13th Pharmaceutical Solid State Research Cluster (PSSRC) meeting in Dusseldorf, Germany in early September, where he is giving a talk on compression-induced destabilization in amorphous glasses.

Joe and Georgina are attending the Time Resolved Vibrational Spectroscopy (TRVS) symposium, Auckland in November and Georgina is giving an invited talk on *Application of time-resolved vibrational spectroscopy in the study of multichromophoric donor-acceptor complexes*. Samanali is attending the Asia-Pacific Optical Sensors Conference (APOS) symposium, Auckland, in November.

WAIKATO

NZIC Analytical Chemistry Competition 2019

This annual event was held on 11 June. Invitations were sent to schools in the wider Waikato/Bay of Plenty region to send teams of four students to the university for the day to carry out an analysis. Twenty-four teams of four students from seventeen schools entered this year's competition.

The task was to analyse a sample of barium chloride using a gravimetric procedure for Ba^{2+} and a volumetric method for Cl^- and to use these values to determine how many water molecules were associated with each barium chloride molecule. "Although this was quite a challenging task in the time available, it was very close between the top few teams and the winning team produced results which were closest to the true values," said competition judge and key organiser, Michèle Prinsep.

The competition allowed enthusiastic Year 13 chemists to spend a day in the university laboratories working on an experiment that would be beyond the resources of their schools. Although rivalry was fierce, the main emphasis was on enjoying the experience of working in a chemistry laboratory at the university and meeting students from other schools. The winning team received $240 and a trophy, with prize money also awarded to all other place-getters thanks to the generosity of the sponsors.

The day involved many of the Chemistry Department staff in setting up the competition and supervising the labs. Bryant Hall and Student Village provided excellent lunches (sponsored by the Waikato Branch of the NZIC) and Hill Laboratories and the Waikato Branch of the NZIC generously donated the prizes. Results were:

1st Prize: Waikato Diocesan School for Girls: (Keely Bowler, Elizabeth Chan, Joyce Hu, Harper Smith)

2nd Prize: Tauranga Girls' College 1: (Parvi Goundar, Jessie Huang, Holly Ryan, Holly Topp)

3rd Prize: Tauranga Girls' College 2 (Rebecca Eggersglusz, Jordan Gilby, Myosung Gwak, Christine Kim)

4th Prize: Otumoetai College 1: (John Austin, Grace Blissett, Alice Cerdeira, Daniel Lee)

Waikato Diocesan School for Girls, first place winners at the 2019 NZIC Analytical Chemistry Competition (from left: Harper Smith, Elizabeth Chan, Joyce Hu and Keely Bowler)

5th Prize: Whakatane High School 1 : (Renee Jay, Jean-Daniel Rosset, Hugh Spence, Katera Tutua)

Scion

Drs Florian Graichen, Dawn Smith, and Kate Parker along with Mr Marc Gaugler have been busy outlining and discussing with industry, government, other research institutes, and universities how to transition New Zealand to a circular bioeconomy. This is allowing us to contribute to solutions for climate change, replacement of finite materials with sustainable and renewable alternatives and how to tackle the plastic waste issue on our land and in our waterways and oceans. Aligned with this, Mr Jamie Bridson has been developing FTIR-based methods to quantify the micro-plastics on our beaches.

Dr Florian Graichen was interviewed on the Kim Hill RNZ show to discuss the problem of tackling plastics in NZ (see: https://player.fm/series/rnz-saturday-morning-2010844/dr-florian-graichen-tackling-plastic-waste).

Drs Ilena Isak and Miruna Petcu have been carrying out work chemically profiling wine and looking at the use of native wood in creating 'aged' wines. Unfortunately, this has involved many litres of wine and a few wine tastings, all in the name of replication of course.

Drs Mathias Sorieul and Stefan Hill travelled to Europe and the UK where they picked up some fully ^{13}C labelled pine trees (IsoLife, Holland; with a price tag equal to the GDP of a small island nation), transported them to Wurzburg University (Germany) to carry out ^{13}C MRI experiments, and then finally to Warwick University (UK) to use high-field solid-state NMR to investigate the chemical nanostructure of plant secondary cell walls.

Dr Angel Greene was awarded an NSC (National Science Challenge) grant to investigate novel methods for chemical sequestration with a molecular sponge, inspired by the field of soft-robotics that uses photochemically or electrically-controlled mechanical motion to selectively trap waste and then release waste products with a material that can repeat this filtration process indefinitely.

Dr Kelly Wade was also awarded NSC funding to develop 3D printing processes and polymer chemistry that integrates additive manufacturing and bioparticles that provide 3D printed objects with functional anti-bacterial activity. These novel 3D printable polymers could deliver patient-specific medical devices with in-built anti-bacterial function against pathogens and prevent biofilm formation.

Drs Laura Raymond and Stefan Hill attended the NZPPS (New Zealand Plant Protection Society) conference in Auckland, where they presented on NMR and LC-MS based metabolomics to detect plant diseases.

Dr Stefan Hill was an invited speaker at the 75th LASRA (Leather and Shoe Research Association) conference held in Napier. His topic of discussion was chemical feedstocks from renewable resources in a circular bioeconomy.

Laboratory recreations of Titan's cyanide sky

Courtney Ennis,[1]* Rebecca Auchettl[2]

[1] Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054

[2] ANSTO Australian Synchrotron, 800 Blackburn Road, Clayton, VIC 3168

(email: *courtney.ennis@otago.ac.nz*)

Keywords: *infrared spectroscopy, astrochemistry, complex organics, Saturn, Titan, cyanide chemistry*

Dr Courtney Ennis was appointed Lecturer at the Department of Chemistry, University of Otago, in September 2018. After completing his PhD at The University of Western Australia in 2009, Courtney's independent research career started as a recipient of an ARC Discover Early Career Research Award in 2015, which followed postdoctoral placements within astrochemistry laboratories at The University of Hawai'i (Prof Ralf Kaiser) and University College London (Prof Steve Price), as well as a research role at the Australian Synchrotron (Terahertz and Far-infrared Beamline). Across these placements Courtney has designed and constructed a number of laboratory setups to replicate and study irradiation-driven chemical reactions unfolding in various space environments. A common goal is to understand the formation pathways of complex organic molecules (COM) - the building-blocks of biological material on Earth. In order to study these species and detect them with telescopes, infrared spectra must be compiled for various environments. Focussing on planetary and interstellar ices, specialist equipment at the Australian Synchrotron and University of Otago is currently being used to study COM - data that may help untangle the chemical origins for life on Earth.

The atmospheric chemistry of Titan

As the Cassini-Huygens (NASA/ESA) mission began drawing to a close in September 2017, with the Cassini orbiter performing a final plunge into the Saturn atmosphere, it would not be a long wait for a return trip to Saturn. In June this year, NASA and Johns Hopkins University Applied Physics Laboratory announced the next excursion to the planet's Earth-like satellite, Titan. Featuring an airborne drone named "Dragonfly" (Fig. 1), the mission plans to perform in-depth reconnaissance of the spectacular moonscape and analysis of its chemical composition, prioritising the search for molecules of biological significance.

Fig. 1. Dragonfly mission concept of entry, descent landing, surface operations and flight at Titan (http://dragonfly.jhuapl.edu/). Image: NASA/Johns Hopkins APL.

So why the rush back to Titan with many regions of our Solar System yet to be explored to the same extent? The answer is that over its 13 years in orbit, the Cassini spacecraft and Huygens probe unveiled a chemistry of high complexity unfolding on the cold world shrouded by its distinctive orange haze.[1] Possessing a geologically dynamic terrain with a surface landscape shaped by meteorological activity, Titan has confirmed itself as one of the Solar System's best targets to locate the fundamental agents we associate with biochemistry; molecules such as amino acids, nucleobases and carbohydrates.[2]

From early astronomy and the NASA Voyager fly-by missions, we have known for some time that the upper layers of Titan's stratosphere is processed by ultraviolet photochemistry and chemical reactions driven by energetic particles sourced from Saturn's magnetosphere and cosmic rays. Here, the dominant nitrogen and methane gas is continually converted to larger hydrocarbons and molecules of the cyanide family (collectively nitriles). The extent of this chemistry yields populations (typically hundreds of parts per billion for higher-order species) of products from small volatiles (hydrogen cyanide: HCN and acetylene: C_2H_2) up to nitrogen-containing polymers known as 'tholins', species responsible for the optically thick orange haze.

It is the fate of these cyanide molecules that is of interest to astrochemists and their search for biological building blocks. Although very much a health hazard to life on Earth, HCN is suspected to act as an important precursor in the formation pathways for both amino acids (via Strecker synthesis[3]) and nitrogen heterocycles,[4-5] the latter forming the molecular framework for DNA nucleobases (indeed the HCN pentamer is an isomer of adenine). However, on Titan, it is thought that such complicated mechanisms involving reactions with high activation barriers are unlikely to unfold in the gas-phase at such cold temperatures.

Instead, many laboratory-based astrochemists have focussed on condensed-phase cyanides, where non-equilibrium chemistry can propagate more efficiently to yield chemical products of higher complexity. Similar chemistry has been invoked for thin molecular ices that coat dust grains found in interstellar environments as cold as 10 K. In these regions solid-state reactions are required to account for the abundances of complex organics identified within interstellar molecular clouds and protoplanetary disks by microwave astronomy.

Although not as cold as interstellar space, the temperature of Titan's atmosphere (~ 200 K at its warmest altitudes but reaching as low as 70 K at the lower stratosphere) is sufficiently low to see the condensation of cyanide and hydrocarbon ices and aerosols on tholin nuclei (Fig. 2). With each atmospheric species possessing a characteristic condensation temperature (and therefore altitude at which the molecule "freezes out"), physical models predict interesting architectures for the icy particles as they grow and precipitate through the atmosphere. First, the more polar nitrile compounds form the core layers of the particles at 70-90 km above the surface. Once subsiding to altitudes below 65 km, non-polar hydrocarbons and CO_2 form the outer layers before the aerosols are capped by the dominant CH_4 ice toward the surface. Ultimately reaching micron-size dimensions, these particles of heterogeneous ice provide interesting avenues for condensed-phase chemistry. Within, it is suspected that the interface between domains of different molecular composition allows various pathways to unfold. This chemistry is largely driven by the energy deposited by the high cosmic ray flux in lower atmosphere regions.

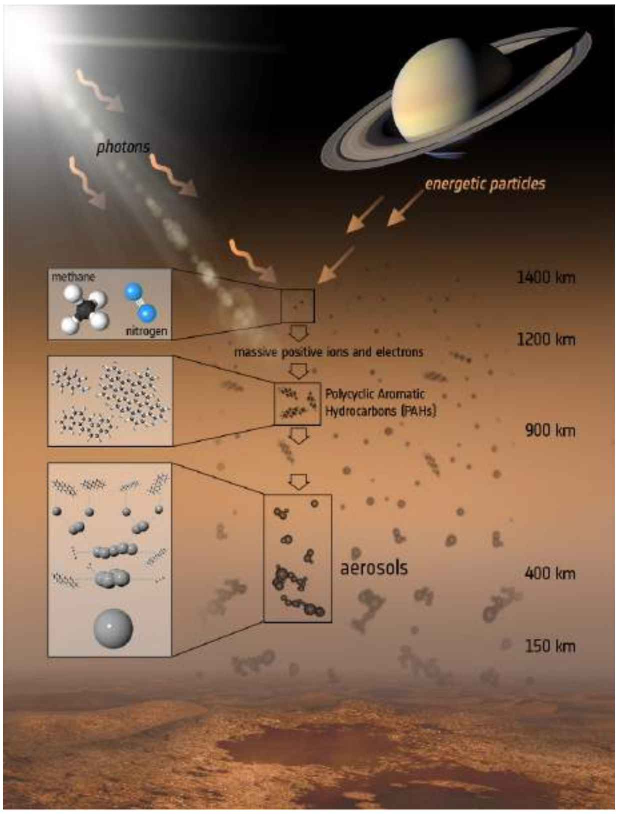


Fig. 2. Chemical reactions leading to the formation of Titan's aerosols. Image: ESA / ATG medialab.

Our workgroup is interested in recreating this exotic chemistry in the laboratory. To do so we use a range of setups to replicate the physical conditions of Titan's atmosphere, its aerosols and its surface ices and apply infrared (IR) spectroscopy to probe chemical properties of Titan's cyanide material. These studies fall into several ongoing projects where we are continuing to build our understanding of Titan's cold chemistry.

Cyanide aerosols at the Australian Synchrotron – Titan's atmosphere in a can

Some of Cassini's more revealing spectra of Titan's atmosphere were obtained using far-IR wavelengths. This region of the spectrum (~ 50 - 500 cm^{-1}) between the terahertz and mid-IR regions is infrequently used for terrestrial investigations, due to limited light sources, issues with the thermal background and the need for helium cooled detectors. It is, however, the region best suited to investigate both the chemical composition and morphology of icy surfaces, being rich in low-lying 'fundamental' molecular vibrations as well as lattice modes. These are associated with intra- and inter-molecular interactions in crystalline materials respectively. Such molecular information was retrieved by Cassini's on-board composite infrared spectrometer (CIRS) where the far-IR region was used to identify signatures of many volatile nitriles (HCN, cyanogen C_2N_2, and cyanoacetylene HC_3N) and unsaturated hydrocarbons (diacetylene C_4H_2 and methyl acetylene C_3H_4). In amongst these fine gas-phase lines were broad features associated with condensed material, the most notable of these being an intense, symmetric peak at 220 cm^{-1} labelled the "haystack" (Fig. 3).[6]

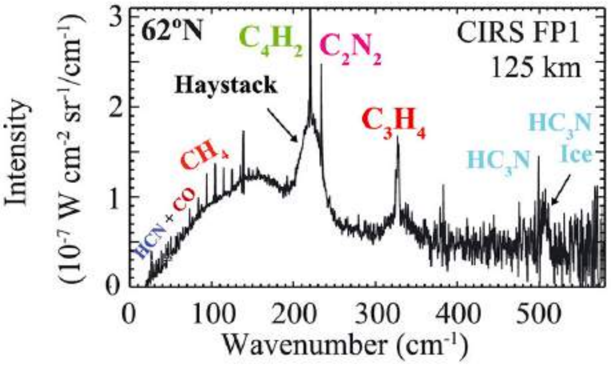


Fig. 3. Cassini-Huygens CIRS Instrument far-IR spectrum of Titan atmosphere revealing gas-phase products, condensed ice and the "haystack" feature at 220 cm^{-1}. Image from reference 6 with permission.

The haystack feature has been closely scrutinised over the duration of the Cassini mission, a period that spanned Titan's northern winter to summer solstice. Over time the intensity of this band was directly linked to Titan's seasonal variation in UV flux; either depleted under full solar glare or growing with the accumulation of ice material when shielded from the harsh radiation field. This pattern was balanced by the appearance and disappearance of ice at southern latitudes. This seasonal variation in band intensities provides compelling evidence that photolysis products were indeed the material forming ices and aerosols at lower altitudes to further validate atmospheric models. However, to this day the specific chemical carriers of the haystack feature remain unconfirmed; no pure ice system characterised to date has provided a compelling fit for the distinctive band position and profile.

The far-infrared beamline at the Australian Synchrotron is the ideal instrument to investigate Titan's cyanide ices at these wavelengths.[7-8] Here, the beamline spectrometer is coupled to the intense far-IR light source and a large gas cell that closely replicates the conditions of the lower Titan stratosphere when filled with the appropriate pressure of nitrogen cooled to 80-130 K (Fig. 4). Into this vessel we saturate nitrile gases to allow our cyanide aerosols to instantly nucleate and grow under the simulated Titan air. By doing so we can track over time the evolution of these particles, first using mid-IR light scattering to measure the aerosol size distribution under different conditions aligned with Titan altitudes. These measurements coincide with the far-IR absorption spectra where the amorphous (small particles) to crystalline (large, micron size particles) nitrile ice can be observed to alter as the material coagulates.

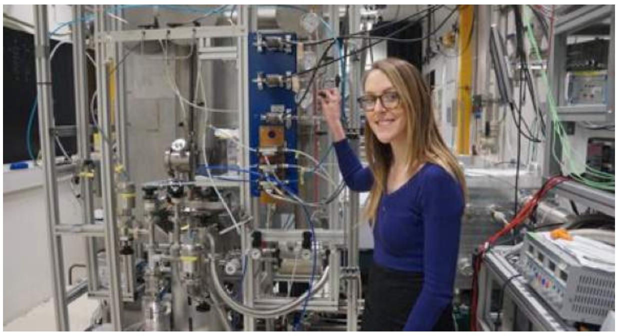


Fig. 4. *Dr Rebecca Auchettl in front of the Titan aerosol experiment at the Australian Synchrotron*

Our early synchrotron work focused on the formation of pure nitrile particles of 'secondary' nitrile species such as acetonitrile and ethyl cyanide (propionitrile). However, their low frequency spectra proved poor comparisons to the Cassini mission spectra (Fig. 5). Our ongoing research toward Titan aerosols is now targeting heterogeneous ice mixtures that better mimic layered ice architectures, where we have experimented with core-shell and mixed ice compositions generated by sequential pulses of gas into the cold cell. By honing this method, we are converging on an understanding of how physical parameters such as aerosol size, shape and morphology - in addition to the chemical composition of the aerosols that may include several co-deposited species - can influence the nitrile ice spectra. We hope to crack the cold case of Titan's haystack composition over our coming visits.

The processing of Titan's cyanide ices - avenues to more complex organics

Trapped within the aerosol matrix, we are now able to explore the solid-state chemistry of Titan's cyanides. Nitriles, extending from the simplest HCN, the unsaturated vinyl cyanide C_2H_3CN and species with multiple CN groups such as diaminomaleonitrile (DAMN), are all proposed reactants for astrochemical pathways leading to biomolecules such as amino acids and nucleobases.[9] As molecular ices, we are particularly interested in non-equilibrium chemical processes where the bombardment of high energy photons and fast particles can efficiently cleave covalent bonds or strip away electrons within molecules. The irradiation of surfaces can therefore generate large populations of trapped reactive species in the solid-state, where subsequent radical-radical and ion-neutral reactions can then unfold without barriers at low temperature (Fig. 6).[10] The result of this processing is a continual increase in complexity of the molecular material within the ice as hydrogen efficiently diffuses from the surface leading to a corresponding increase in C, N, and O bonding. A suite of higher-order organics can now be located in the ice matrix.[11]

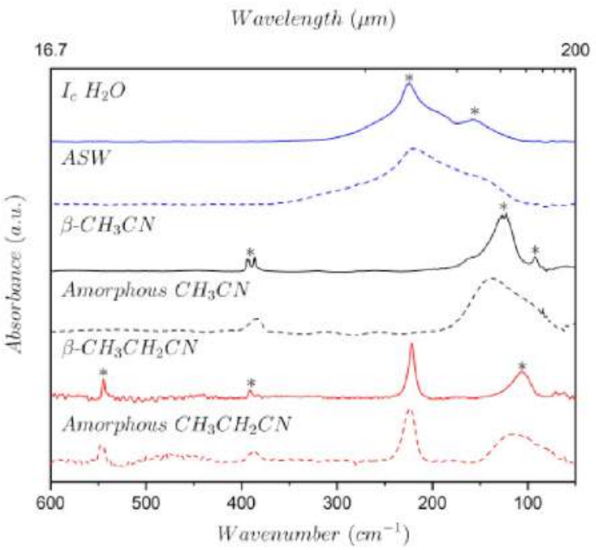


Fig. 5. Far-IR spectra of pure H_2O (blue), pure CH_3CN (black) and CH_3CH_2CN (red) in their amorphous (dashed line) and crystalline (solid line) phases from 600 - 50 cm^{-1}. Potential crystalline-phase tracer free from spectral overlap with other molecules are indicated using an asterisk (*). Note symmetric band of ethyl cyanide at 225 cm^{-1}, a possible candidate for the haystack feature.

Replicating this chemistry in the laboratory requires (ultra) high vacuum and low temperature equipment (Fig. 7) appropriated from surface science to grow molecular ice thin-films simulating planetary and interstellar ice surfaces.[12] Once formed from chemical vapour deposition, ice layers typically several hundred nanometres in thickness can be exposed to whatever radiation source is at hand; from UV lamps and lasers to electron and ion sources of typically keV to MeV energies.[13] The energy of these impinging photons and particles can initiate a number of physical processes, from ionisation to homolytic bond cleavage and implantation of atoms. The chemical alteration of the ice can be tracked on-line by IR spectroscopy, where diminishing precursor signals coincide with the rise in vibrational signatures of new products.[14-15] The changes in these peak areas can be quantified to determine solid-state kinetics as a function of dose; useful information for astrochemical models.

Often, the formation of new organic molecules is shrouded by the bulk precursor ice. In such cases the low mass volatile material can be removed to the gas-phase by temperature programmed desorption mass spectrom-

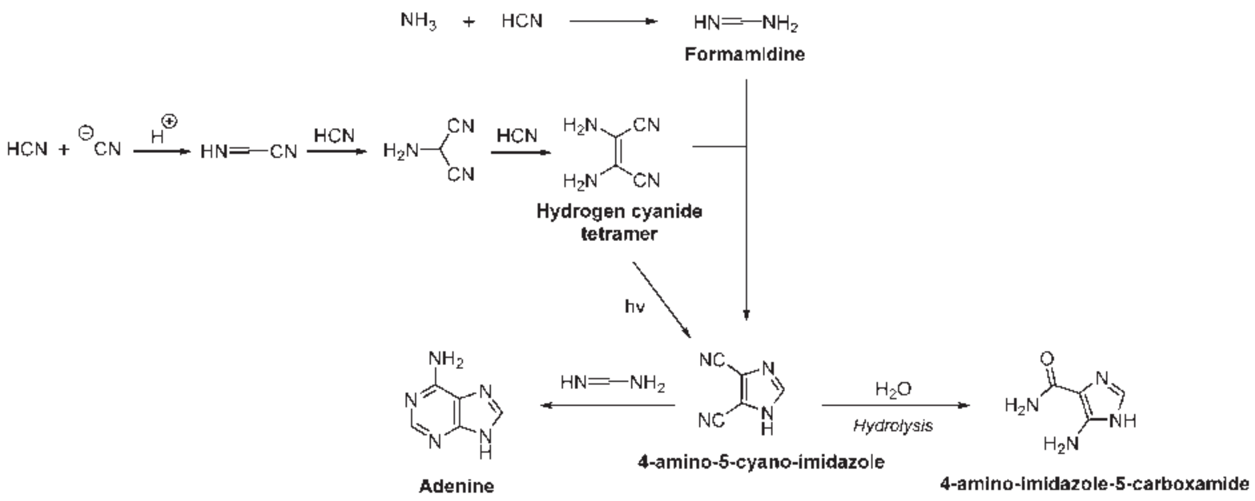


Fig. 6. Possible prebiotic synthesis of adenine from hydrogen cyanide. Image from reference 10 under Creative Commons License CC BY 4.0.

Fig. 7. Cyanide thin-film photochemistry at the Australian Synchrotron. A similar apparatus has been completed at the University of Otago to perform UV photolysis of thin-films, however, characterised using the mid-IR region.

etry (TPD-MS) where the substrate is heated at a controlled rate and the individual ice components can be recorded by mass spectrometry once sublimed. The high sensitivity of quadrupole and time-of-flight mass spectrometers may even help determine the identity of trace irradiation products once released to the gas-phase, provided the ionisation method is sufficiently 'soft' to avoid excessive fragmentation. This ice sublimation is actually representative of the evolution of interstellar dust grains, where grain mantles can be warmed as UV flux increases over time in cloud environments and complex organics are released to the gas-phase enabling telescope detection.

In terms of elucidating chemical reaction mechanisms that unfold in planetary ices, IR spectroscopy can identify the vibrational signatures of reactive radicals and ions. The temporal populations of these species (OH, NH_2, CN, HCO) can be monitored and even quantified, allowing us to construct intricate reaction networks and determine rate constants. The result of numerous aligned studies, a complete kinetic model can interlink the formation and destruction of all molecules observed within a planetary or interstellar environment, as well as predict the existence of as yet unidentified species to be the target of the next astronomical search (Fig. 8).[16]

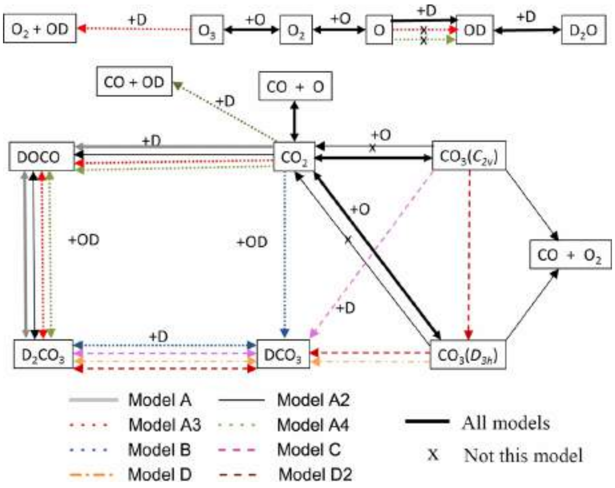


Fig. 8. Summary of the alternative reaction pathways investigated by various kinetic models for the formation of (D_2)-carbonic acid from deuterium ion irradiated CO_2 and O_2 ices. Image from reference 13 with permission.

The refinement of astrochemical models is a collaborative endeavour between many international laboratories, each specialised in perhaps a certain space environment or class of compounds. Our contribution is squarely focussed on the role of cyanide molecules in solid-state chemistry as relevant to Titan's ices, in the hope of confirming pathways to biomolecule synthesis beyond Earth. One should note that cyanides are of increasing interest to other planetary regions, such as distant trans-Neptunian objects that are the source of long period comets.[13] These icy Solar System bodies are also rich in nitrogen and methane and have been revealed by the recent NASA New Horizons spacecraft to harbour cosmic ray-driven surface chemistry. Could complex organics formed on comet surfaces have been delivered to an early Earth *via* cometary impact? By replicating this chemistry in the laboratory we can provide evidence to either prove or disprove this theory.

Laboratory astrochemistry is an incremental science. At the University of Otago we are continually honing our expertise in recreating these icy planetary systems and learning the chemical intricacies of nitriles in the condensed-phase. Although there is a finite number of astromolecules that could find themselves mixed in a cyanide-containing Titan aerosol, the pathways to form molecules such as a nitrogen heterocycle are numerous, some conducive to photochemistry while others may only be possible from particle irradiation. However, as our experience with these systems builds, we are always excited to observe what organic product will next emerge from the ice. Looking forward, we hope that our laboratory results will converge with the observations of Dragonfly during its planned exploration of Titan in 2034 and are thankful for a sporting head-start to uncover any life-bearing molecules from the icy terrain.

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Chemical speciation models: simplifying the complexity of the ocean

Anna C. Lunde Hermansson

Department of Marine Sciences, University of Gothenburg, Gothenburg, Sweden & Department of Chemistry, University of Otago, Dunedin, New Zealand (email: *gusherana@student.gu.se****)***

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Anna is an MSc student in the Marine Sciences Department, University of Gothenburg, Sweden. She is currently at the University of Otago as a visiting student, working with Dr Christina McGraw for a one-year project in the chemistry department finishing her MSc degree in marine chemistry. As a marine sciences BSc student, Anna realised early that she was especially interested in the chemical aspect of the marine environment, leading to her BSc thesis covering the chemical speciation of copper with a primary focus on natural organic ligands.

Introduction

Since the beginning of the industrial revolution, humans have, by our way of living, changed the environment around us. Increasing anthropogenic pressure, largely due to the usage of fossil fuels, has led to a changing climate and global warming. This means that the ocean has become warmer and its pH has decreased. These changes are directly affecting the distribution of ions and molecules, i.e. the chemical speciation, in the ocean. The global ocean absorb about 30% of the CO_2 released into the atmosphere.[1-2] The CO_2 is hydrated, forming carbonic acid (H_2CO_3) which dissociates to form bicarbonate (HCO_3^-) carbonate (CO_3^{2-}) and hydronium ions (H_3O^+) (Eq. 1). The oceanic uptake of CO_2 is the driving force of hydronium ion formation and lowered pH, known as ocean acidification. The total dissolved inorganic carbon (DIC) pool of the ocean in equilibrium at current conditions consists of approximately 90% of HCO_3^-, 9% of CO_3^{2-} and 1% of the combination of CO_2 and H_2CO_3 (Fig. 1). Adding more CO_2, this equilibrium is shifting and pH decreases, affecting both the organic and inorganic chemistry of the ocean (Eq. 1).[3-4]

$$CO_2 + 3H_2O \rightleftarrows H_2CO_3 + 2H_2O \rightleftarrows$$
$$HCO_3^- + H_3O^+ + H_2O \rightleftarrows CO_3^{2-} + 2H_3O^+ \qquad \text{(Eq. 1)}$$

The chemical speciation determines the reactivity and bioavailability of all compounds that constitute the "chemical soup" of seawater. Semi-empirical models, built to calculate the solution composition, are necessary when we want to evaluate how current and future scenarios affect the state of the ocean and, possibly, how to manage these changes.

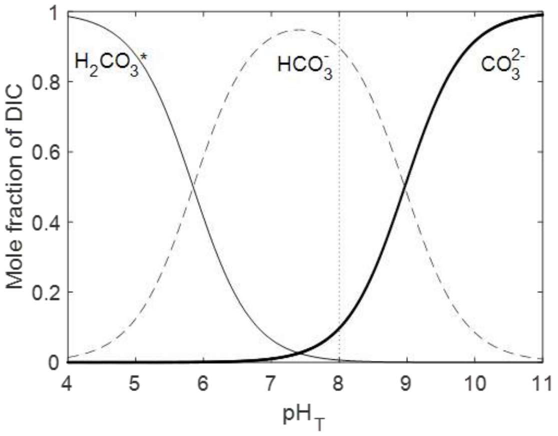

Fig. 1. The molar distribution of the dissolved inorganic carbon (DIC) species determined by pH. CO_2 and H_2CO_3 are combined in the $H_2CO_3^*$pool. pH_T (pH total) is a definition of pH often used in the marine environment to include the activity of bisulphate ions (HSO_4^{2-}) in addition to the activity of hydronium ions (H_3O^+). The dotted line equals the distribution found in the ocean at pH_T=8.

In this article, a combination of two well-established models is proposed as a new method when unravelling the complexity of seawater. One part accounts for the inorganic speciation and the other the organic speciation of compounds. Together they produce a more comprehensive and accurate reflection of ocean chemistry.

Copper – a toxic nutrient

Trace metals are important micronutrients affecting the productivity of the ocean.[5] 50% of the oxygen we breath originates from marine primary producers such as plankton and seaweed. As with all living things, a balanced uptake of nutrients is important for the organisms to function properly. Copper, a trace metal in the marine environment, is interesting to study since it is an essential nutrient but, at the same time, toxic at rather low concentrations.[4, 6] This means that in the case of copper, only a narrow concentration range is permitted to sustain life; concentrations which are too high or too low could thus limit an entire ecosystem. The toxicity and bioavailability of copper is proportional to the free cupric ion, not the total copper concentration. It is therefore important to determine the distribution of copper species rather than only looking at the total concentration.[7-11]

The primary sources of copper and other trace metals in the ocean are from rivers, the atmosphere and hydrothermal vents (Fig. 2). The primary sinks are biological uptake, precipitation, scavenging and burial in sediments.[4, 12] Anthropogenic impact is mostly visible in coastal areas but is seen worldwide.[12]

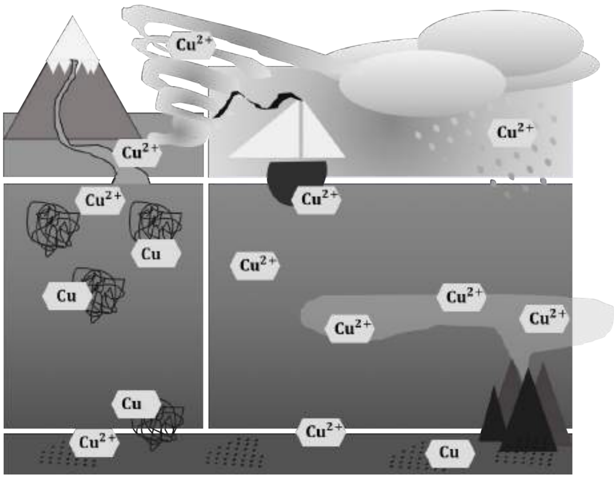

Fig. 2. Examples of sources (rivers, dust, rain antifouling and hydrothermal vents) and sinks (agglomeration and burial) of copper to and from the ocean

In the ocean, surface concentrations of dissolved copper (dCu_{TOT}) is about 1 nmole/kg.[4] Elevated levels of copper can be found in coastal areas which is often due to, for example, antifouling and riverine input.[4, 12-13] The dCu_{TOT} pool includes the free cupric ion (Cu^{2+}), inorganic complexes, such as $CuCO_3$ and $Cu(OH)_2$, and chelates with dissolved organic material (CuL or Cu-DOM) (Fig. 3).[4,7,14] The most important inorganic copper complexing ligands are CO_3^{2-} and, to a lesser extent, OH^-.[10] The speciation is, however, dominated by stable organic complexes.[4, 11] Most CuL complexes are considered strong and not bioavailable.[15] Mobility, solubility, speciation and bioavailability (toxicity and nutritive) of CuL is largely determined by the binding to the functional groups of the organic matter.[16-19]

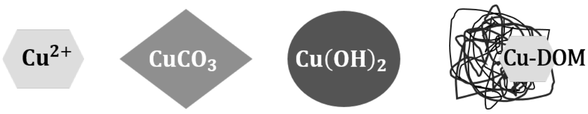

Fig. 3. Different forms (i.e. chemical species) associated with dissolved copper in the marine environment. From the left: free cupric ion, $CuCO_3$, $Cu(OH)_2$ and copper forming complexes with dissolved organic ligands

The free cupric ion can be toxic at picomolar (10^{-12} M) levels.[5, 15] Cu^{2+} concentrations below 10^{-14} M, on the other hand, could be biolimiting, by inhibiting the uptake of iron which will affect the productivity of the ocean.[16] In addition to its role as a micronutrient, copper constitutes an important part of the enzymatic processes covering both the carbon and nitrogen cycles as well as the intercellular transportation of iron.[5, 20-21]

Since copper is strongly bound to CO_3^{2-}, the inorganic speciation will be affected by pH induced changes in chemical speciation.[4, 15] As CO_3^{2-} continues to decrease, less is available to bind to copper, which is expected to result in an increase of the toxic, free cupric ion. Similarly, the decrease in OH^- will also add to the potential increase of the free cupric ion. Millero *et al.*[15] predicted a doubling in the Cu^{2+} concentration if pH drops from 8.1 to 7.8, equal to an estimated pH decrease predicted by the end of this century. The estimate is based on calculations that did not include organic matter as potential ligands. Since a large fraction of the dissolved copper forms a complex with DOM, new calculations are necessary to give better predictions of the future. The ocean consists of an intricate food web where alterations have great effects of both known and unknown dimensions. The change in copper availability not only affects the microorganisms at the bottom of the trophic levels but the entire ecosystem.

Copper and organic ligands

Organic ligands can act as a buffer and control the availability of many essential nutrients as well as neutralise otherwise toxic ions by forming complexes that thus become unavailable and harmless to marine biota. Many researchers agree that more than 99% of dissolved copper is bound to organic ligands (CuL).[4, 7-8, 14-15] The heterogeneity of organic ligands is a complicating factor when determining complexation; the ligands not only exhibit different shapes and sizes, but also different affinities to different elements.[8, 22]

Natural organic matter (NOM) is common in all natural waters and consists of a complex composition of compounds.[4, 17-19, 22] NOM can be fractionated based on size into particulate (POM) and dissolved (DOM) organic matter. The dissolved fraction can be further divided into a colloidal fraction and a truly dissolved fraction.[23] An additional way of grouping DOM is to distribute the ligands in discrete classes, defined by the ability and strength of the ligands to form complexes with the metal in question. These classes consist of various types of DOM where L1 is considered the strongest binding ligand class followed by L2, L3 and so on.[11, 23-24] The definition of these classes should be treated as a tool to separate the otherwise unknown DOM based on a single common denominator, the binding strength. The strongest binding ligands are present in the truly dissolved fraction while weaker ligands are part of the colloidal fraction.[4] When organic ligand concentrations are greater than the copper concentration, which is usually the case, the stronger ligand class has the largest impact on copper speciation.[8]

Examples of natural ligands are extracellular polymeric substances (EPS), nanofibrils, humic acids (HA) and fulvic acids (FA).[23] HA and FA are common NOM in the colloidal/dissolved fraction and are important when considering metal complexation in natural waters.[25] There are different functional groups associated with HA and FA, but the two considered most important are carboxylic (COOH/COO^-) and phenolic (OH/O^-) groups.[15, 17-19] Oxygen is a key element in these functional groups and the fraction of oxygen relative to carbon in an organic ligand can give information about the reactivity of the molecule.[26] Dissociation of the functional groups is determined by pH and electrolyte concentration, usually resulting in a net negative surface charge of the molecule in ambient conditions.[15, 26] Both carboxylic and phenolic groups are common and have great influence in the binding of different cations.[17, 26] The phenolic site is thought to be the primary determinant of copper speciation while calcium and magnesium are more associated with the carboxylic sites.[17] This would indicate that the competitive effect between copper and the major cations of is low.

Complexation between copper and dissolved organic matter is determined by the concentration and the physiochemical properties, e.g. ionic strength (I), pH and competition.[9, 27] The natural organic ligand and copper complexes are very stable in environments where the ligand concentration is high.[28] Dissolved organic ligands are found throughout the entire water column but with the highest levels at depths corresponding to the chlorophyll maximum depths, indicating a strong connection to biological productivity.[23] Fungi, algae and bacteria are capable of producing metal binding ligands (e.g. thiols), which have been shown by excretion in cultures.[4, 9, 13] Production of copper binding ligands maintains the cupric ion concentration below toxic levels even if the total concentration is above normal.[4, 7] Organic ligands are especially important in coastal areas where the copper concentration often reaches elevated, and potentially harmful, levels.[7-8, 15] A positive correlation between the total dissolved copper concentration and the free cupric ion is not always the case, indicating a buffer capacity by the organic ligands.

Having now highlighted the importance of organic ligands associated with copper speciation, the next section of this article will explain how two models of inorganic and organic speciation can be combined to simulate copper speciation in an improved way.

Inorganic speciation – where activity coefficients are key

Inorganic speciation is relatively straightforward when conditional stability constants can be calculated and concentration can be measured.[10, 24] In order to calculate the speciation of elements in solutions under non-ideal conditions, e.g. high ionic strength, the activity must be used instead of the concentration. The activity is defined to account for the non-specific effects in solutions and can be explained as the active part of the concentration, the effective concentration.[29] The activity is related to the concentration via the activity coefficient (γ) according to Eq. 2:

$$a_i = c_i \gamma_i \qquad \text{(Eq. 2)}$$

where a_i is the activity and c_i is the concentration of substance i. γ_i describes the non-ideal behaviour of ions due to interactions and is determined by the composition of the media.[30-31] The values of the activity coefficients depend on ionic strength, temperature and pressure. In ideal solutions, the activity coefficient is equal to one and the activity is therefore equal to concentration.[29] The Debye-Hückel theory and the Davies extension are among the most common approaches when calculating activity coefficients (γ) in equilibrium models of dilute solutions.[26] When working with solutions of higher ionic strength, like seawater, one must apply another approach to calculate γ with more accurate results. One example is the Pitzer model where the Pitzer equations are used to calculate the activity coefficients in natural waters of higher ionic strength, thereby determining the inorganic speciation of compounds, as a function of concentration, temperature and ionic strength.[31]

The Pitzer model

The Pitzer model is a well-developed chemical equilibrium model, which calculates activity coefficients in solutions as a function of temperature and ionic strength while accounting for the specific ion interactions of high ionic strength media.[26, 31-33] The Pitzer equations are derived from the relationship between solution composition and excess Gibbs energy. The activity coefficient of an ion (i) can be described by Eq. 3:

$$\ln \gamma_i = D.H + \sum_{ij}(m_i m_j B^{\gamma}) + \sum_{ijk}(m_i m_j m_k C^{\gamma})\ldots \qquad \text{(Eq. 3)}$$

where D.H is a Debye-Hückel term expressing the limiting law, $m_{i,j,k}$ is the molality of different ions and B and C are parameters that describes the binary and ternary interactions of the ions.[33] These parameters are empirically derived and dependent on ionic strength and temperature.[34] The equations cover two types of interactions: (1) the interactions between ions of opposite charge, which has the greatest influence, and (2) the binary interactions between ions with the same charge combined with the ternary interactions adding an ion of the opposite charge.[35]

Parameters for several elements and interactions have been estimated and the model is now often used for inorganic speciation of trace element in natural waters.[33] When γ is known, conditional stability constants of each ion-ligand complex, needed for the speciation of metals, can be determined. The stability constants are then used when determining the competition between different ligands and thus species composition.[15]

Exploring heterogeneity and complexity of organic speciation with the NICA-Donnan model

When determining speciation of trace metals in natural waters it is important to incorporate a model that describes the organic interactions. This introduces a new challenge associated with both calculations and interpretations due to the inhomogeneous nature of organic matter.[13] It is extremely difficult to develop accurate models of the interactions occurring between DOM and other ions. Although, there are several examples of models attempting to do this, they are only valid at low ionic strength.[36] One example of such is the NICA-Donnan model, a combination of two models: the Non-Ideal Competitive Absorption (NICA) model and the Donnan model, a combination that has been used successfully to evaluate the interactions between trace metal and humic substances in low ionic strength media.[17, 19, 22]. The NICA model is an analysis tool, which handles the complexity related to the binding properties of dissolved organic matter (DOM), while adding the Donnan part accounts for the non-specific, electrostatic, interaction.[17, 19]

Combining the Pitzer model, for calculation of activities, with NICA-Donnan, to determine the amount bound to organic compounds, is a significant step towards developing a model that can describe the composition of the non-ideal marine environment correctly.

The Donnan component accounts for electrostatic interactions

The main parameter in the Donnan part of the NICA-Donnan model is the Donnan volume (V_D) which is related to the Donnan potential (Ψ) and dependent of the ionic strength of the solution.[17, 19] The concentration and interaction of interest is considered within the Donnan volume V_D (Fig. 4), close to the binding sites, instead of the total bulk solution.[17] Organic matter is considered as being a gel-phase, where the heterogeneity is "smeared out" over the molecule.[18] This assumption makes it possible to avoid determination of shape and size of the substance.[19] Three aspects of ion binding are described by the electrostatic interaction within the volume:[18-19]

- The effect of the ion strength on local potential, which affects the proton and metal binding
- Non-specific ion binding due to residual charge of the organic molecule
- Second order effects of interactions elsewhere, e.g. binding at a phenolic site affects the properties of the carboxylic site

The Donnan model assumes that charged groups, belonging to the DOM, are neutralised by ions within V_D that surrounds the DOM.[17-19] The potential is considered to drop to zero outside of the Donnan volume, leading to Eq. 4:[18]

$$\frac{q}{V_D} + \sum_i z_i(c_{i,D} - c_i) = 0 \qquad \text{(Eq. 4)}$$

where q represents the charge of the molecule, V_D the Donnan volume, z is the charge of ion i, c_i is the concentration of ion i in the bulk solution and $c_{i,D}$ is the concentration of ion i within the Donnan volume, derived from the Boltzmann equation, shown in Eq. 5 as:

$$C_{i,D} = c_i \exp^{\frac{-zF\Psi}{RT}} \qquad \text{(Eq. 5)}$$

where zFΨ is given by electrostatic interactions between ions (z is the valence, F the Faraday constant and Ψ the Donnan potential), R is the gas constant (8.31 J/mole/kg) and T is the temperature (Kelvin). To solve the Donnan potential (Ψ), when the charge and concentration are determined, the Donnan volume must be calculated. The Donnan volume does not change with pH and can be expressed as a function of ionic strength, I (Eq. 6).[17]

$$\log V_D = b(1 - \log I) - 1 \qquad \text{(Eq. 6)}$$

where I is the ionic strength, which is described by a function of the concentration (c_i) and charge (z_i) of all ions in a solution ($I = \frac{1}{2}\sum c_i z_i$), and b is a positive parameter that can be adjusted and changes depending on the organic substance considered.[19] Milne et al. (2003)[37] sets b to 0.57, which is an often-used value for FA. The activity of compound i within the Donnan volume is used in the NICA part of the model to calculate the amount of ion i bound to the organic substance. The concentration (activity) is now corrected by the Boltzmann factor (= exp(-FΨ/RT)).[17, 19]

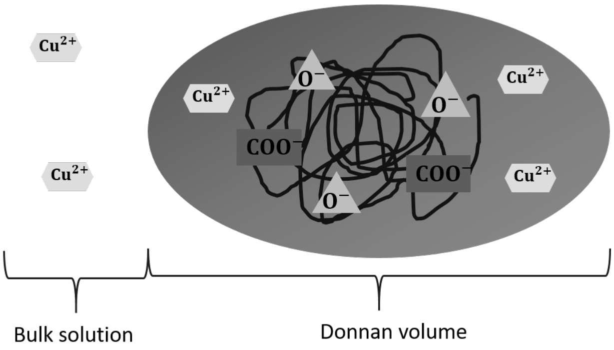

Fig. 4. An illustration of the concept of the Donnan volume (V_D). The Donnan volume surrounds the dissolved organic matter (DOM), with its functional groups (COO^- and O^-), and the associated cations (here represented by copper).

The NICA component accounts for heterogeneity

The NICA part of the model can be interpreted as a competitive binding model in heterogenic systems.[18] By using continuous distribution of the site affinities of DOM it is possible to account for the heterogeneity of the binding sites.[17] The model can predict competition between different cations such as trace metals, protons and alkali-earth metals by adjusting parameters to different heterogeneities and binding stoichiometry.[19, 22, 37] The NICA model is derived from the Hill equation where the fraction of compound i bound to sites is expressed as a function of an affinity constant (K), activity of ion i (a_i) and the stoichiometry of the binding reaction (n).[16-18] Although a simplification, the distribution of affinity sites is described as a continuum where the general shape of the proton and metal affinity distributions are expressed with the same expression, i.e. have the same shape, but can be shifted along an affinity axis (Fig. 5).[18] The affinity spectrum does not reflect reality as ligands should be considered as discrete components. The distribution peak corresponds to the affinity constant (K) that is most probable to control metal complexation.[25]

The NICA component accounts for heterogeneity

To describe the heterogeneity of the sites, only one more variable (the Sips parameter (p)), specifying the width of the affinity spectrum, must be added.[19] Eq. 7 describes the specific fraction covered by compound i in a multi component system.[19]

$$\theta_i = \left(\frac{(K_i a_i)^{n_i}}{\Sigma(K_i a_i)^{n_i}}\right)\left(\frac{\Sigma(K_i a_i)^{n_i})^{p}}{1+(\Sigma(K_i a_i)^{n_i})^{p}}\right) \qquad \text{(Eq. 7)}$$

where the first part on the right side describes the fraction of binding sites covered by ion i and the second part calculates the total number of sites that are occupied by any ion.[19] n is ion specific and describes the non-ideality of the ion (examples given in Fig. 6). p represents the heterogeneity of the organic compound and has the same value for all ions considered.[17] The total amount (Q_i) of metal bound to organic matter can be expressed as Eq. 8:

$$Q_i = n_i \theta_i Q_{max,i} \qquad \text{(Eq. 8)}$$

where Q_{max} is the maximum sites that can be occupied by ion i and n_i is the again non-ideality parameter. To keep the model thermodynamically consistent and describe the exchange ratio between metal bound and protons released, the maximum number of sites that can be occupied by ion i is scaled to the non-ideality parameter of protons (n_H) changing the expression to Eq. 9:

$$Q_i = \frac{n_i}{n_H} \theta_i Q_{max,H} \qquad \text{(Eq. 9)}$$

where $Q_{max,H}$ is the maximum amount of affinity sites that can be occupied by protons. The absorption maximum Q_i is thus ion specific and connected to the non-ideality term of the ion.

When n_i/n_H is less than 1, multidentism occurs, which means that the maximum amount that can be bound is less than the total site of protons. If n_i/n_H is more than 1 this is called cooperativity where the maximum amount that can be bound is larger than the total site of protons.[18] The exchange ratio describes the interconnection between protons released/bound with metals bound/released.[18] When investigating proton affinity distribution with FA and HA there are two broad peaks, illustrated in Fig. 5, corresponding to two different binding sites: one weaker, low affinity, with lower pK_a (the carboxylic group) and one stronger, high affinity, with higher pK_a (the phenolic group).[17-18] Combining equation 7 with equation 9 and accounting for the bimodality, i.e. the two different binding sites (carboxylic=1, phenolic=2), gives the final equation (Eq. 10):[26]

$$Q_{i,T} = \frac{n_{i1}}{n_{H1}} Q_{max1,H}\left(\left(\frac{(K_{i1} a_i)^{n_{i1}}}{\Sigma(K_{i1} a_i)^{n_{i1}}}\right)\left(\frac{\Sigma(K_{i1} a_i)^{n_{i1}})^{p_1}}{1+(\Sigma(K_{i1} a_i)^{n_{i1}})^{p_1}}\right)\right) +$$

$$\frac{n_{i2}}{n_{H2}} Q_{max2,H}\left(\left(\frac{(K_{i2} a_i)^{n_{i2}}}{\Sigma(K_{i2} a_i)^{n_{i2}}}\right)\left(\frac{\Sigma(K_{i2} a_i)^{n_{i2}})^{p_2}}{1+(\Sigma(K_{i2} a_i)^{n_{i2}})^{p_2}}\right)\right)$$

(Eq. 10)

where Q is site density, $K_{i,x}$ are the median affinity constants, $n_{i,x}$ are stoichiometry between the ions and binding sites and p_x are the widths of the affinity distributions. These parameters are independent of pH, salinity and metal concentration.[19] Table 1 shows previously empirically determined parameters of the NICA model, describing interactions between the fulvic acid and four different cations. The NICA-Donnan model separates the effects due to the generic heterogeneity, which are the same for all ions, from the effects that are ion specific. The specific interactions are the bindings between the cation and the negatively charged functional groups associated with the organic matter while the non-specific interactions are the residual negative charge of the entire molecule.[17]

Preliminary findings and final remarks

During simulations of voltammetry experiments (reversed titrations), where labile copper con- centration was determined using salicylaldoxime (H_2SA) as a ligand, the combination of the two models resulted in some interesting findings. Usually, a calibration curve is constructed based on the response from the voltammetry analysis and a known amount of $Cu(HSA)_2$ in the solution. Comparing experimental data with the model simulation revealed that at low pH and low concentration of H_2SA, the calculation does not correspond to the measured data. Adding chloride (a major ion in seawater) as a potential ligand means that two complexes ($Cu(HSA)_2$ and CuClHSA) cause a response, and incorporating this into the model resulted in a much better fit between model and reality (Fig.7). The best way to evaluate and simulate

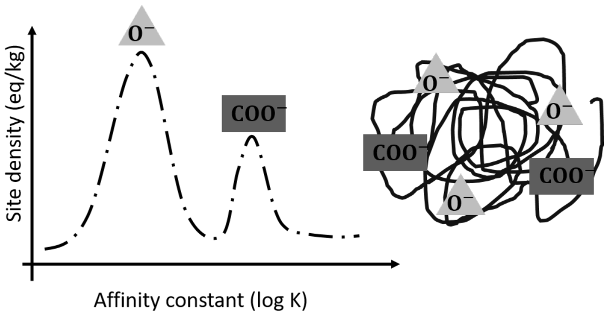

Fig. 5. A representative affinity spectrum of a fulvic acid, with its two most prominent binding sites, phenolic and carboxylic functional groups, highlighted

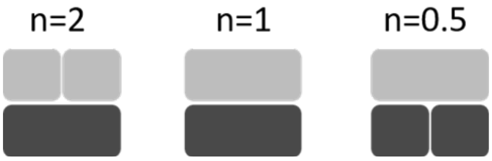

Fig. 6. An illustration of three examples of the stoichiometry of the binding reaction. The functional group(s) are the dark squares and the binding cations are the light squares.

Table 1. Table showing previously determined constants for the NICA model describing the behaviour of fulvic acid with one strong and one weak type of binding site. These constants are determined empirically through fitting of experimental data. For more information and additional determined parameters, see Milne *et al.* (2003).[37]

	Weak sites (COO-)		**Strong sites (O-)**		**References**
	$Q_{max, H1}$	p_1	$Q_{max, H2}$	p_2	
	5.88	0.59	1.86	0.7	Milne *et al.* (2003)[37]
	$logK_1$	**n_1**	**$logK_2$**	**n_2**	
H^+	2.34	0.66	8.60	0.76	Milne *et al.* (2003)[37]
Ca^{2+}	-2	0.85	-3	0.8	Milne *et al.* (2003)[37]
Mg^{2+}	-2.1	0.77	-2.4	0.59	Milne *et al.* (2003)[37]
Cu^{2+}	0.26	0.63	5.26	0.56 (0.36*)	Avendaño *et al.* (2016)[38] (*determined by author)

the experimental data, where both inorganic and organic speciation at high ionic strength must be described properly, is by combining the Pitzer model with the NICA-Donnan model, described throughout this text. This method can provide a new tool for analysing the chemistry of complex solutions such as seawater. The preliminary finding of a potential additional electroactive ligand (Fig. 7) could not only change the way voltammetry results should be interpreted but also highlights the advantage of using models to investigate knowledge gaps and simulate scenarios without consuming large amount of time and money.

More knowledge regarding the most common organic ligands and their properties must be prioritised in order to construct generic models for the marine environment. The Pitzer model and the NICA-Donnan model can be combined successfully, accounting for the high ionic strength of seawater and simplifying the complex behaviour of organic ligands. All models and analytical methods include fitting of parameters and/or constants and should therefore be tested, evaluated and developed by large high-quality datasets which have been produced in controlled ways following identical procedures. All sampling and *in situ* measurements are snapshots of the reality we live in and it is therefore important to gather as many snapshots as possible if we want to be able to develop and use generic models to predict future scenarios.

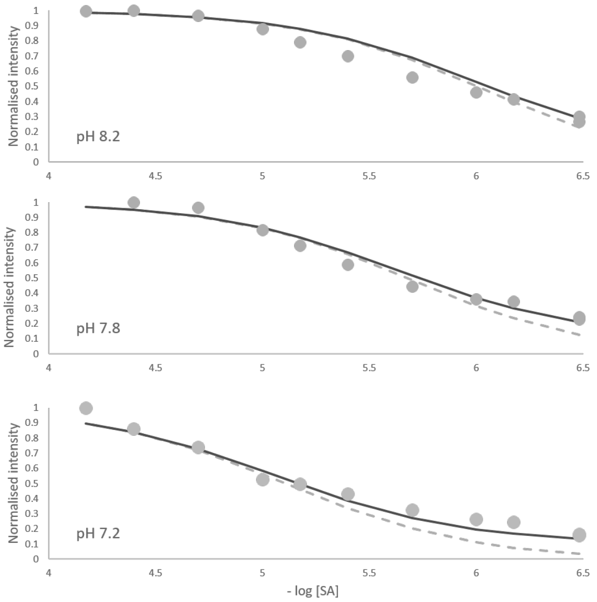

Fig. 7. An illustration at different pH of how models can be used to improve our understanding of experimental results. The experimental data (grey filled circles) can be compared with simulation of the experiment using a model accounting for organic speciation only (dashed line) and with a model that incorporates an additional electroactive complex (CuClHSA) described by both inorganic and organic speciation (solid line).

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Determining the provenance of the water source by measuring strontium isotope abundance ratios in beer and cider made in Dunedin, New Zealand

Tayla Hill

Department of Geology, University of Otago, PO Box 56, Dunedin (email: *hilta674@student.otago.ac.nz*)

Keywords: *isotopes, strontium, provenance, water source*

Growing up in Taranaki, I intuitively had an appreciation for the natural environment. This resulted in me pursuing a degree in geology and oceanography at the University of Otago. I am currently a 3rd year student with a particular interest in using geophysical techniques to study the seafloor. Undertaking a geochemical study on beer and cider was very different for me but nonetheless something I quickly grew passionate about.

Introduction

The isotopic composition of strontium (Sr) is not just a useful indicator of the ages of rocks and minerals, but it also contains information about the origin of igneous rocks and about the geological processes that have affected their chemical composition. Strontium is an alkaline earth element. Its ionic radius (1.18 Å) is very similar to that of calcium. Sr tends to substitute for Ca in minerals such as gypsum. Sr has four naturally occurring isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. All four of these isotopes are stable, with the fraction of ^{87}Sr subject to variation due to the radioactive decay of ^{87}Rb.[1] It is relatively widely distributed in groundwater, as well as in some surface waters near coastal regions.[2] The relative proportion in groundwater can allow for the determination of relative proportions of materials entering and leaving an ecosystem.[1] Recently there has been growing interest in the provenance of beverages, with beer being one of the largest shares in the global alcoholic beverage market, there are few studies that have been performed in terms of elemental and isotopic composition.[3]

The aim of this study was to investigate the claim that a local brewery uses spring water sourced from a basaltic aquifer. During the brewing process, it is likely spring water is used directly from the aquifer, as well as a mixture of other additives to the water. The strontium isotopic value of the spring water from the aquifer was compared with the beer brewed on site. It was hypothesised that the spring water collected from the tap on site would have fairly similar values to that of the beer, as this water is supposedly used during the brewing process. We also measured the strontium isotopic values of hops and malt, which in New Zealand are all sourced from the Nelson/Motueka region. This was to investigate if they have any effect on the Sr isotopic values in beer and cider.

Methods

The experiment began by collecting the beer, cider and spring water directly from a local commercial brewery. The spring water was collected both in a plastic 1.25 L bottle and an acid washed bottle (referred to hereafter as SSW and AW respectively). The samples were then brought back to the clean lab where they were prepared for analysis. Weighed splits of the samples were then dried down in a Teflon digestion vessel and the weight was measured and recorded. Then 5 mL of concentrated nitric acid was added into the sample and transferred over to autosampler vials and submitted to the Centre of Trace Element Analysis. From the data obtained from the Centre, the concentration data was determined for the second split.

Based on the concentrations obtained from the trace element analysis, the mass of each sample required to be dried down in order to gain 2000 ng of Sr was calculated. This was because in order to prepare the samples for isotopic analysis a minimum of 1000 ng of strontium was needed, so a split of 2000 ng was prepared. For the solid samples, instead of leaching 400 g of hops to obtain 5 µg Sr, a new split was weighed out and completely digested. An appropriate amount of sample was then measured out and again dried down at 120°C. Once dry, 10 mL of concentrated nitric acid was added to the sample and left to heat overnight at 80-90°C, allowing for reflux to occur. Adding the nitric acid was necessary as it oxidises as much of the organic matter as possible to avoid issues with subsequent steps. The solutions were then transferred into microwave digestion vessels, and transferred to a microwave oven to digest any excess organic matter.

The samples were then once again dried down on hot plates. 1 mL of 7N nitric acid was added to the dried down sample. The digested samples were then run through a Teflon column containing 250 µl of Sr-specific ion exchange resin, which allowed for ion exchange chromatography to occur. Essentially, this was done to remove any impurities and interfering ions within the strontium split. The isotope masses of Sr that were being measured in this experiment were 84, 86, 87 and 88. There is a direct isobaric inference of ^{87}Sr with its parent isotope ^{87}Rb, which would lead to an overestimate of the ^{87}Sr/^{86}Sr of the sample. Therefore, it was critical to remove Rb from the Sr sample using the resin. If there was still a high Rb concentration left in the split after ion exchange, the ion exchange step had to be repeated a second time prior to mass spectrometry.

The data were then finalised and ranked from highest to lowest isotopic composition. A comparison between the tap beers and the spring water was then made. Further comparisons were made with an independent brewer's beer, which was a local home-brewed beer using standard Dunedin tap water. From this, it could be determined which samples might be related to the use of different ingredients or ingredients from different sources.

Results and discussion

The Sr concentration and isotopic data are presented in Fig. 1.

Fig. 1, a plot of Sr isotopic composition versus Sr concentration, shows a negative trend. As the concentration increases, the ratio of ^{87}Sr/^{86}Sr decreases. The most notable aspect of the samples in Fig. 1 are that the range of the Sr isotopic composition of all the beer and cider samples are similar to each other but all are significantly different from the spring water samples (SSW and AW). The beer and cider samples are together, ranging from 0.707846- 0.709174, showing a homogenised relationship. Amongst the cluster is the local brewer's beer (Fig. 1); this sample fits within the same range as the commercial brewer's beer, even though the local brewer uses tap water from a different aquifer.

Fig. 2 shows that the ^{87}Sr/^{86}Sr ratio of the spring water collected in the acid washed bottle (AW) and the standard plastic bottle (SSW) are the same to 4 decimal places. This ratio was higher than that of the basalt in the area which is approximately 0.703.[4] All measurements were within the range of Dunedin volcanic rocks.

The origin of water used in brewing, whether from carbonate or silicate rock, can be detected using ^{87}Sr/^{86}Sr ratios.[5] The ratios for the spring water collected in the plastic bottle and the acid washed bottle in this study were the same (Fig. 2). This implies that when collected, the samples of beer and cider were not contaminated in any way by the bottles given to us by the brewery. The spring water and acid washed bottle were within the same range of the ^{87}Sr/^{86}Sr ratio of basalt rock in the area, with a value of ~0.703. This shows that the aquifer is associated with the basalt, but not purely in contact with it.

It was perplexing to find that the beer and cider samples which are supposedly made using the spring water had significantly higher values for isotopic ratio, but lower Sr concentration compared to the spring water. This was thought to potentially be due to other factors used throughout the brewing process such as ingredients e.g. malt and hops. If the spring water was indeed the primary source of the brewing water, these results suggest that somewhere through the process, the strontium concentration is lost. It had been expected that the general trend of the data would show that as the concentration of Sr increased, so would the ^{87}Sr/^{86}Sr ratio but Fig. 1 shows the opposite trend. This could be due to the Sr being adsorbed onto the solid materials with which it is in contact, such as the malt and hops.

As seen in Fig. 1, the malt and the hops have a higher ^{87}Sr/^{86}Sr ratio in comparison to the spring water. Since the values of the beer range between 0.708180- 0.709174, and the malt lies at 0.708895, this could potentially mean that the Sr ratio increases due to a source from the malt. However, previous studies analysing the ^{87}Sr/^{86}Sr ratio in red wine showed that neither biological nor winemaking and ageing processes are able to change the ^{87}Sr/^{86}Sr values.[6] This implies that there is not enough Sr in either yeast or bentonite to affect the Sr isotopic composition of red and white wine. When the ^{87}Sr/^{86}Sr ratio in red and white wine associated with two different volcanic rocks was compared, it revealed that isotopic values throughout

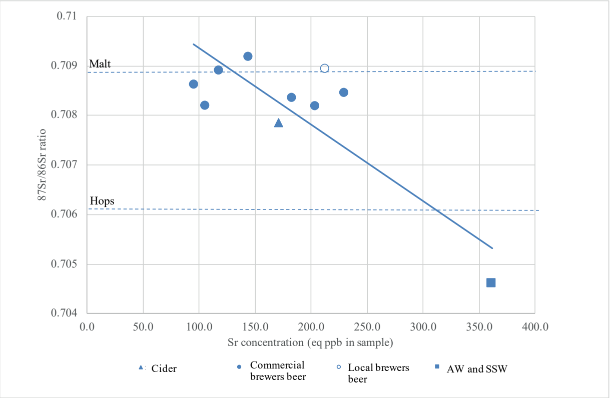

Fig. 1. Concentrations of strontium in ng/ml (ppb) in 5mL dilution of sample against the ^{87}Sr/^{86}Sr ratio normalised to the International Standard SRM 987

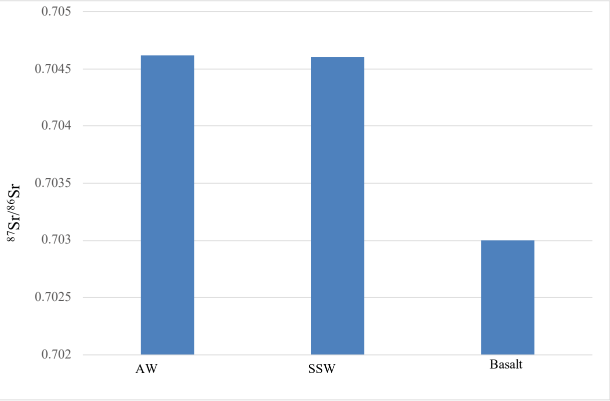

Fig. 2. Comparison of ^{87}Sr/^{86}Sr ratios in spring water and local basalt rock

the years were in a narrow interval at different levels dependent upon the vineyard of provenance rather than the addition of either yeast or bentonite.[6]

Plotted within the cluster is the local brewer's beer (Fig. 1). This was interesting because the local brewer uses Dunedin tap water in their beer, sourced from a different aquifer to the commercial brewer's beer. Potential reasons to explain why the Sr value is higher than expected could be because the water treatment applied to Dunedin city tap water includes addition of calcium sulfate (gypsum) and calcium chloride. The mean $Sr^{87}/^{86}Sr$ ratio for carbonates is 0.7065 + 0.0003.[7]

Another interesting find was that the Sr concentration in cider coincided with the clustered values for beer. The process used to make cider is completely different to making beer, as cider is fermented where beer is brewed. It also has no traces of hops or malt in its ingredients. This provides further evidence that the addition of these ingredients is unlikely to affect the strontium concentration.

Another potential reason for the Sr concentration being significantly different from the spring water value could be due to the dilution of water through the brewing process. The water used in the brewing process must be free of taint and be sterile. This is normally achieved through treatment of the water by passing it through a purpose-built plant involving a trap filter to remove the solids. A carbon filter is used to remove chlorine residues and inert gas stripping or vacuum stripping to remove oxygen.[8] Water used in breweries can be treated more than once to adjust the composition. These treatments can include reducing or increasing the number of organic compounds in beer, with calcium ions in particular influencing the mashing processes – a term for the hot water steeping process which hydrates barley and converts the grain starches into fermentable sugars. With the local brewer's beer revealing a similar Sr concentration and ratio as the commercial brewery, it could be possible that they treat the water in a similar way as the Dunedin tap water by adding calcium sulfate. In brewing, this tends to be added to the mash in order to increase the hardness of the water as well as lowering the pH.

Conclusions

The comparison of Sr concentration between the beverages, spring water, hops and malt indicate that the local commercial brewery products do not relate in a simple way. When the Sr value of the spring water collected from the aquifer was compared to the beer brewed on site, it was recognised that the aquifer had a much lower Sr ratio than the beer. This proved to be very different from what was originally hypothesised, as it was believed they would have similar values. The measured Sr values from the malt and hops also proved to have no direct impact on the isotopic composition of the beer. It is more likely that the additives to the water, as well as the treatments that are applied, such as the removal or addition of certain chemicals and minerals, are more likely affecting the Sr values.

Outstanding questions that could be investigated further in the future could include comparing the Sr values of the spring water with the Dunedin city tap water, as they both come from different sources in at least some cases. A potential investigation into different chemical components in the different aquifers around Dunedin would also be interesting. An investigation into the origin of the hops and malt and the Sr isotopic values from them could also be investigated as they potentially have an independent value determined by their geographic origin.

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Celmisia, New Zealand's alpine daisies: assessing a sticky situation to "trichome" up with some answers

David Rubin

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin (email: *rubda327@student.otago.ac.nz*)

Keywords: *natural products*, Celmisia, *trichomes*

I moved to Dunedin with my family in late 2016 from Fort Dodge, Iowa, to study at Otago University. Having recently completed my BSc majoring in chemistry, I decided to pursue a Master's degree. I enjoy studying chemistry due to its versatility. It is a great tool for appreciating one's place in the world. When I am not at the university I enjoy attending to the needs to my three little children and making my wife laugh. If you would like to know what my Master's inquiry is about keep reading.

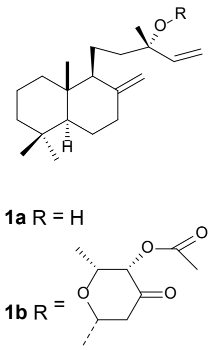
Introduction

Celmisia, New Zealand's alpine daisy genus, belongs to the Asteraceae plant family. This is the second largest family (after Orchidaceae) of flowering plants, comprising over 25,000 species and nearly 1300 genera.[1] *Celmisia* comprises sixty one species endemic to New Zealand, with a further eight endemic to Australia.[2] *Celmisia*, known as tikumu or puakaito to Māori, is an important genus, adding unique character to the alpine regions of New Zealand. The distinct, yet familiar, flower heads that arise in many species of this genus give credence to the colloquial name, New Zealand mountain daisies.[3-4] The genus has a diverse range of leaf morphologies which are a wonder to behold (Fig. 1).

Celmisia viscosa is a New Zealand endemic subshrub with very viscid (sticky), 6-8 cm leaves. A 2013 study by Sansom *et al.*, of Plant and Food Research at the University

Fig. 1. Morphological differences can be clearly observed between the four species of *Celmisia* shown. Top left: C. *prorepens*; top right: *C. viscosa* from the Rock and Pillar Ranges, Otago. Bottom left: *C. semicordata*; bottom right: *C. hookeri*. (Images courtesy of Janice Lord).

of Otago, reported a high yield of epimanool (Fig. 2), an unexpected find, from the leaves of *C. viscosa*.[5]



1a R = H

1b R =

Fig. 2. Structures of epimanool (**1a**) and 2,6-dideoxy-hexopyran-3-acetate (**1b**)[5]

The ecology of *C. viscosa* was investigated in 2006 by Thomas Long, a PGDipSci student of Dr Janice Lord of the Botany Department at the University of Otago.[6] Long's research focused on the insect-plant interactions of *C. haastii* and *C. viscosa*. Long sought to understand whether insect herbivores alter plant distributions in alpine environments. His research found that external microscopic structures known as trichomes affect the feeding patterns of these insects with those in captivity preferring to be on *C. viscosa* leaves but preferring to feed on *C. haastii* leaves which had trichomes selectively removed. Trichomes originate from the epidermal cells of a plant and are found on many species of *Celmisia*. Trichomes have been characterised as those that produce secretions and those that do not. Large quantities of these secretory trichomes accumulate on plant surfaces, perhaps serving defensive purpose.[6-7] Long's study backed up this claim, inferring that trichomes protected against predation.[6] The chemical properties of trichomes which lead to the predation patterns observed are of interest to my research.

Celmisia and its historic uses

Māori used *C. spectabilis* and *C. semicordata* to produce clothing such as raincoats, cloaks and hats. The stiff and leathery leaves of these two species act as a fire retardant. Māori found that dried woven leaves act as good leg protectors while the soft under leaves could be used to produce water proof clothing. Other uses included hair decorations and ear adornments. Tūhoe transplanted puakaito, *C. spectabilis*, for use as a perfume.[4,8]

European settlers found the plant fibres, equivalent to fine cotton, useful for wound dressings.[4] Otago settlers found *C. prorepens* and *C. angustifolia* leaves a worthy substitute for tobacco and an antiasthmatic.[8]

Utilising natural product chemistry for knowledge and profit

Today it is possible to study the chemical properties inherent to *Celmisia* which gave it utility. Natural product chemistry studies secondary metabolite products of plants, animals, insects and marine organisms and microorganisms. Secondary metabolites have a broad range of structures and functions. Classes of these compounds include alkaloids and flavonoids.[9] Flavonoids contribute to plant colouration and assist plants in forming symbiotic relationships while alkaloids are believed to act as repellents toward predators, parasites and other plants. A widespread and ancient flavonoid, flavonol (Fig. 3), acts as a signalling molecule to a wide range of stress-inducing agents while a commonly ultilised alkaloid, nicotine (Fig. 3), is an antiherbivore compound.[9]

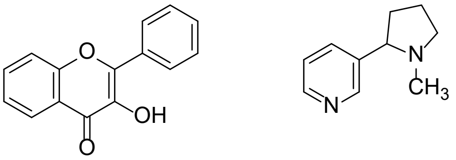


Fig. 3. Structures of flavonol (left) and nicotine (right)

Secondary metabolites are not essential to survival, playing no direct role in reproduction and growth, yet they assist organisms to diversify thereby gaining an evolutionary advantage.[10] An understanding and subsequent utilisation of natural products is important for many human endeavours, due to their biological activities. These compounds are used for enhancing crop production and producing pharmaceuticals; in fact 34% of clinically used pharmaceuticals are derived from natural products. Furthermore, they also offer a wealth of industrial applications such as production of novel flavours, fragrances and resins.[10]

Aside from the potential profits to be had in utilising the chemistry of a plant, a wealth of knowledge can be derived by understanding how the underlying chemistry places plants in relation to each other, a discipline known as chemotaxonomy. Chemotaxonomy is a method of biological classification, categorising organisms based on production of similar chemical compounds.[11] Chemotaxonomic findings can be informed by the groupings of plant taxonomy as well as historical documentation of plant uses.[4,8]

Factors impacting plant chemistry

A number of studies have been undertaken quantifying the amounts of secondary metabolites present in various plants as a function of environmental conditions. As differing classes of secondary metabolite are biosynthesised by varying biochemical pathways, the production of these compounds is strongly affected by a range of abiotic and biotic factors which inevitably leads to either a reduction or over-production of these metabolites depending on the role they play for the plant.[12]

Abiotic effects such as temperature, altitude, light exposure, carbon dioxide levels, drought and over- and under-nutrition have all been shown to impact production of various secondary metabolites. Research has shown that light exclusion acts to enhance purine alkaloid levels in tea leaves.[13] Another study found positive correlations between light intensity, quality and duration and the amount of ginsenoside, a saponin, produced.[14] Elevated CO_2 levels have been found to increase the concentration of phenol compounds, such as tannin, while there is a negative correlation between these compounds and altitude.[15-16]

Biotic effects on the chemotaxonomic profile of plants is more complicated than abiotic effects. The plant interacts with a range of microorganisms and insects all of which impact the chemical makeup of the plant. Further, plants have an intricate physiology, the study of which is known as phenology.[17] Plants have a range of key life cycle events which are influenced by seasonal and interannual variations in climate and overall habitat. Plant physiology is deeply influenced relative to the time of year with distinct phenophases being seasonally distributed, the variation is commonly mischaracterised as seasonal variability, failing to characterise plants ultradian rhythms. These variations have a cumulative affect over the life time of the plant.[17]

Previous research on *Celmisia*

Abiotic effects on the chemistry of various *Celmisia* species, particularly *C. viscosa*, have been studied. Seasonal variation was characterised for the carbohydrate and lipid cycles of *C. viscosa* and other species of *Celmisia* in a 1974 study by Hadley *et al.* of the University of Illinois.[18] Carbohydrate and lipid build-up and depletion was observed throughout the plant over the growing season, with particular depletion occurring during late summer to early autumn. At the beginning of winter carbohydrates accumulated in some tissues ceasing soon after while lipids increased throughout winter.[18]

Other abiotic effects have been studied by White-Monsant *et al.* of La Trobe University. Changes in vegetation composition due to antecedent fire and experimental warming were invetigated.[19] Extraction of *C. pugioniformis* found a decreased nutrient composition of the plant with carbon composition of the leaves decreasing upon environmental warming but not antecedent fire. If an accurate chemotaxonomy of *Celmisia* is to be obtained such seasonal changes and the effects of environmental warming needs to be accounted for in modelling.

Biotic effects of plant chemistry are much more subtle and require an understanding of how plants are affected by other organisms in their environment. With the right application findings can be used to infer chemical properties. In a recent conversation, Dr Daryl Rowan, who completed his PhD at the University of Otago and currently works for Plant and Food Research, informed us that the feeding patterns of the takahe bird had been studied extensively in the 1970s. This research found that *C. petriei* is a vital source of nutrition for takehe who prefer eating the sugary leaf bases of the plant. It is conversations such as these which lead to a vast source of further information when conducting research.

Some natural products chemistry has been established in part for three species of *Celmisia*. Epimanool, a diterpenoid secondary metabolite that exhibits antibacterial properties in plants is also an epimer (C-13) of a starter in the perfume industry, manool, a compound studied extensively by Professor Peter Grant and his students at the University of Otago.

Epimanool (Fig. 2, **1a**), and an epimanool derivative with 2,6-dideoxy-hexopyran-3-acetate (Fig. 2, **1b**) were extracted from a *C. viscosa* plant from Mt Terako, Marlborough with structural elucidation achieved using high field ^{1}H NMR and ^{13}C NMR for **1a** and the further use of COSY and HMBC correlations for **1b**, with NOE interactions and coupling constants used to determine the stereochemistry. Successful growing and harvesting of *C. viscosa* may create a useful, sustainable alternative to pink pine.[5]

Saponins, which may enhance nutrient absorption on plant surfaces, have been reported from two species of *Celmisia*.[20-21] Saponins, for example that in Fig. 4, are a class of natural products which have surface active properties. These molecules, although toxic, can lower plasma cholesterol in humans, playing an important role in reducing the risk of many lifestyle diseases.[22-23] The exhibition of cytotoxic effects against cancer cell lines indicates potential anticancer activity.[23]

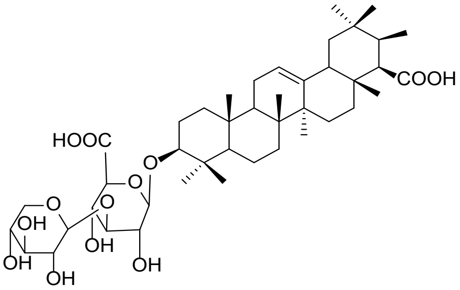


Fig. 4. Triterpenoid saponin[24]

Two distinct noroleanane saponins (Fig. 5) were extracted from the underground parts of *C. spectabilis* plants collected from Mount Terako, Canterbury and two distinct saponins were extracted from the leaves of *C. petriei* plants collected from the Murchison Mountains in early autumn and late spring by researchers at Humboldt University, Germany and the University of Otago respectively. The saponins from the *C. spectabilis* extracts were successfully isolated from alcoholic extracts using column chromatography and preparative HPLC. They were structurally characterised using ^{1}H NMR and mass spectral data. The saponins from *C. petriei* were detected using a TLC antifungal bioassay system with isolation achieved using column and droplet counter current chromatography. Acid hydrolysis was used to identify arabinose and glucose sugars in a 2:1 ratio. This finding aided in the characterisation of the structures when analysing mass spectrometry, ^{13}C NMR and T_1 measurements. Hence, the sugar sequence and most of the linkage positions were confidently ascribed. The structure of the second saponin was further confirmed using a base hydrolysis conversion to the first saponin.[21] A question of interest in my MSc is whether unique saponins exist in other species of *Celmisia.*

Compound extraction was achieved with ethanol or chloroform. A range of techniques was utilised for further purification including silica column chromatography and reverse phase flash chromatography. Structural elucidation is achieved through the use of ^{1}H NMR, ^{13}C NMR, 2D NMR data and mass spectrometry, with stereochemistry confirmed through interconversions or data matching techniques.

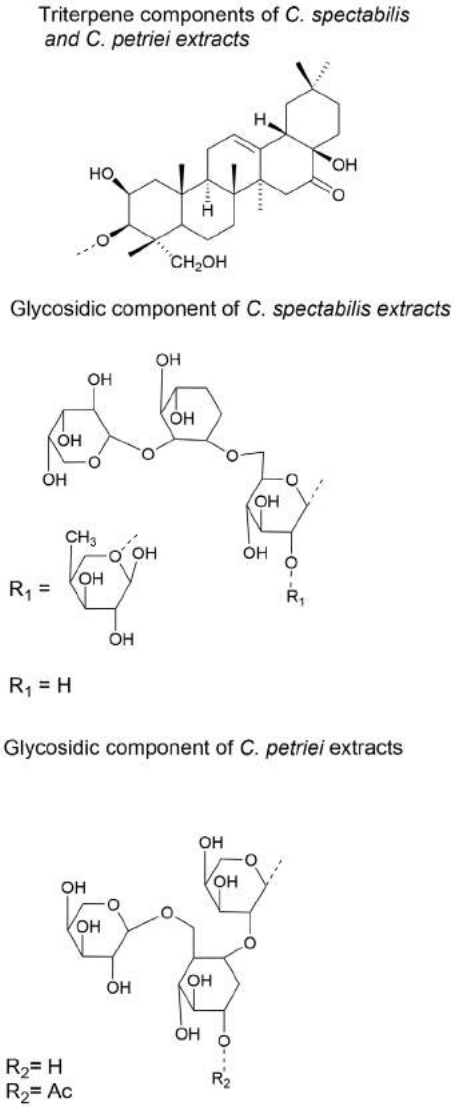


Fig. 5. Noroleanane saponins from *C. spectabilis* and *C. petriei*[21]

Previous chemotaxonomy study of a New Zealand plant, *Pseudowintera*, finds novel sesquiterpene dialdehydes

Sesquiterpene dialdehydes have a range of biological properties which protect organisms against various fungi. They also enhance the antifungal activity of actinomycin D and rifampicin antibiotics. [25] A commonly studied example of a sesquiterpene dialdehydes is polygodial (Fig. 6).

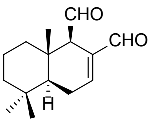


Fig. 6. A common sesquiterpene dialdehydes, polygodial

Pseudowintera, otherwise known as horopito, is a New Zealand endemic, genus of woody flowering trees and shrubs. Wayman *et al.* of Humboldt State University, investigated the chemotaxonomy of one *Pseudowintera* species, *P. inseprata*. Two sesquiterpene dialdehydes were characterised (Fig. 7), using the same methods discussed previously.[26]

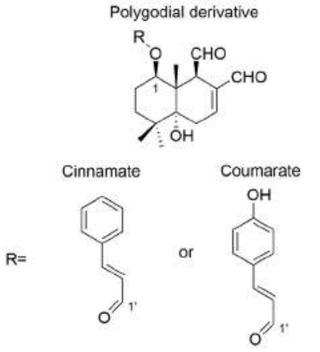


Fig. 7. A polygodial derivative extract with a minor component of cinnamate (left) and a major component of coumarate (right) at C-1

Conclusions

Previous research on the *Celmisia* genus has yielded a few novel results. Further study of the chemistry of *Celmisia* will utilise a range of analytical methods to characterise the chemical profile of these plants.

Any further novel chemotaxonomic findings from investigating *Celmisia* might be helpful in Māori product development from historic perfume uses. Furthermore, they may inform other ecological and taxonomic studies, thereby helping scientific disciplines to better understand evolutionary processes.

Results have started coming in and are yielding some interesting chemistry.

Acknowledgements

I thank Dr Janice Lord and Patricio Perez, Botany Department University of Otago, for images and *Celmisia* samples and also Professor Nigel Perry and Catherine Sansom of Plant and Food Research Otago for guidance and training.

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Happy 50th anniversary, Jim!

Professor Jim Simpson celebrates 50 years at Otago Chemistry

This year in 2019 we celebrate Professor Jim Simpson's 50th year in the Department of Chemistry at the University of Otago. Many people nowadays do not even stay in the workforce for 50 years, let alone at the *same* workplace, making this achievement all the more remarkable. Professor Jim Simpson is a true asset to and an integral member of all the chemistry that happens at the University of Otago. Originally from the UK, Professor Simpson obtained his BSc(Hons) degree (1964) and PhD (1967) from the University of Southampton before making the move to New Zealand to take up a lecturer position at the University of Otago in 1968. This offer was clearly important to Professor Simpson as he has kept a copy of his letter of offer to this day. The letter reads:

> *"Dear Dr. Simpson,*
>
> *I have pleasure in offering you appointment as Lecturer in the Department of Chemistry at the University of Otago…*
>
> *The commencing salary I am authorised to offer you is at the rate of $NZD 3,800 per annum.., increasing to $NZD 4,000 per annum..."*

Here's hoping he got paid a little more at the end of his career!

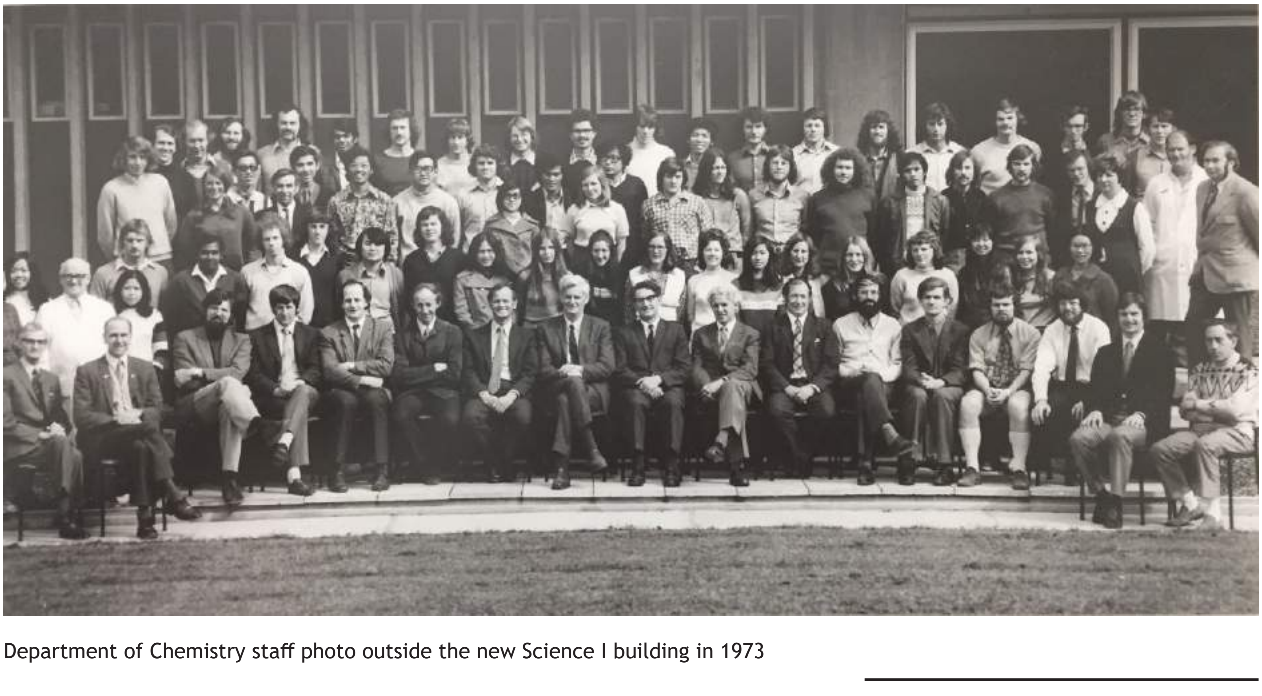
Coincidentally, Jim began in the Chemistry Department at the University of Otago just prior to the opening of the then state-of-the-art Science I building, which has very recently undergone a huge upgrade to be transformed into the brand new Mellor Laboratories (see the following article in this issue by Lyall Hanton). It was also the University of Otago's 100th anniversary and he is now witnessing the 150th.

In 1995, Jim Simpson was promoted to Professor and in 2015 became an Emeritus Professor of Chemistry at the University of Otago. Jim has had a very diverse career with noteworthy achievements including being Head of the Department of Chemistry from 1998-2004 and Head of Department of Botany for a year in 2010. During his time as Head of Department in Chemistry, Jim Simpson hosted New Zealand's second Nobel Prize winner in Chemistry, Professor Alan MacDiarmid. Jim was also involved in the approval of the installation of two NMR spectrometers, which, at the time, allowed the University of Otago to boast the most powerful NMR spectrometers in New Zealand. These instruments, and others, have allowed world class science to be carried out at this far flung corner of the globe.

Over his time working as a chemist, Jim has developed many research interests which include (but are by no means limited to) paramagnetic species derived from metal cluster carbonyls, organometallic compounds with multiple redox centres, fluorescent organometallic species, fluorescent polymers, polymer gels, X-ray structure determination and molecular graphics. However, some of his most interesting work has been surrounding validation and fraud prevention in X-ray crystallography.

Jim has this to say about his work regarding crystallographic fraud:

> *"In the early 1990s I became involved with the International Union of Crystallography (IUCr) and the Asian Crystallographic Association (AsCA). I helped organise and run AsCA conferences in Thailand and Malaysia and for many years was the NZ representative on the*



Department of Chemistry staff photo outside the new Science I building in 1973

Professor Jim Simpson (left) with Professor Alan MacDiarmid, winner of the 2000 Nobel Prize in Chemistry

Professor Jim Simpson helping undergraduate students with crystallography

AsCA Council. In 2004 I was invited to become a co-editor of the IUCr Journal, Acta Crystallographica Section E. Two years later I became a Main Editor of the same Journal. This editorial role led to involvement with fraud in X-ray publications. In 2008 we were alerted to some unusual similarities between papers from the same institution. A year of investigation, new software and increasing incredulity at the scale of the problem led to an Editorial announcing the frauds to the scientific community. Subsequently I was asked to take on the role of checking other possible frauds reported to the IUCr. This is a role I still have today but fortunately involves only a handful of investigations in a year, most of them from the time when such cheating was rife in the early 2000's or alternatively papers from totally incompetent authors! More recently I have been helping staff from the Cambridge Crystallographic Data Centre who are beginning to check their million entry database for similar problems. In 2015 I was appointed an inaugural Main Editor of IUCrData, a journal aiming for fast peer reviewed publication of structures that otherwise might not be seen in the public domain."

Jim's contribution to the Chemistry Department at the University of Otago is further exemplified through his huge contribution to teaching and developing the next generation of scientists through his supervision of 18 PhD students, 8 MSc students and 34 BSc(Hons) students. Furthermore, Jim has an outstanding 332 peer reviewed journal publications and has put New Zealand on the map through numerous international collaborations with other academics throughout North America, Asia, the Middle East and Europe.

Jim is a huge asset to the Chemistry Department and his long serving efforts are highly valued and he continues to make meaningful contributions both at the University of Otago and to the global scientific community.

From ugly duckling to real swan: transformation of the Science I chemistry laboratories into the new Mellor Laboratories at the University of Otago

Lyall Hanton

Department of Chemistry, University of Otago, PO Box 56, Dunedin
***(email:** lhanton@chemistry.otago.ac.nz)*

Keywords: *chemistry buildings, Mellor laboratories, laboratory refurbishment*

After nearly 47 years of use, the old Science I building, which housed all of chemistry's undergraduate teaching and some specialist research laboratories, has been transformed into a modern and effective teaching and research space. Science I has been renamed the *Mellor Laboratories*, in honour of Joseph William Mellor; one of the University of Otago's most distinguished alumni (see *Chemistry in New Zealand*, **2014**, *78(2)*, 85-89).

Joseph William Mellor CBE, FRS (1869-1938) was an Otago graduate (BSc and MSc) who became a ceramicist, a cartoonist, and a famous chemist. Indeed, his single-handed effort to complete his 16 volume definitive work '*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*' (1922-1937), amounting to over 16 million words, has never been equalled. From humble beginnings and self-initiated study at King Edward Technical School, Mellor obtained a place at the University of Otago, where he won a scholarship to study at Owens College, Manchester. As Principal of the Technical College (now part of Staffordshire University) at Stoke-on-Trent, he worked on refining refractory processes, especially high-temperature ceramics relevant to the steel industry. Mellor was elected Fellow of the Royal Society in 1927. Because of his contribution to the World War I effort he was offered a peerage, which he turned down.

The $56m refurbishment of the Science I building involved Leigh's Construction stripping the old building back to its bare-bones and rebuilding it, while adding a new air-handling system, new windows, a new roof and new exterior cladding and including "living walls" of ivy and a new pop-out extension from the first and second floors to house offices and student break out space. The ground floor of the building houses two flexible "super-labs" for Health Science First Year students. One of the labs used by chemistry can be divided into two for flexible teaching and includes iPads at each lab station. The ground floor also has a breakout space with 232 student lockers, each with a USB port for charging phones, a power socket and LED lighting. Students swipe their student ID cards at the locker terminal to be allocated a free locker – when they remove their belongings, the locker can be reassigned.

Among the improvements within the laboratories themselves was the installation of 67 fume cupboards mainly in the advanced chemistry teaching laboratories. The fume cupboard exhausts were combined for the first time nationwide because of a change in the regulations.

Advanced teaching laboratories

The 67 fume cupboards, which in the past had a single manifold exhaust fan that ran at a constant speed regardless of need, now have a single manifold with a tri-stack that has four fans (with three operating at any one time) servicing all cupboards that each automatically change speed or stop to reflect demand. Previously, if an exhaust fan failed, the cupboard failed. Now, if a fan on the tri-stack fails, three still operate. Because the exhaust duct is bigger, less fan power is needed to move air and disperse it into the sky. Those plumes are up to 50 metres high, so odours and contaminants are dispersed effectively. The rescue helicopter has been instructed to avoid the area when landing at Dunedin Public Hospital because of the force of the updraft from the tri-stack. Gone are the porcupine fume stacks of old. The fume cupboards now automatically draw minimal air if a lab is unoccupied, so not as much air is extracted from labs, reducing the need to replace air.

Controlling internal temperatures and air changes became more difficult as the building aged but now lab technicians can monitor air flow and quality with a system that signals green (good), amber (problems) and red (evacuate until issue resolved). The user-friendly controls also let technicians flick air exchange rates from ‘background’ to ‘full exhaust’ during rare incidents.

The building’s exterior promotes science and chemistry on campus for the first time. A central campus-facing entrance has large-scale steps and a 12.5 tonne steel three-storey, three-sided, abstract network and is the Division of Sciences’ gateway. It is both art and science but there has been controversy about the valence of some of the atoms depicted in the network. However, one chemist described it as a perfect representation of a random polymer network. A highway-facing wall has a 1.5 tonne metal lit-up representation of a laurenene molecule. This molecule has a unique chemical structure as it has four rings sharing a central flattened carbon atom. It is extracted from the rimu tree and was discovered by Otago PhD chemistry student Denis Lauren (1970) and named after him.

The building’s interior also references chemistry and colour. Foyer strip lighting represents molecules such as caffeine and adrenaline. The atrium hanging lights change colour and look like diatomic molecules. A hexagonal carpet pattern and hexagonal tiles reference graphitic or benzene-type materials. Window decals have a chemical network theme. Large lab windows let people inside and outside the building see science at work, including through a striking yellow-framed foyer window.

Left: southern exterior of the new Mellor Laboratories. Right: western exterior of the new Mellor Laboratories, featuring the structure of laurenene.

Interior of the Mellor building. Left: communal locker space; right: atrium.

Left: Clean Laboratory Suite vestibule. Right: ducted laminar flow cabinets and clean evaporation area.

The University was committed to people with disabilities being able to use this building as easily as everyone else. Swipe card access automatically allocates an accessible locker to students registered with Disability Information and Support. In the labs, there are some benches with buttons to lower to wheelchair height. There are fire refuges provided for people with disabilities that are impermeable to smoke, can withstand about 200˚C and are connected to campus security.

The Mellor laboratories also contain a new world class Clean Laboratory Suite that is virtually free of metals and produces filtered air 100,000 times cleaner than outside air. It is a timber-framed vinyl box, with vinyl walls to the bottom of the concrete floor above. Structural engineers worked hard to think of replacing metal securing pipes and wires in earthquakes with glass reinforced plastic. All pipes are plastic. Many screws are nylon or covered. The lab withstands strong acids used to extract trace elements from a wide range of substances – such as water, rock, food and agricultural products – to identify the underlying processes at work across a diverse range of applications from archaeology to climate change to biomedical research. Sensitive equipment identifies the concentration and isotopic makeup of trace elements down to the parts per trillion level or even lower in substances, so contamination from other metal specks, such as dust and rust, can be devastating. The lab now has two clean rooms – one for substances with higher metal contents and another for substances with lower metal contents, to avoid cross contamination. Experiments include examining rare meteorites for the solar system's origins, when second chances are rare. Air washes down over experiments in the lab's special 16 laminar flow cabinets – and people beside them – into vents that expel the air and potential contaminants.

Remarkably, the architects Parker Warburton Team Architects with Lab-Works Architecture transformed the building's brutalist concrete façade into a contemporary research institute. A student told the Otago Daily Times the labs make him feel like a "real scientist". At the New Zealand Architecture Awards in 2019 the Mellor Laboratories won the Southern Architecture Award and the Resene Paint award in the Education category.

Davy and the voltaic pile

Richard Sorrenson (email: *r.sorrenson@auckland.ac.nz*)

This article is one of a series on the history of chemistry authored by Richard Sorrenson. Richard is General Manager of the University of Auckland Foundation. He gained an MSc in chemistry from the University of Auckland and a PhD in the history of science from Princeton University.

The invention of the voltaic pile, what we now call a battery, originated from studies on animal electricity in Italy in the late eighteenth century and is one of the more unlikely stories in the history of science. Prior to its invention, no chemist could demonstrate with any persuasive force that chemical reactivity and electricity had anything much to do with each other. Electrical fluids were confined to animals (like electric eels) or could be generated by static electricity machines and poured into Leyden jars, but these fluids could not be poured out of the jars to influence chemical reactions.[1]

The battery changed all this. Despite not having been invented to be a tool of chemical analysis, it turned out to be one of the most powerful and influential instruments in the history of chemistry, revealing a host of elemental substances in the first decade of the nineteenth century.

That decade produced romantic heroes like Beethoven in Germany and Napoleon in France, men who rose from humble origins to great fame by dint of their genius, effort and self-promotion. It also produced one of the most remarkable of chemists, Humphry Davy in England. For Davy, a scientific genius was a "conqueror of nature, a discoverer of laws and a commander of instruments."[2]

Sir Humphry Davy (1778-1829), by Sir Thomas Lawrence (1769-1830), c.1821, oil painting on canvas in the possession of the Royal Society of London

The instrument that Davy commanded was a series of ever more powerful batteries that he deployed at the Royal Institution in London with significant funding from private patrons. He reported his findings in a series of papers to the Royal Society of London. His most famous paper outlined the results of using two batteries in combination – one of "100 plates of [zinc and copper] 6 inches [square]" and another of "150 of 4 inches" – on barely moist potash placed on "an insulated disk of platina."

The results were astounding and completely novel: at one of the points of electrification, "small globules having a high metallic lustre … appeared, some of which burnt with explosion and bright flame." In a similar experiment with soda and just the 100 plate battery of 6 inches square, he produced a substance which became "solid on cooling, and appeared to have the lustre of silver."[3]

In Davy's hands the battery reduced the formerly irreducible alkalis to "new & extraordinary bodies" which constituted the bases of soda and potash.[4] He confirmed this by a simple "synthetical experiment," namely, that the "metallic lustre of the substance [derived] from potash immediately became destroyed in the atmosphere" and the white crust which formed, "I soon found to be pure potash."[5] Both bases had a metallic lustre and were excellent conductors of electricity and heat and therefore appeared to be metallic despite their low specific gravity. A drop of basis of potash demonstrated a "beautiful" phenomenon when brought into contact with a drop of water, decomposing with "great violence" and an "instantaneous explosion" producing "a brilliant flame, and a solution of pure potash."[6]

With so extraordinary an instrument at his command, Davy reasoned that "barytes and strontites … through [to] lime, magnesia, glucina, alumina, and silex" would by means of batteries "sufficiently strong … yield … to the methods of analysis by electrical attraction and repulsion."[7]

Davy then procured a very powerful battery of "500 pairs of double plates of six inches" and learned (by means of a letter from the Swedish chemist Berzelius received in June 1808) that barytes and lime, when combined with mercury, could be reduced by a battery to a metallic amalgam. Davy confirmed this outcome and applied it to strontites and magnesia as well.

Davy however was not content with the amalgams; he wished to remove the mercury and did so through a series of very clever "distillations" which reveal him at the height of his chemical brilliance.[8]

Davy noted:

> *"These new substances will demand names: and on the same principles as I have named the bases of the fixed alkalies, potassium and sodium, I shall venture to denominate the metals from the alkaline earths barium, strontium, calcium, and magnium; the last of these words is undoubtedly objectionable, but magnesium has already been applied to the metallic manganese, and would consequently have been an equivocal term."*[9]

In just one volume of the *Philosophical Transactions* for the year of 1808, Davy announced six new elemental substances, one of the most remarkable bursts of creativity and productivity in the history of chemistry. None of this could have occurred without a completely new and unexpected instrument – the battery.

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7. *Ibid*, p 42.
8. Humphry Davy, "Electro-Chemical Researches, on the Decomposition of the Earths …" *Philosophical Transactions*, Vol 98 (1808), pp 333-370; Section III, pp 341-346 deals with the distillations to remove the mercury from the amalgam.
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