



# Chemistry

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Identifying natural products from their biosynthetic roots

Gertrude Elion: pioneer of drug discovery

Wastewater treatment in New Zealand: zeolites as a potential low-cost solution for heavy metal removal

Developing a periodic table for earth scientists

Priestley's new airs

Graeme Baxter Russell, 1937 – 2019

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**The New Zealand Institute of Chemistry  
Incorporated**

PO Box 13798  
Johnsonville  
Wellington 6440

Email: [nzic.office@gmail.com](mailto: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](mailto:catherine.nicholson@branz.co.nz)

**Publisher**

Rebecca Hurrell

Email: [rebeccajhurrell@gmail.com](mailto:rebeccajhurrell@gmail.com)

**Advertising Sales**

Email: [rebeccajhurrell@gmail.com](mailto: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>



15<sup>th</sup> International Symposium on Macrocyclic and Supramolecular Chemistry  
12<sup>th</sup> - 16<sup>th</sup> July 2020 **Sydney**

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## Comment from the President

Welcome to the New Year and the first issue of *Chemistry in New Zealand* for 2020. I am writing this the day after the close of the **NZIC2019 national conference**, and what a phenomenal conference it was. Our plenary and keynote speakers gave wonderful presentations to all the conference attendees, the invited streamed sessions were brilliant and our students did an amazing job in the oral competition. The poster session was buzzing with so many people presenting and others asking questions. Everyone seemed to have a great time at the conference dinner held in Christchurch Town Hall, with the band commenting that they've never seen such committed dancing from so many delegates at a conference! The conference was trending on Twitter each day and I had a lot of messages from those who couldn't come indicating that they were really sorry to be missing out.

On a more serious note I want to **reinforce the great stats we achieved in terms of equity**, with 57% female plenary speakers, 40% female keynote and invited speakers and nearly 50% female session chairs. This is a mark of our **commitment to the NZIC equity, diversity and inclusion policy** that was introduced in 2019.

It was a privilege to be able to give many students the opportunity to present oral contributions at the conference, and pleasing that many academics complemented the quality of their presentations. Congratulations to **Emma Wrigglesworth** who won the Best Oral Communicator student oral competition, and to **Sidney Woodhouse, Michael Meijlink, Lynn Lisboa, Hannah Johnston, Rami Elsayed** and **Daniel Chong** who all won prizes for their wonderful posters.

It was an honour to welcome **Cara Birch, Thimeth Wijesinghe** and **Isobel Masters** to the opening ceremony to collect their prizes for the IYPT2019 schools video competition. Cara and Thimeth were joint winners of the senior section and Isobel was highly commended in the junior section. Congratulations to you all.

I had a wonderful team of helpers in the lead up to the conference, with **Paul Kruger, Vladimir Golovko** and **Jan Wikaira** on the organising committee, and **Dr Samantha Bodman, Nic Bason, Hector Mancilla Diaz, Sarah Guy, Belinda Grashuis** and **Aliyu Ja'o** all doing an excellent job keeping the conference running smoothly and dealing with issues in a very professional manner. Great job, team!

Thank you again to all of you who came to the conference and contributed to its success, and for all your kind messages. A conference is as good as the delegates who participate, and it's fair to say that this one was excellent which is a wonderful reflection on you all. I'm looking forward to the next conference in Auckland in 2021; keep a look out for the save the date!

The **NZIC AGM** was held during the conference where we launched two new student prizes, formalising the **Stu-**



**dent Oral Communicator Prize**, which is contested during the conference, and introducing the **Brian Halton Award** for the best paper in the field of chemistry published by a New Zealand university student. It is a fitting tribute to the work that Brian did promoting students in New Zealand that this award is named in his honour. Details are available on the NZIC website and Council looks forward to receiving lots of strong nominations in June next year. The revised rules for the Institute were ratified at the AGM which is a big step forward for us. Michael Mucalo (Waikato) was confirmed as the incoming Vice President and I look forward to working with him on Council over the next few years. Council will be reconvening in February next year and I look forward to welcoming any new delegates to Council at that meeting. A reminder that the rest of our Council meetings are now done through Skype to enable us to reduce our travel commitment and also achieve more through smaller focussed discussions.

At the AGM we formally announced the winners of the 2019 NZIC prizes. Congratulations to **Justin Hodgkiss** (Maurice Wilkins Centre Prize for Chemical Science), **Bill Hawkins** (Easterfield Medal), **Russell Frew** (Shimadzu Prize for Industrial and Applied Chemistry) and **Richard Hartshorn** (sciPAD Denis Hogan Chemical Education Award). It is very pleasing that again the field for these awards was strong and the decisions took a lot of discussion. This is a reflection of the strength and depth of talent in chemistry in New Zealand.

With the conference done my attention now turns not only to the work I should have done this year (!) but also to representing the NZIC at the **20<sup>th</sup> General Assembly of the Federation of Asian Chemical Societies (FACS)** immediately before the **18<sup>th</sup> Asian Chemical Congress (ACC)** in Taiwan.

In 2020 I will be undertaking the traditional **President's tour** of the branches. This will be a great opportunity to reinforce the connections made at the conference, to meet lots of members and to interact with everyone throughout the year.

2020 will culminate in **Pacificchem** in Hawaii and I encourage you to start thinking about what sessions you will attend and how to get as many NZIC members there as possible. Remember, the more members who attend, the better the financial return to NZIC, which will subsequently allow us to do more as an Institute to support our members.

I hope you had a relaxing Christmas break and are raring to go for another year of great chemistry in New Zealand.

**Sarah Masters**

*NZIC President*



## New Zealand Institute of Chemistry

*supporting chemical sciences*

### January News

#### International Year of the Periodic Table competition results

To celebrate 2019 as the International Year of the Periodic Table, NZIC held two element-themed competitions. One was to compose a limerick and was open to chemistry and poetry enthusiasts of all ages. The other was to put together a video and was open to NZ students in Years 1-13.

#### Limerick competition results

Entries were assessed on originality and creativity, accuracy of the chemistry featured in the limerick and composition, including rhythm and rhyme. We got so many excellent entries for this competition – thanks to all of the participants!

The prize winners were:

First prize: Anna Greaney

A brown liquid you'll find in a jar

To distinguish between  
An alkane and alkene  
Orange to colourless – ta da!

Second prize: David Perl

A hydrogen all on its own  
has a wavefunction, perfectly known.  
But combined with another,  
As Erwin discovered,  
a solution just can't be shown.

Third prize: Delene Holm

"It's better to give than receive"  
said hydrogen, aiming to please.  
"My electron is yours.  
Please take it because  
I'm positive after it leaves."

#### Student video competition results

Students were asked to submit a video about their favourite element of the periodic table. Again, there were some amazing submissions and the

judges had a hard time deciding on winners. For that reason, a decision was made to award first equal and third equal prizes, as well as several highly commended videos. The winners were:

#### Junior Group (Years 1-8)

**First equal prize (yes, they are sisters!)** Kaite M (Year 6, Glenbrook School) for her video on radium  
Lara M (Year 4, Glenbrook School) for her video on copper

**Third equal prize** Dani Simmons and Caitlin Murphy (Year 7, Dannevirke South School) for their video on silver  
Rhian, Siena, and Laila Telfer (Year 6, 6, 4, Wanaka Primary School, College St. Normal School and Wanaka Primary School respectively) for their video on titanium

**Highly commended** Stefan Foster (Year 8, home schooled) for his video on oxygen  
Joshua Crowley (Year 6, St Clair School) for his video on gallium

Abigail Crowley (Year 3, St Clair School) for her video on boron Zander Lyall and Ritcheson Bamola (Year 7, ACG Strathallan) for their video on helium Ella Sexton and Arizona Rogerson (Year 7, Blockhouse Bay Intermediate) for their video on tin Isobel Masters (Year 4, St Margaret's College) for her video on helium

### Senior Group (Years 9-13)

**First equal prize** Thimeth Wijesinghe (Year 10, Christ's College) for his video on neodymium Cara Birch (Year 9, St Margaret's College) for her video on chlorine

**Third prize** Emily and Matthew Smith (Year 11 and 10, Cornerstone Christian School), for their video on radium

**Highly commended** Calvin Pooley (Year 10, Mount Albert Grammar School) for his video on sodium Poppy Gunson (Year 12, Kamo High School) for her video on carbon Jessica Dixon (Year 11, Botany Downs Secondary College) for her video on bismuth

All videos (including entries that did not win a prize) can be viewed on the NZIC YouTube channel at: [https://www.youtube.com/channel/UCatB-st0teRenhA\\_cS4zjy\\_w/videos](https://www.youtube.com/channel/UCatB-st0teRenhA_cS4zjy_w/videos)

### NZIC PRIZES

The fields nominated for each award were extremely strong again this year and the selection committees had a very difficult time deciding on the awards.

### Easterfield Medal

The winner for 2019 was **Dr Bill Hawkins, University of Otago**. The Easterfield award takes the form of a medal that was donated by the Royal Institute of Chemistry (now the Royal Society of Chemistry) in honour of the late Sir Thomas Hill Easterfield KBE MZ (Cantab) PhD (Wurzburg) FRSNZ FRIC HonFNZIC who was well known for his contribution in the field of chemistry. Sir Thomas was the first chairman of the New Zealand section of the Royal Institute of Chemistry and also one of the early Presidents of the New Zealand Insti-

tute of Chemistry (NZIC). The award winner will be requested to deliver a lecture on the subject of her/his research at an NZIC conference (or on some other suitable occasion) and will carry out a short lecture tour, hosted by the Royal Society of Chemistry, in the United Kingdom.

### Maurice Wilkins Centre Prize for Chemical Science

The winner for 2019 was **Professor Justin Hodgkiss, Victoria University of Wellington**. This is the premier prize of the NZIC and is awarded to a candidate based on the excellence and impact of their chemistry.

### Shimadzu Prize for Industrial and Applied Chemistry

The winner for 2019 was **Professor Russell Frew, University of Otago**. The Industrial and Applied Chemistry Prize was first awarded in 1978 to encourage and support applied chemical research in New Zealand. The prize is awarded for meritorious achievement in the field of industrial or applied chemistry.

### sciPAD Denis Hogan Chemical Education Award

The winner for 2019 was **Professor Richard Hartshorn, University of Canterbury**. The NZIC Denis Hogan award for Chemical Education recognises excellence in teaching chemistry. The award is made to a person who has made an important contribution to Chemical Education in New Zealand.

### BRANCH NEWS

#### AUCKLAND

#### The University of Auckland

##### Events

##### Open Day

The annual University of Auckland Open Day was held on Saturday 31 August for prospective students. In addition to talks about programmes and activities within the School of Chemical Sciences, visitors were also able to experience a "smoothie bike" and chemistry demonstrations.

### School of Chemical Sciences Seminars

The School of Chemical Sciences at the University of Auckland hosted several seminars between September and November 2019 and launched a weekly School of Chemical Sciences Seminar Series:

Professor **Christian Hartinger** (University of Auckland): *Inorganic compounds for cancer treatment and mode of action studies*.

Dr **Dan Furkert** (University of Auckland): *Natural product synthesis – a crucible for new method discovery*.

Professor **Paul Kilmartin** (University of Auckland): *PEDOT electrochemical sensors for antioxidants in beverages*.

Dr **Geoff Wilmot** (University of Auckland): *Nanofluidics and dynamic microfluidics*.

Dr **Nadine van der Heijden** (University of Auckland): *Patterning nanomagnets; towards bottom-ups synthesis of magnonic crystals*.

Dr **James Brady** (University of Auckland): *Technology, teaching, and me*.

Dr **Zoran Zujovic** (University of Auckland): *The power of solid-state NMR*.

Emeritus Professor **Laurie Melton** (University of Auckland): *CRISPR gene editing: How can it be used to solve the world's health and food problems?*

Professor **Ralph Cooney** (University of Auckland): *Green anchored antibacterials: surface chemistry*.

Associate Professor **Tilo Söhnel** (University of Auckland): *Materials chemistry using single crystal and powder X-ray and neutron diffraction*.

Dr **Andrea Kolb** (University of Auckland): *Impact of interfaces on crystallization of phase change materials thin films revealed by in situ scanning transmission electron microscopy*.

Dr **Shanghai Wei** (University of Auckland): *Transmission electron microscopy (TEM) at University of Auckland*.

Dr **Joel Rindelaub** (University of Auckland): *Air quality, amphet-*



Photos from the University of Auckland Open Day

*amines, and other adventures in analytical chemistry.*

Professor Yuji Mikata (Nara Women's University): *Development of fluorescent sensors for specific detection of metal ions and phosphate species with a quinoline/isoquinoline platform.*

Professor Jas Pal Badyal (Durham University): *Scalable functional nanocoatings for technological and societal applications.*

Professor Nils Metzler-Nolte (Ruhr

University Bochum): *Bioorganometallic chemistry of rhenium – in and around peptidic structures.*

Dr Kang **Huang** (University of Auckland): *Innovative processing technologies and advanced materials for improving safety and quality of food products.*

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

The University of Auckland hosted the following NZIC Auckland Branch Seminars between September and November 2019:

Dr Megan **Grainger** (University of Waikato): *Sticky business: my research journey with Mānuka honey.*

Dr Vanessa **Morris** (University of Canterbury): *The good, the bad and the fibrillar: amyloid fibrils in health and disease.*

The University of Auckland also hosted the Royal Society of Chemistry Australasian Lecture co-hosted by the NZIC Auckland Branch:

Professor Keith **Gordon** (University of Otago): *From ultrafast processes*

*in solar cells to prediction of meat quality: using spectroscopy and computational methods to understand complex systems.*

The University of Auckland, Auckland branch of the NZIC and the Centre for Green Chemical Science co-hosted a public lecture by Dr **Pete Myers**: *Are plastics a threat to human health?*

## Staff Successes

### Hector Medal

Professor **Jadranka Travas-Sejdic** was awarded the Hector Medal by the Royal Society of New Zealand Te Aparangi for her research on nano-materials and advanced polymers used for biosensing, biomedicine and bioelectronics. The Hector medal is given to a researcher who “has undertaken work of great scientific or technological merit and has made an outstanding contribution to the advancement of the particular branch of science.” Her research identifies and characterises new materials based on conducting polymers, and develops new sensors with applications ranging from health monitoring to detection of pest species.

### Pickering Medal

Professor **Cather Simpson** was awarded the Pickering Medal by the Royal Society of New Zealand Te Aparangi for her pioneering research and commercialisation of innovative photonic technology using ultrafast lasers. The Pickering Medal is awarded “to a person, who while in New Zealand, has through design, development or invention performed innovative work the results of which have been significant in their influence and recognition both nationally and internationally, or which have led to significant commercial success.” Cather started up the Photon Factory “to enable the research of all New Zealand scientists – academic, industrial, CRI-based and student-led”. This approach has resulted in multiple research contributions for NZ companies, formation of the spin-out companies Engender Technologies and Orbis Diagnostics, and research publications ranging from femtosecond spectroscopy to laser beam shaping.

## Clinical Trials

Neuren Pharmaceuticals has just announced that trofinetide has commenced Phase 3 clinical trials (12 week LAVENDER study then 40 week LILAC study) in the US for treatment of Rett Syndrome. The first study will involve about 180 girls and young women with Rett Syndrome. In addition, another drug from the **Brimble** group, NNZ-2591, should enter clinical trials for treatment of three childhood disorders in 2020.

## MBIE Funding Success

The School of Chemical Sciences had a number of successes in the latest MBIE round. Dr **Alex Risos** and Professor **Cather Simpson** were awarded a Smart Ideas grant for a project to monitor pathogens in water. Associate Professor **Paul Harris** and Distinguished Professor Dame **Margaret Brimble** were awarded a Smart Ideas grant to develop new approaches for boron capture therapy. In addition, **Margaret Brimble** has subcontracts with two large University of Otago-based MBIE platform grants in precision antimicrobials and new frontiers in animal development, and Associate Professor **Geoff Waterhouse** has a subcontract with a Smart Ideas grant on nano-catalytic surfaces led by GNS.

## Marsden Fund Success

Congratulations to Dr **Davide Mercadante** on receiving a Marsden Fast Start grant for his research project, *Looking at the dark side of the proteome: how do post-translational modifications control highly disordered proteins for the regulation of genetic transcription?*

## New Zealand-China Emerging Researcher Fellowship

Congratulations to Dr **Lisa Pilkington** who has been awarded the New Zealand-China Emerging Researcher Fellowship. The fellowship will allow Lisa to travel and undertake research with academics at Sun Yat-sen University in Guangzhou and Peking University in Beijing as well as attend conferences in China in 2020.

## Auckland Medical Research

## Foundation Postdoctoral Fellowship

Congratulations to Dr **Hannah Holtkamp** for being awarded a two-year Auckland Medical Research Foundation Postdoctoral Fellowship for her project, *Probing the biochemistry of skin with lasers, light scattering and molecular ionisation*. This project continues to build on the Photon Factory’s success in applications of spectroscopic imaging and analysis.

## Sir Charles Hercus Fellowship

Congratulations to Dr **Muhammad Hanif**, who has been awarded a prestigious Sir Charles Hercus Fellowship by the Health Research Council. This four-year fellowship gives him the opportunity to explore whether metallodrugs can cause an antitumour immune response that might be useful in anticancer treatment. Muhammad will be working on this project in cooperation with Professors **Christian Hartinger** and **Rod Dunbar**.

## Rutherford Postdoctoral Fellowships

We congratulate Dr **Lisa Pilkington** and Dr **Emma Davison** on being awarded prestigious Rutherford Foundation Postdoctoral Fellowships for the next two years. Lisa intends to combine data science with medicinal chemistry to develop new statistical methods for establishing quantitative structure-activity relationships. Emma is developing flow synthesis methods that could be used to produce personalised cancer immunotherapies. These fellowships continue their scientific successes – both Lisa and Emma were previously awarded the L H Briggs Prize for the top PhD thesis in our School (Lisa in 2016 and Emma in 2019).

## Zonta New Zealand Women of Achievement Award

Distinguished Professor Dame **Margaret Brimble** was awarded a Zonta New Zealand Women of Achievement Award by the Zonta Club of Auckland. Zonta is an international non-profit organisation, and its awards programme aims to recognise NZ women who have been em-

powering other women and girls. The description of her achievement reads: "Dame Margaret has received many recognitions for her science and educational achievements including being elected a Fellow of the Royal Society London (2018) and inducted into the American Chemical Society Medicinal Chemistry Hall of Fame (2019). She was named the L'Oreal-UNESCO Women in Science Laureate in Materials Science for Asia Pacific in 2007 and has encouraged and influenced girls and young women to develop their abilities to reach their full potential. She's a role model in New Zealand and around the world who actively empowers women around her to reach their full potential in both academic science and commercial research. She has discovered several drugs in phase 2/3 human clinical trials for neurodevelopment disorders and has co-founded a spin out company in the USA working on cancer vaccines."

### Publications

Congratulations to Dr *Ivan Leung* and Associate Professor *Jon Sperry*, along with Dr Ghader Bashiri, for leading the research resulting in a paper on isocitrate lyase activation in *Nature Communications*.

Congratulations to Dr *Muhammad Hanif* for his article in the 2019 Emerging Investigators Issue of *Chemical Communications*. Muhammad's invited article reports on multidisciplinary research on the design and development of dinuclear RhIII(Cp\*) and IrIII(Cp\*) complexes with potent *in vitro* anticancer activity while exhibiting low toxicity in haemolysis studies and *in vivo* zebrafish models. This project included contributions from the SCS (Key contributors are *Christian Hartinger*, *Tilo Söhnel*, *Viji Sarojini*), the Auckland Cancer Society Research Centre (Euphemia Leung, Stephen Jamieson) and the School of Medicine (Jonathan Astin).

Congratulations to Dr *Ali Bagheri* and Dr *Jianyong Jin* for co-authoring a paper on 3D and 4D printing that was published in *Angewandte Chemie International Edition*.

### Student Successes

#### Faculty of Science Postgraduate Research Poster Competition

Congratulations to *Hannah Matthews* who was awarded 2nd prize in the People's Choice award in the Faculty of Science Postgraduate Research Poster Competition 2019.

### Blues Awards

Congratulations to *Rebecca Jelley*, co-founder of the company Ultimate Bowls Championship, for winning the Most Outstanding Contribution (Innovation) Award at the 2019 Blues Awards. The Blues Awards Ceremony was held on 27 September to celebrate students who have achieved in sports, the arts and culture, innovation, and service and leadership.

### Publications

Congratulations to PhD student *Rory Devlin*! His work on the biomimetic synthesis of the nudicaulin pigments has been published in *Chemical Communications* and highlighted in the Royal Society of Chemistry magazine *Chemistry World*.

### Velocity Challenge

Team eMpowder from Food Science is now a finalist in the Velocity \$100k Challenge 2019 (New Ventures Category). "The endeavour is to empower your gut health against self-reported dairy intolerances. We are doing this by formulating eMpowder: a novel manuka honey milk powder with the added power of probiotics. Be ready to prepare a wholesome milk drink, which you will find is delicious and surprisingly easy-to-digest!"



Team eMpowder - Velocity \$100k Challenge finalists. Left to right: Ina Guo (Bioscience Enterprise), Xuan Dong (BSc. Hons.), Phoebe Leung (Food Science), SzeMun Tan (Chemical & Materials Engineering), Anand Mohan (PhD Candidate), Hengjie Wang (Co-founder, Kami). Not pictured: Associate Professor Siew-Young Quek (Supervisor).

### PhD Completions

Congratulations to the following students who successfully defended their thesis:

**Courtney Davy**, whose PhD thesis is entitled, *Development of catalytic systems for green oxidation chemistry*. Courtney's research was supervised by Professor **James Wright**.

**Ben Lu**, whose PhD thesis is entitled, *Synthesis of novel TLR2 agonist for self-adjuvanting peptide vaccines*. Ben was supervised by Distinguished Professor Dame **Margaret Brimble**. He is now working on a commercial contract in the **Brimble** group developing new treatments for migraine and diabetes, funded by Living Cell Technologies.

**Aubrey Dosado**, whose PhD thesis is entitled, *Upconversion phosphors for efficient solar energy harvesting*. Aubrey was supervised by **Geoff Waterhouse** and **Dongxiao Sun-Waterhouse**.

**Danilo Correddu**, whose PhD thesis is entitled, *Studies on human proteins involved in deregulated translation in Parkinson's disease*. Danilo was supervised by **Ivanhoe Leung** and co-supervised by **Johannes Reynisson**.

**Fithra Nisa**, whose PhD thesis is entitled, *Influence of low-frequency ultrasound homogenisation on the physicochemical properties of some*

*dairy-based systems*. Fithra was supervised by **Fan Zhu** and **Yacine Hemar**, and co-supervised by **Conrad Perera**.

**Matheus Vargas**, whose PhD thesis is entitled, *Advances in microfluidics: a lab-on-disk approach to solve dairy industry problems*. Matheus was recommended to be passed "as is" with no corrections at all! He was supervised by Professor **Cather Simpson** and Professor **David Williams**.

**Sesha Manuguri**, whose PhD thesis is entitled, *Proteins, polymers and nanoparticles: self-assembly towards functional nanostructures*, supervised by Dr **Jenny Malmstrom** (Chemical and Materials Engineering) and Professor **David Williams**.

**Ayiya Bikimi Bitrus**, whose PhD thesis is entitled, *The development and study of new chelating ligands with combinations of PYA and remote-NHC donors as supporting ligands for homogeneous metal catalysts*. Ayiya's research was supervised by Professor **James Wright**.

**Rachel Mathew**, whose PhD project in applied ceramics was supervised by Professor **Ralph Cooney**. She is currently working with Professor **George Franks** as a Postdoctoral Research Fellow in the Faculty of Engineering at the University of Melbourne.

### Massey University (Auckland Campus)

Dr **Debbie Jordan** was voted Massey Albany's Student Association Lecturer of The Year (LOTY) 2019 at a recent awards ceremony. The LOTY award is an established tradition on the Albany campus and is the students' way of recognising teaching excellence and supporting academic quality. This is an across-campus award encompassing staff from all four colleges at Massey Albany – a great result for chemistry and the College of Science!

Associate Professor **John Harrison** returned from a visiting professorship at Stanford University's chemistry department where he continued his long standing collaboration with Professor **Richard Zare**. While there he was involved in pioneering experiments developing 'photon catalysis', where an intense pulsed electric field from a non-resonant laser directly manipulates the potential energy surface and the outcome of chemical reactions.

Distinguished Professor **Peter Schwerdtfeger** is now Head of the New Zealand Institute for Advanced Study. This does not mean that he is getting out of research - read the latest *Angewandte Chemie* paper on copernicium (just below mercury) and if it is a liquid metal or not.



Debbie Jordan receives her LOTY award

Postgraduate students **Alex O'Neil** (PhD with **Jon Kitchen**) and **Jade Pope** (PhD with **John Harrison**) and MSc students **Nethmie Jayasooriya** and **Alex Burton** presented their research at the annual School of Natural and Computational Sciences Postgraduate Student Conference. Congratulations to **Alex O'Neil** who won best poster.

**Jon Kitchen** welcomes Gaby Sansom to his group for a Summer Internship where she will be working on luminescent materials development. Gaby was also the recipient of the

SNCs Chemistry Prize at this year's prize giving for top chemistry student.

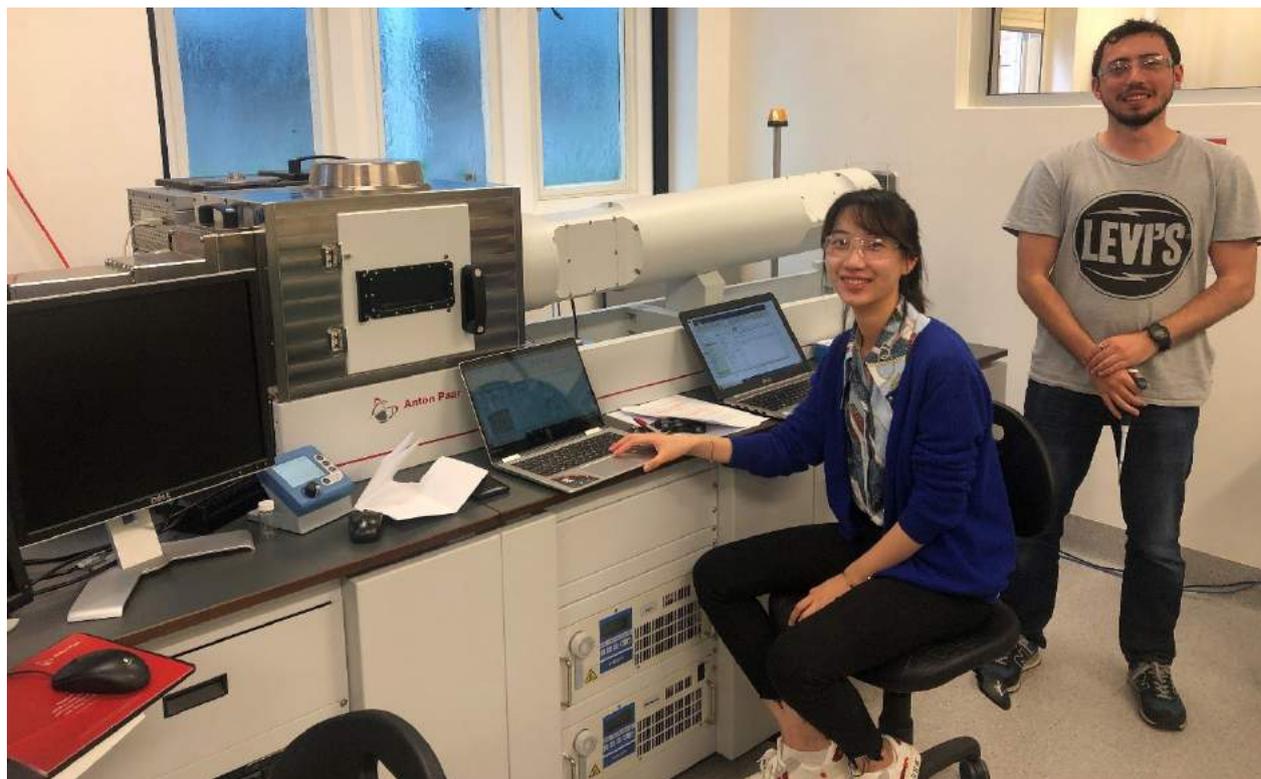
During the high school holidays, Dr **Debbie Jordan** piloted a crash-course style chemistry tutorial for year 13 students from Long Bay College, Western Springs College and Albany Senior High School. The tutorial was for an NCEA organic chemistry external standard. 47 students spent a total of 4 hours over 2 sessions on the Albany campus. After running 6 successful streams, and having received e-mails from students

at other schools wanting the same experience, Debbie is thrilled by the results. As a direct result of teachers talking to each other after the success of the programme, Debbie spent 2 days at Liston College running the same tutorial programme.

**Erin Moffet**, **Jade Pope** and **Debbie Jordan** were involved in a fantastic engagement with 35 Year 10-12 Northland students who had come to our Auckland campus for a science "taster day". Big thanks to our colleagues Margaret Peace, Dr Patrick Bowman and Dr Sam Tuttle from



Staff and students from Massey Albany make a human Periodic Table



Chloe Zhijun Ren and Pablo Solís Muñana with the SAXS instrument at the University of Sydney

physics for their combined input.

**Debbie Jordan** and **Jon Kitchen** have been using innovative ways of celebrating the UN's International Year of the Periodic Table (#IYPT2019). Earlier in the year this was done using staff and students from the School of Natural and Computational Sciences to make a human periodic table.

## Auckland University of Technology

### New Faces

We welcome new PhD student **Fouad Ismael** from Kurdistan, Syria, who will be working with Professor **Nicola Brasch**. Fouad has been awarded a PhD stipend from the Dodd-Walls Centre.

### Events and Invited Talks

#### NZIC Branch Talks

AUT hosted the NZIC Auckland Branch AGM as well as two NZIC seminars between September and November 2019:

Dr **Erin Leitao** (University of Auckland): *Towards the next generations of polymeric materials.*

Dr **Viji Sarojini** (University of Auckland): *Peptide sciences and technologies –turning the tide in medicinal chemistry & much more.*

Dr **Jack Chen** and his PhD students **Pablo Solís Muñana** and **Chloe Zhijun Ren** travelled to Sydney to perform small angle X-ray scattering experiments in the labs of Professor Gregory Warr at the University of Sydney and Paul Fitzgerald at Sydney Analytical.

### Congratulations

Professor **Nicola Brasch** and her PhD Student **Vinay Bharadwaj** published a paper on 2-nitrobenzyl photocaged N-hydroxysulfonamides in the *Journal of Photochemistry and Photobiology A* (DOI: 10.1016/j.jphotochem.2019.112033).

Professor **Nicola Brasch's** PhD students **Dominique Rwizinkindi** and **Vinay Bharadwaj** were awarded Dodd-Walls travel grants to attend the New Zealand Institute of Chemistry conference in November.

Dr **Jack Chen's** PhD students **Pablo Solís Muñana** and **Chloe Zhijun Ren** were awarded NZIC travel grants to attend the New Zealand Institute of Chemistry conference in November.

Recent BSc graduates **Jess Robinson**, **Bronte Carr** and **Roisin Mooney** were awarded Faculty of Health and Environmental Sciences Summer Studentships to work with Professor **Nicola Brasch**, Dr **Jack Chen** and Dr **Marcus Jones**, respectively.

## CANTERBURY

### University of Canterbury

To mark 2019 as the year of the Periodic Table, Radio New Zealand (RNZ) Nights with Bryan Crump teamed up with the MacDiarmid Institute to produce *Element of the week*. On 30 August, **Richard Hartshorn**, Professor of Chemistry at University of Canterbury, and Secretary General of the International Union of Pure and Applied Chemistry, talked about the element rutherfordium. The RNZ interview can be found here: <https://www.rnz.co.nz/national/programmes/nights/audio/2018711203/element-of-the-week>

On 17 October, a UC Connect public lecture was given by Associate Professor **Sarah Masters** on *Essential elements – where would we be without the Periodic Table?* Sarah introduced the periodic table, explored its evolution to become what we currently know and accept, and pondered what might have happened had Russian chemist Dmitri Mendeleev and German chemist Julius Lothar Meyer not organised the elements into some form of repetitive table. The lecture also looked at some of the greatest achievements that have arisen from our understanding of the periodic table, from medicine to materials to our understanding of space.

### NZIC

A Christmas-themed NZIC Canterbury branch AGM was held on 2 December.

A Joint RSC-NZIC morning tea was

held on 1 November at which Professor **Keith C. Gordon**, University of Otago, Department of Chemistry, gave a presentation as part of the Royal Society of Chemistry Australasian Lecture Series entitled, *From ultrafast processes in solar cells to prediction of meat quality: using spectroscopy and computational methods to understand complex systems*. More about Prof Keith Gordon and his research can be found here: <https://www.otago.ac.nz/chemistry/people/otago668566.html>

An NZIC public lecture was given by Professor Sir Colin Humphreys (University of Cambridge, UK) on gallium nitride and graphene on 26 September at the University of Canterbury entitled, *Gallium nitride and graphene: the amazing new materials that can save energy, save lives, create jobs and improve our health*. You can read more about Professor Humphreys and his research here: <https://www.gan.msm.cam.ac.uk/directory/humphreys>

## MANAWATU

**David Shillington**, Associate Professor of Chemistry, has retired from his position at UCOL, Palmerston North. David was also the treasurer for the Manawatu Branch of NZIC for nearly two decades. The branch thanked him profusely for his years of dedicated service.

On 1 August, **Ben Munro** successfully defended his PhD Thesis titled, *Structure and properties of tunable Pickering emulsions*. He was jointly supervised by **Simon Hall** and **Catherine Whitby**. Ben is now working in R&D chemistry at Hexion, Tauranga.

**Vyacheslav V. Filichev** delivered an invited talk during a symposium on *Chemistry meets biomedicine* at the Skolkovo Institute of Science and Technology (Moscow, Russia, 19-21 September 2019).

**Omid Taheri** successfully defended his PhD thesis on *Gas separation with metal-organic frameworks*. Omid was supervised by **Shane Telfer**. His thesis was nominated for the Dean's List.

**David Nixon** defended his PhD thesis



David Shillington retired as Treasurer of the Manawatu Branch of the NZIC. Here he receives a thank you gift from Catherine Whitby

entitled, *Catch  $_4\text{Be}^9$  if you can: exploiting second sphere hydrogen bonding toward chelation of beryllium*. David was supervised by **Paul Pleiger** and **Gareth Rowlands**. He has now also completed a post-graduate qualification in secondary school teaching and has started his first post at Fielding High School.

The **Pleiger** group celebrated the graduation of **David Nixon** (PhD) and **Sidney Woodhouse** (MSc). Sidney worked on complexation of salicylal-doxime ligands.

On 1 Oct, **Yiming Zhang** joined the **Telfer** group as a PhD student. Yiming will be working on gas separation using MOF membranes.

Shikeale Harris gave a presentation on *Fluorescent MOFs and chiral sensing* as part of her BSc. Honours and submitted her thesis.

Between 22-25 October, **Nisansala Bandara** and **David Perl** attended the MESA Boot Camp at Waihi Beach, Bay of Plenty.

Between 27-30 October, **Joel Cornelio** and **Bernhard Auer** attended EuroMOF 2019 - 3<sup>rd</sup> International Conference on Metal Organic Frameworks and Porous Polymers in Paris, France. Joel gave a presentation on *Photophysical studies of multicomponent metal-organic frameworks*. Bernhard presented a poster on *Multicomponent MOFs with tunable pore-environments for catalysis*. Both Joel and Bernhard were funded by NZIC travel grants.

**Lauren Macreadie** was successful in being appointed for a three-year term as a Lecturer in Chemistry at Massey University.

**Jenna Buchanan** has joined Massey

for a one-year term as a Research Officer, working for **Paul Pleiger**, Head, School of Fundamental Sciences.

The APOBEC3 team led by **V. Filichev**, **E. Harjes** and **G.B. Jameson** described the first APOBEC3B selective inhibitor in the article published in *Organic & Biomolecular Chemistry* in November 2019. The article was chosen to feature on the front cover of the journal and a press release was issued by Worldwide Cancer Research describing the importance of these findings.

On 5 November, **Joel Cornelio** gave a talk on *Some aspects of multicomponent MOFs* at the Felix Bloch Institute for Solid State Physics, Leipzig University, Germany. He was hosted by Professor Andreas Pöpl of the same Institute.

**Brodie Matheson** spoke on *The development of hydroquinone-based ligands for metal-metal communication* as part of his BSc Honours and submitted his thesis.

**Adil Alkaş** and **Nisansala Bandara** attended the MacDiarmid Annual Symposium held between 20-22 October at Victoria University, Wellington.

**Catherine Whitby** gave a keynote talk at Okinawa Colloids 2019, held between 3-8 November, at Nago, Okinawa, Japan.

The Massey-Victoria Chemistry Symposium was held on 8 November at Massey University. **Sam Brooke** and **Yongdong Su** of Massey with **Matthew Evans** of VUW served as organisers. The event featured 14 talks by students. **Matthew Evans** of VUW won the Best Talk Prize for *synthesis and Reactivity of N-heterocyclic germanimines*. **Leonie Etheridge** (Massey) spoke on *the synthesis and chemistry of planar chiral amino acids derived from [2.2]paracyclophane* and **Thomas Bird** (VUW) spoke on *synthesis and extended linker analogues of risperidone*. Both Leonie and Thomas won runners-up prizes.

**Adil Alkaş**, **Leonie Etheridge**, **Hari-krishnan Kurup**, **Suraj Patel**, **Rebecca Severinsen**, **Marrylyn Donaldson**, **Sidney Woodhouse**, and **Tyson Dais** attended and presented posters at the NZIC Conference in Christchurch.

*Paul Plieger* attended the NZIC Conference and also the 18<sup>th</sup> Asian Chemical Congress (Taipei, Taiwan) representing New Zealand as an Asian Chemical Editorial Society board member.

## OTAGO

### University of Otago, Department of Chemistry

There have been a number of well-deserved awards won by staff from the Department of Chemistry this quarter. Congratulations to *Bill Hawkins* for being awarded the 2019 RSC/NZIC Easterfield Medal. The award is made biennially to a chemist in New Zealand in recognition of the quality and originality of their research. In addition to a medal, Bill will also visit the UK to deliver lectures at a number of universities in order to promote scientific links between New Zealand and the UK.

Hearty congratulations to *David Warren* who received the Award for Distinguished Contribution to Chemical Education from the Federation of Asian Chemical Societies (FACS). The award is “presented to an eminent chemist who has made distinctive contributions to the advancement of chemical education in the Asia Pacific.” Included with the award was assistance with the costs to attend the 18<sup>th</sup> Asian Chemical Congress in Taipei, Taiwan in December, where Dave presented a talk on chemical education.

At the end of October *David McMorran* travelled to Parliament to be awarded with one of this year’s Ako Aotearoa Tertiary Teaching Excellence Awards, in recognition of his teaching and community engagement efforts over the years. The award was presented by the Minister of Education, the Hon. Chris Hipkins. Anyone who has come through the Otago Chemistry programme will have experienced Dave’s teaching first hand and will no doubt agree he is an incredibly well-deserved recipient of this prize!

Congratulations to *Sally Brooker* who was made one of the inaugural Sesquicentennial Distinguished Chair appointments to mark the 150th



Matthew Evans (left) receives the Best Talk Prize from Barry Scott of DKSH (centre) and Vyacheslav Filichev (right).



Thomas Bird (left) won the Runner-Up Prize in the BSc Honours category. Also pictured are Barry Scott of DKSH (centre) and Vyacheslav Filichev (right).



Leonie Etheridge (centre) receives her Runner-Up Prize in the PhD category from Barry Scott of DKSH (left) and Vyacheslav Filichev (right).

anniversary of the founding of the University of Otago. This award recognises Sally’s fantastic scholarship in the field of chemistry, particularly her interests in solar fuels research, and inspiring students. She is also keen to develop a more inclusive and diverse workplace for students and staff.

*Anna Garden* was awarded an Early Career Award for Distinction in Research from the University of Otago. This is recognition of the hard work of all in the Garden Group – especially the tireless students!

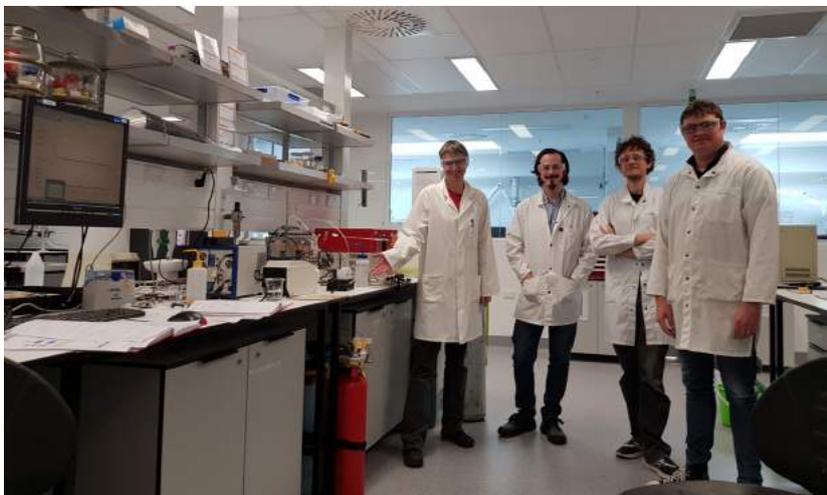
*Jaydee Cabral* gave an oral presentation entitled, *Wound healing bioma-*



Dave McMorran receiving an Ako Aotearoa Tertiary Teaching Excellence award from Hon. Chris Hipkins



Participants in the mid-term IAEA coordination meeting representing Vietnam, Indonesia, Cambodia, India, Sri Lanka, Singapore, Myanmar, Philippines, Fiji, Malaysia, Japan, Bangladesh, Thailand, Pakistan, Korea, New Zealand and Australia



Left to right: Sally Brooker, Michael Bennington, Johan Hamonnet and Aaron Marshall very happily watch bubbles of carbon dioxide reduction products steadily being produced by Sally's molecular catalyst and then analysed

terials as cell and bioactive delivery vehicles at the International Conference on Nanospace Materials, University of Queensland, St. Lucia, Australia, 1-4 October 2019.

Two new students have joined the Plant & Food Research Bioactives team in the Chemistry Department. **Lani Aloï** has started a PhD working on natural products from Samoan medicinal plants. Her main supervisor is **Nigel Perry**, with **Dave Larsen** and **Joel Tyndall** (Pharmacy) also involved. Lani completed an MSc at Otago Chemistry with Guy Jameson, and is now a lecturer at the National University of Samoa. **Asena Foliaki** has started a Plant & Food Research summer studentship. She is researching a rapid method for analysing the vanillin and glucovanillin contents of vanilla pods, which are being grown in Tonga working with the New Zealand company Heilala. Asena will be working with Plant & Food Research agronomist Bruce Smallfield, the Plant & Food Research natural products chemists, and spectroscopists in **Keith Gordon's** group.

**Russell Frew** has been in Hanoi chairing the mid-term coordination meeting for an International Atomic Energy Agency (IAEA) project he is leading. The project aims to help countries in the Asia-Pacific region implement food authentication and traceability systems based around nuclear and complimentary techniques. There are 19 countries involved, each working on projects of national importance and contributing to the over-arching programme of work. Nuclear techniques have been shown to be very effective in authenticating food products (i.e. detection of adulteration or counterfeit), and in discriminating foods with different geographical origins. These systems have the potential to provide verification of information-based traceability systems and provide information on the integrity of the food product itself. For example, isotope analysis of the foodstuffs can provide an indication of point of origin and serve in the detection of adulteration.

**Sally Brooker** has been on research and study leave in the laboratory of Aaron Marshall (Canterbury) this se-

mester. Sally and Aaron have been testing some of Sally's molecular CO<sub>2</sub> reduction catalysts, with promising results so far. Watch this space!

Congratulations to **Sara Miller** for her recent grant success. Sara has been successful with both an MBIE Smart Ideas grant and Marsden Fast-Start grant. These complementary grants will explore the use of spectroscopic techniques to diagnose gastrointestinal diseases *in vivo*, via endoscopy, to minimise the need for biopsy collection. These studies are to be carried out in collaboration with colleagues in the Dunedin School of Medicine, University of Auckland and University of Exeter. The work will look at endoscopic probe development and the creation of robust algorithms for identification of healthy and non-healthy tissue.

Congratulations to **Keith Gordon** for being awarded the 2019 MacDiarmid Medal for his creative use of light and spectroscopic techniques in helping in the understanding of a wide range of systems, varying from conducting polymers and donor-acceptor systems to fish oils and pharmaceuticals. Keith has been speaking extensively in Australia and New Zealand during his Royal Society of Chemistry Australasian tour. Keith gave two invited talks at SciX in Palm Springs. He talked about *Time-resolved (ten millisecond) low frequency Raman spectroscopy: a method of evaluating dynamic behaviour in drug formulations* and *Time-resolved resonance Raman studies of Re(I) complexes with blended intraligand and metal-to-ligand charge-transfer states.* He also spoke at the 8<sup>th</sup> Asian Spectroscopy Conference 2019 in December.

## WAIKATO

### University of Waikato

Nearly 180 students from 22 schools in the greater Waikato and Bay of Plenty region participated in the annual ChemQuest competition, held at the University. This was a fun-filled evening for students studying NCEA level 2 chemistry and a hard-fought contest. Prizes were shared right across the region and were awarded as follows:

**1st Place: Whakatane High School:** (Manaakiao Hahipene, Ruby Stuart and Michael Williams)

**2nd Place: Hamilton Boys' High School:** (Finlay Buckell, Levi Craven, Richard Neale)

**3rd Place: Te Awamutu College:** (Hayden Absalom, Logan Cooper, Nathaniel Short)

**4th Place: Tauranga Girls' High School:** (Talia Moore, Katrina Opie, Georgina Wooller)

**5th Place: Otumoetai College:** (Sarah Dixon, Bethany Lake, Amy Meidema)

The quiz was generously sponsored by the Waikato Branch of NZIC (major sponsor), Hill Laboratories and the School of Science, University of Waikato. The question master was **Michèle Prinsep**, ably assisted by numerous other chemistry staff and students.

The School of Science Postgraduate Conference, held in October, was well attended and there were some interesting talks and poster presentations. A number of chemistry students were awarded prizes as follows:

Mark T. Mitchell Award for Most Innovative Presentation: **Rose Swears** - *Project ARIELLE: ASV (Anodic Stripping Voltammetry) remote investigation of electrochemically-labile life-supporting elements.*

NZ Institute of Chemistry (Waikato Branch) Award for Best Chemistry-

Related Oral Presentation: **Stevie Noe** - *Nectary photosynthesis contributes to the production of mānuka (Leptospermum scoparium) floral nectar.*

Waikato Science Club Prizes for Best Poster: **Kaitlin Button** - *Rapid maturation of whiskey.*

Former Waikato branch secretary **Onyekachi Raymond** has just started a new job as a senior scientist with the Forensic Specialised Analytical Services Group (F-SAS) at ESR in Porirua. **Bill Henderson** has been appointed as the academic team leader for Chemistry & Applied Physics within the School of Science.

### Scion

As part of Scion's Ministry of Business, Innovation and Employment supported Smart Idea, Dr **Marie-Joo Le Guen**, Dr **Miruna Petcu** and **Maxime Barbier** sampled geothermal water to test new heavy metal removal technology. Professor Neil Ward from the University of Surrey, a specialist in heavy metals characterisation and particularly in arsenic speciation, joined the team, which sampled the pools of Wai-O-Tapu Thermal Wonderland, mapped out initially by analytical researcher Gillian Lord.

Thanks to Ngati Tahu-Ngati Whaoa Runanga Trust, the landowner and mana whenua of the area for their support and allowing access, and to Wai-O-Tapu Thermal Wonderland, the tourist park operator, for their



Whakatane High School's winning team with sponsors (from left): Alister Kennedy (Hill Laboratories), Olivia Underwood (Hill Laboratories), Michael Mucalo (President, Waikato branch, NZIC) Ruby Stuart, Michael Williams, Manaakiao Hahipene, Michèle Prinsep (quiz organiser) and teacher Karen Asquith.

flexibility and help during the visit.

Scion has recently acquired a new LC-MS (Agilent 1290 Infinity II UPLC coupled to a 6545XT AdvanceBio Q-ToF with a 1260 Infinity II SFC system) giving much needed new capability to Dr *Christine Karbiwnyk*'s MS-Suite. This, along with a new Bruker Hyperion 3000 FTIR microscope, is finding application in quantifying microplastic contamination under *Jamie Bridson*. Jamie presented some of his work at WasteMinz conference in Hamilton in September.

Scion staff were recognised at the Science New Zealand Awards with a Team Award going to the polymer chemistry group and Dr *Roya Rezanavaz* picking up an Early Career Researcher Award.



Marie-Joo Le Guen braves one of the smaller geothermal pools



Lake sampling in action



Scion staff with the Minister for Research, Science and Innovation, Dr Megan Woods

# Identifying natural products from their biosynthetic roots

Lewis J. Dean

School of Science, University of Waikato, Hamilton 3240 (email: [ljd22@students.waikato.ac.nz](mailto:ljd22@students.waikato.ac.nz))

**Keywords:** *natural products, secondary metabolism, biosynthesis*

Every person, creature, microbe and other assorted earthly lifeform can consider themselves a highly efficient synthetic chemist. Within the cells of all known living organisms, a series of fundamental chemical reactions are constantly running to produce and utilise the chemical compounds that are essential for life as we know it.<sup>1</sup> These are the carbohydrates, nucleic acids and amino acids that are ubiquitous throughout nature and used to drive the proper functioning of all metabolic and reproductive cellular processes. Larger macromolecules such as proteins, enzymes, lipids, and other essential structural compounds are biosynthesised from these compounds and along similar chemical routes. Taken together, all of these compounds are known as the primary metabolites and represent the vast majority of an organism's metabolic output. The combination of the chemical pathways that produce, utilise and recycle primary metabolites makes up any given organism's primary metabolism.<sup>1,2</sup>

Despite the often immense physiological and ecological differences between the different domains of life, in many ways the pathways that make up primary metabolism are found to be remarkably similar. All organisms rely on RNA and DNA for coding genetic information,<sup>3</sup> and many of the core metabolic pathways such as glycolysis (for carbohydrate breakdown), the pentose phosphate pathway (that produces many important building blocks) and the citric acid cycle (for energy production) are present in some form, either wholly or in part, across all the branches of life.<sup>4</sup> The commonality of these pathways suggests that they are some of the earliest developed biochemical processes, with their origins in the early Archean Eon some 4 billion years ago.<sup>4,5</sup> This ubiquity of certain chemical pathways and compounds across all known life has attracted a great deal of research and so the exact biochemical roles and interactions of primary metabolites are typically well studied and understood.<sup>1,2</sup>

In addition to the primary metabolites, many organisms are known to utilise their biosynthetic apparatus to produce a variety of compounds which are seemingly unnecessary for any of their essential cellular processes. These compounds are the secondary metabolites, or natural products, and unlike primary metabolites, their synthesis deviates from primary metabolic processes and their biochemical roles are often poorly understood.<sup>1,2</sup> Despite being unnecessary for the life of an organism, a natural product is instead assumed to confer some ecological advantage, as there would seemingly be no reason to expend cellular resources in their production otherwise.<sup>6</sup> In this way, the production of a particular natural product can be viewed as a response to an evolutionary pressure. As such, the various biochemical pathways that make up an organism's secondary metabolism, and hence the natural products an organism can produce, are often unique

to that organism, reflecting its own evolutionary history.<sup>6</sup> Therefore, the distribution of natural products across different species is considerably narrower than for primary metabolites.<sup>2</sup> Certainly there are some secondary metabolites known to be produced only within a single genus, others by a single species and in some cases, only within a distinct population of a species.

As natural products are assumed to confer some ecological advantage, they are often considered the products of an evolutionary chemical arms race between an organism and its environmental competitors.<sup>6</sup> Deducing the exact biochemical role of a secondary metabolite is often a difficult exercise, but where the ecological roles of natural products are known, they are often found to induce a biochemical change in an organism other than the one that produced it.<sup>6</sup> Thus secondary metabolites are frequently implicated as key drivers of chemical ecological interactions.<sup>7</sup> As such, there are many examples of natural products that have been found to deter predation (through toxicity or some other repulsive mechanism), prevent fouling from colonising species, inhibit ecological competitors, aid in predation (through poisons, toxins and the like) and facilitate inter- and intra-specific communications.<sup>7</sup> Natural products can be said to enhance the survivability of an organism and, whilst not essential for the life of the organism, can be considered to improve its life.

Natural products are highly diverse, from both a structural and biochemical viewpoint, covering a range of structural scaffolds with all manner of bioactive properties reported.<sup>2</sup> This is reflective of the various ecological functions that natural products have been evolved to perform. The structures of secondary metabolites are also frequently complex, being functionalised far beyond what is seen in most primary metabolites, despite natural products commonly being relatively small molecules, typically less than 1500 Da.<sup>8</sup> This diversity and complexity arises despite the relatively small pool of biologically available precursors and fundamental reactions from which compounds can be synthesised. Indeed, the chemical origins of many natural products can be traced back to acetate or select amino acids (tryptophan, phenylalanine, tyrosine, ornithine and lysine in particular).<sup>8</sup>

That such structural variability can arise from a relatively limited range of precursors is not unexpected if one recalls that natural products are not strictly essential to the life of the producing organism. Although the synthesis of secondary metabolites occurs along more specialised chemical pathways, they are all built from precursors found within primary metabolism (Fig. 1).<sup>9</sup> The utilisation of metabolites and intermediates that are already produced by an organism through its own primary me-

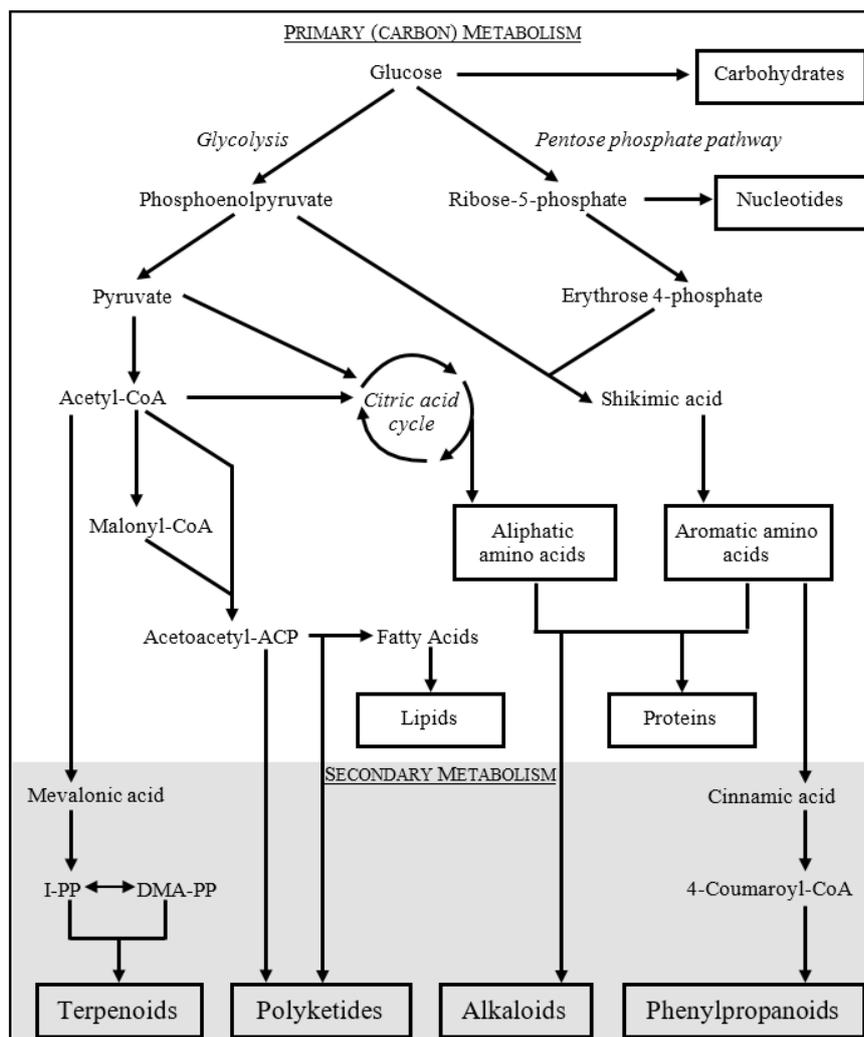
tabolism is an efficient use of cellular resources. That secondary metabolic pathways are themselves largely modified from existing primary pathways also ensures that the metabolic cost of synthesising a natural product is significantly lessened relative to the cost of utilising an entirely separate reaction chain, divorced from all other cellular processes.

There are four broad structural classes of natural products: the terpenoids, polyketides, phenylpropanoids and alkaloids. Each class of natural products is derived from a distinct primary metabolic precursor (Fig. 1), which results in a characteristic chemical backbone.<sup>8</sup> Whilst the initial biosynthetic steps towards a natural product generally proceed along partially understood pathways, once the backbone has been assembled, more complicated chemical modifications are applied. This occurs via the organism specific reactions and enzymatic processes that make up its own secondary metabolism and frequently makes use of methylation, acetylation, cyclisation and oxidation/reduction processes.<sup>10</sup> Here follows a brief overview of the biosynthesis and chemical backbones of the natural products.

## Terpenoids

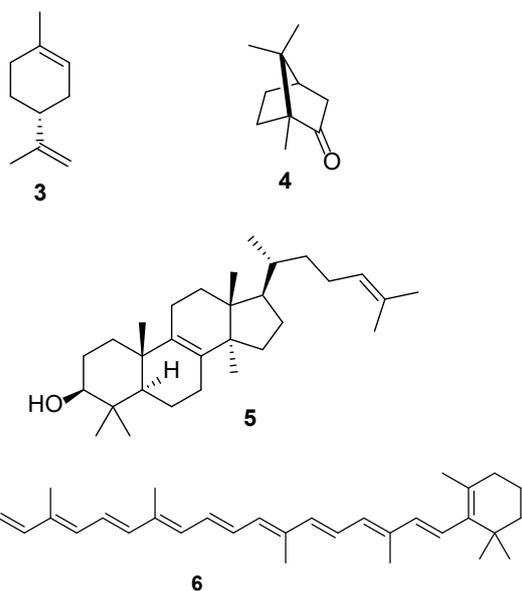
Terpenoids, sometimes called isoprenoids or simply ter-

penes, have been isolated from virtually every branch of life and represent the largest class of reported natural products.<sup>11</sup> The ubiquity of terpenoid synthesis is accountable in large part to the synthesis of steroids occurring via the isoprenoid pathway.<sup>12</sup> Many of the other known terpenoids are found in the volatile components of plants, giving rise to distinctive aroma and flavour profiles.<sup>13</sup> There are two distinct secondary metabolic pathways that give rise to the terpenoids. The first is the mevalonate pathway (as summarised in Fig. 1) that operates in eukaryotes by combining units of acetyl-CoA before reduction to mevalonic acid.<sup>14</sup> The second pathway, found in prokaryotes and some plants, is the 2-C-methyl-D-erythritol 4-phosphate (MEP) pathway that begins instead with pyruvate and does not produce the acid.<sup>15</sup> Both routes are derived from precursors of primary glycolysis, and the end products from each pathway are the same: the two isomers isopentenyl (**1**) and dimethylallyl (**2**) pyrophosphates.<sup>14,15</sup> The resulting five carbon isoprene unit derived from these structures forms the characteristic backbone of all terpenoids.



**Fig. 1.** A generalised overview of the four main secondary metabolic pathways as derived from primary metabolite precursors. Arrows are not necessarily indicative of a single step reaction nor are all inputs shown. (CoA = coenzyme A; ACP = Acyl-carrier-protein; I = isopentenyl; DMA = dimethylallyl; PP = pyrophosphate). Adapted from Schmidt *et al.*, 2005 with permission.<sup>9</sup>

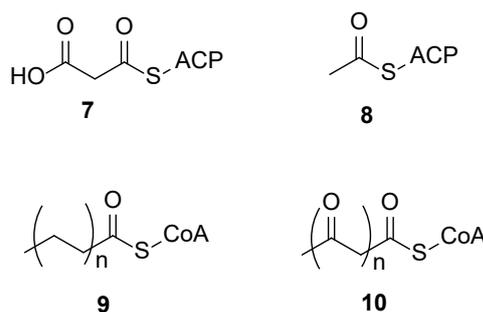
The next step in the formation of a terpenoid natural product is typically to combine the isomers of **1** and **2** in a linear (head-to-tail) fashion giving rise to successive terpene chains of 10, 15, 20 or 25 carbons.<sup>16</sup> These smaller terpene chains can in turn be combined (typically in a head-to-head fashion) to yield longer chains of 30 or 40 carbons, though sometimes longer. It is by the chain length that terpenes can be further classified into mono- ( $C_{10}$ ), sesqui- ( $C_{15}$ ), di- ( $C_{20}$ ), sester- ( $C_{25}$ ), tri- ( $C_{30}$ ), tetra- ( $C_{40}$ ) and poly- ( $C_{>50}$ ) terpenes respectively.<sup>16</sup> These backbones are subjected to extensive modification in the form of additional functionalities and often undergo enzyme mediated cyclisation reactions, which can result in the formation of enantiomers.<sup>17</sup> It is the many different cyclisation pathways that have developed which gives rise to such a variety of terpenes. Consider that both limonene (**3** - found in various citrus fruits)<sup>18</sup> and camphor (**4** - from the bark of camphor trees and rosemary leaves)<sup>19</sup> arise from the same monoterpene backbone. The cyclisation of larger terpenoids can give rise to even more complex scaffolds as with the steroids, of which lanosterol (**5** - the precursor to all steroids in animals and fungi) is a prime example.<sup>12</sup> Other terpenoids retain a mostly linear character and as such are able to utilise the extensive conjugation for pigments and photosynthetic compounds, as is seen with the carotenoids ( $\beta$ -carotene, **6**, for example).<sup>20</sup> That such variety and complexity can arise from such a simple precursor goes some way to explain the abundance of terpenoid secondary metabolites in nature.



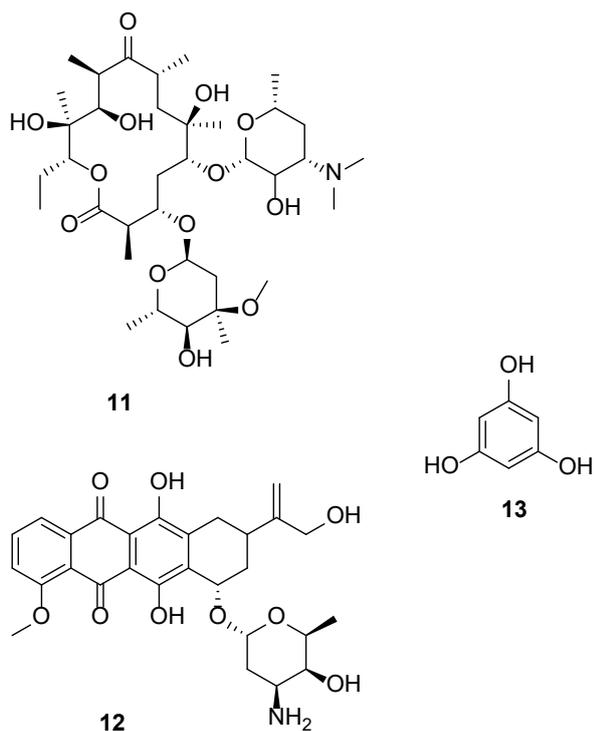
## Polyketides

The precursors for polyketide synthesis are also derived from the glycolytic pathway and are formed via the acetate-malonate pathway.<sup>21</sup> This initial part of polyketide biosynthesis resembles the same primary metabolic process that produces fatty acids. Long carbon chains are built by adding acetate groups sequentially through an initial enzyme mediated, Claisen-like condensation of malonyl-ACP (**7**) with acetyl-ACP (**8**) to yield a  $C_4$  precursor (acetoacetyl-ACP) with the elimination of  $CO_2$ , after which a repeated Claisen condensation

of malonyl-ACP builds the chain to the desired length.<sup>22</sup> During the synthesis of fatty acids, the  $\beta$ -keto oxygen is reduced and eliminated in between each acetate addition such that only an aliphatic chain and the terminal carboxylic carbonyl remains (**9**).<sup>22</sup> However, in the synthesis of polyketides, the acetyl oxygens are left as they are, or else only reduced at selected sites, such that a highly oxygenated poly- $\beta$ -ketone (**10**) precursor is produced.<sup>21</sup> The variation in length, and the degree to which this precursor is reduced, form the basis for the variety observed in final polyketide structures. Additional structural complexity can be obtained by utilising a non-acetate starting unit or a different acetate repeating unit (for instance by adding a branched chain form of malonyl-ACP).<sup>21</sup>

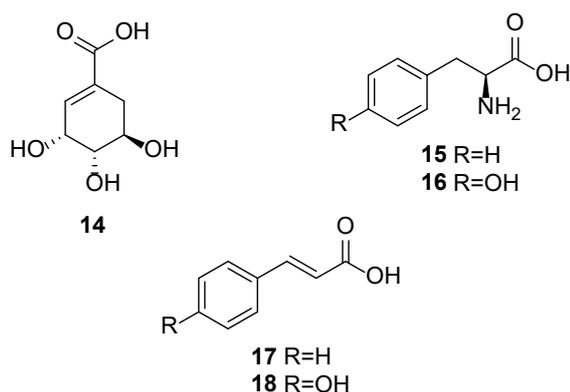


Polyketides are produced extensively by fungi, bacteria and plants via specialised polyketide synthase (PKS) enzyme clusters.<sup>21</sup> These enzyme clusters are responsible for catalysing the condensation reactions described above, as well as cyclising the poly- $\beta$ -ketone precursor into the final polyketide product. The PKS enzyme clusters come in one of three classes (I, II & III) that differ in their catalytic mechanisms and hence each tends to produce a different type of polyketide structure. The first class of enzyme clusters (PKS I) are comprised of large multi-functional enzymes that tend to reduce the poly- $\beta$ -ketone precursor to a greater extent than the other classes and typically produce lactone rings and larger macrocyclics,<sup>23</sup> of which the core of the antibiotic erythromycin (**11**) is an example.<sup>24</sup> Class II PKS clusters are comprised of discrete enzymes and almost always found to produce aromatic polyketides,<sup>25</sup> as found with doxorubicin (**12**) a bacterial polyketide with anti-neoplastic activity.<sup>26</sup> Finally, the class III PKS enzymes, which are not really clusters but rather a single enzyme formed from a homodimer of a peptide,<sup>27</sup> tend to give rise to smaller aromatic compounds, such as phloroglucinol (**13**), a precursor to the polymeric phlorotannins known from various brown algae.<sup>28</sup> Despite the differences between polyketide structures as synthesised by the different enzymes clusters, all form cyclic compounds that retain a high degree of oxygenation. Additionally, in most structures, it is also still possible to observe the remnants of the poly- $\beta$ -ketone precursor.



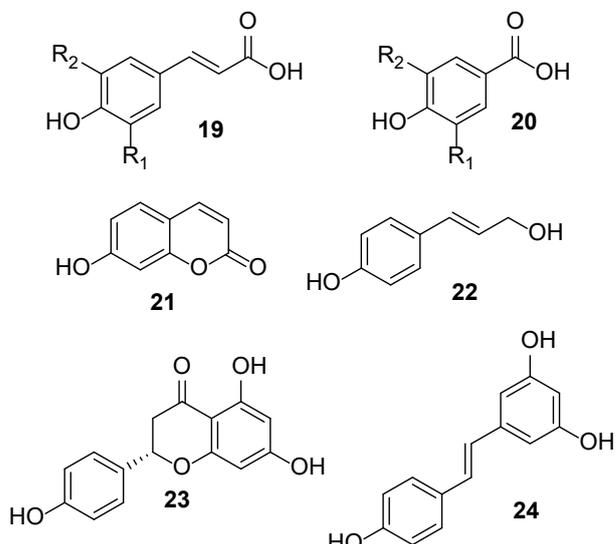
## Phenylpropanoids

The phenylpropanoids are a group of plant exclusive natural products with their biosynthetic origins in the shikimate pathway.<sup>29</sup> This pathway encompasses a series of primary metabolic reactions that give rise to a range of biologically important aromatic compounds all derived from shikimic acid (**14**), the most important of which are the aromatic amino acids: tryptophan, phenylalanine and tyrosine. The shikimate pathway is entirely absent from animal metabolism, which is why animals must obtain the aromatic amino acids through their diet. Despite the presence of the shikimate pathway in bacteria and fungi, they are unable to produce phenylpropanoids, suggesting this pathway developed with the emergence of the plants.<sup>29</sup> As their name may indicate, all phenylpropanoids are phenolic compounds that incorporate a three carbon chain into the molecule. This base structure arises from the deamination of phenylalanine (**15**) or tyrosine (**16**), via an ammonia lyase enzyme, to cinnamic acid (**17**) or 4-coumaric acid (**18**) respectively.<sup>30</sup> Cinnamic acid can itself be further converted into 4-coumaric acid, which when bound as the thioester to CoA (4-coumaroyl-CoA), can be readily modified into the wide range of phenylpropanoids that are known.<sup>31</sup>



The synthesis of phenylpropanoid from 4-coumaroyl-CoA occurs via a number of interconnected, multi-step, enzyme mediated reactions.<sup>31</sup> Depending upon the specific enzyme processes utilised during biosynthesis, phenylpropanoids are further divided into five broad structural sub-classes: phenolic acids, coumarins, monolignols, flavonoids and stilbenes, for which representative structures are given below. The hydroxycinnamic acids (**19**) as derived from 4-coumaroyl-CoA, can be modified to give the hydroxybenzoic acid (**20**) form of the phenolic acid.<sup>32</sup> Both types of phenolic acid are frequently utilised as signalling molecules and are also important precursors to other phenylpropanoid compounds. The coumarins, such as umbelliferone (**21**), are synthesised from the hydroxycinnamic acids by hydroxylation at the *ortho*- position and subsequent spontaneous cyclisation into the lactone.<sup>33</sup> Monolignols, such as 4-coumaryl alcohol (**22**) are also synthesised from the hydroxycinnamic acids by selective reduction of the acid, through the aldehyde, into the alcohol.<sup>34</sup> Monolignols are themselves precursors to lignin (important structural polymers) as well as lignans (a class of antioxidants). Finally, within the phenylpropanoids are the flavonoids and stilbenes, characterised by naringenin (**23**) and resveratrol (**24**) respectively. These are both interesting examples of mixed origin secondary metabolites. Each class is initially synthesised from a 4-coumaroyl-CoA derivative and three units of malonyl-CoA that are added via a different type III polyketide synthase enzyme.<sup>35</sup> The different enzymes result in a different cyclisation reaction and hence structure, with chalcone synthases (CHS) forming flavonoids and stilbene synthases (STS) resulting in stilbenes.<sup>35</sup>

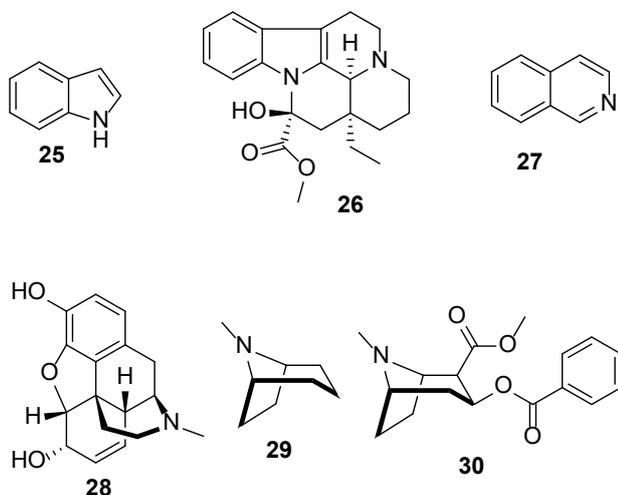
Plants have made extensive use of the phenylpropanoid pathway to produce a large number of aromatic molecules that would otherwise be unobtainable from polyketide synthesis. Lignin in particular, is considered one of the most important molecules that has allowed plants to colonise the terrestrial landscape with such success, due to the rigidity it provides.<sup>36</sup> The reliance of plants on many phenylpropanoids, especially lignin, has led some to argue that the importance of this class of natural products to the survival of plants puts these secondary metabolites on par with the primary metabolites.<sup>37</sup>



## Alkaloids

The final class of natural products are the alkaloids. These are all nitrogenous heterocyclic compounds derived from one or more amino acids, be they aliphatic or aromatic in origin.<sup>38,39</sup> In this way, alkaloids are unique among the natural products in that their structural diversity arises initially from the diversity of potential amino acid precursors. This is as opposed to the other classes of natural products discussed, where structural diversity generally arises from the secondary modification of a single core precursor. There are a multitude of different reaction pathways for which the synthesis of alkaloidal natural products can proceed along and too many to adequately summarise here. The amino acid precursor utilised will naturally alter the biosynthetic options available for the synthesis of any alkaloid. Thus the resulting carbon heterocycle skeleton can be used to infer the synthetic origin of an alkaloid as well as provide a convenient classification system.<sup>39</sup>

Extended aromatic heterocycles can be produced from each of the shikimic aromatic amino acids. Indole alkaloids (**25**) are derived from tryptophan and are also frequently found to incorporate a terpenoid chain into the final structure.<sup>38</sup> This is seen in vincamine (**26**), an alkaloid found in the periwinkle flower, in which tryptophan has combined with a modified monoterpenoid unit.<sup>40</sup> Alkaloids derived from phenylalanine or tyrosine tend to form quinoline or isoquinoline (**27**) backbones.<sup>41</sup> The opioid alkaloids, as typified by morphine (**28**),<sup>42</sup> are perhaps the most famous examples of an isoquinoline. There are of course many non-aromatic alkaloids, particularly those that arise from ornithine, arginine and lysine precursors. Tropane (**29**) alkaloids are derived from ornithine or arginine,<sup>38</sup> of which cocaine (**30**) is a well-known example synthesised via the combination of the tropane heterocycle to a benzoyl group that is obtained from the phenylpropanoid pathway.<sup>43</sup> The complexity of known alkaloids cannot be easily summarised here, although the structural examples outlined should help to highlight this. This variety of alkaloid structures has also led to the reporting of myriad pharmacological effects.<sup>44</sup>



As has hopefully been illustrated, each class of natural products is able to produce highly variable chemical backbones with an immense degree of structural complexity. The suite of chemical and enzyme mediated modifications (such as methylation, cyclisation or oxidation/reduction processes) that can be employed during biosynthesis only work to add further structural complexity to any scaffold. Natural products may be synthesised via a single secondary metabolic pathway, as the examples presented here mostly exemplify, or via a combination of fragments from multiple pathways. There are also some highly specialised and bioactive peptides and polysaccharides produced by a combination of primary and secondary metabolic routes, that can be considered natural products. Although the structures of secondary metabolites may appear overly complex at times, there are always structural remnants in the chemical backbone hinting at the humble origins of a natural product as an offshoot of primary metabolism. That this structural variety and complexity can arise from such simple precursors is testament to the efficiency with which organisms have developed their secondary metabolic pathways.

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# Gertrude Elion: pioneer of drug discovery

Claire Voogt

School of Science, University of Waikato, Hamilton 3240 (email: [clairevoogt123@gmail.com](mailto:clairevoogt123@gmail.com))

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## Life and early career



**Fig. 1.** Gertrude Elion ([https://commons.wikimedia.org/wiki/File:Gertrude\\_Elion.jpg](https://commons.wikimedia.org/wiki/File:Gertrude_Elion.jpg), reproduced under license CC BY 4.0)

Gertrude (Trudy) Elion was, by all means, a woman who beat the odds (Fig. 1). She was born in 1918 to European-Jewish immigrants, who emigrated to New York City in the early 20<sup>th</sup> century, escaping the devastating effects of both World Wars. It is here that Gertrude's life began.<sup>1</sup>

Gertrude was somewhat of a polymath in school, and had her beloved grandfather not passed away from cancer, she may not have pursued chemistry. However, as a teenager, having been forced to watch her grandfather's slow and painful battle, she became determined to dedicate her career to curing diseases to alleviate suffering, and hence pursued a career as a pharmacologist.<sup>1,2</sup>

Gertrude's family were hard workers, and her mother was a determined woman who supported her ambitions to become a chemist, which at the time was somewhat extraordinary. Of her mother Gertrude once said "She had no higher education, but had the most common sense of anyone I knew, and she wanted me to have a career."<sup>3</sup> After graduating from high school at age 15, Gertrude enrolled at Hunter College in New York City, where she earned a BA in chemistry. She graduated *summa cum laude* in 1937, after which she planned to marry her fiancé, a statistics student named Leonard Canter.<sup>4</sup>

In the 1940s Leonard tragically died of a bacterial infection, and Gertrude never married.<sup>5</sup> She said that following marriage, she would have likely succumbed to expectations that a wife should not work, especially in a laboratory. The death of her beloved fiancé further engrained her determination to become a pharmacologist.<sup>4</sup>

The Elion family had lived prosperously throughout the 1920s, but the stock market crash of 1929 bankrupted them, and consequently Gertrude could not pursue graduate studies. Postgraduate fellowships were very rarely offered to women, so instead she opted to work.

Despite her academic success and suitable qualifications, Gertrude could not find any laboratory work. At a time when advertisers bombarded the public with slogans such as "Women don't leave the kitchen!"<sup>6</sup> Gertrude unsurprisingly struggled to be viewed as an equal by her male peers. Gertrude recalls being told, "You're qualified. But we've never had a woman in the laboratory before, and we think you'd be a distracting influence". While she wanted to work as a researcher, she settled for jobs as a secretary, chemistry teacher, and unpaid laboratory worker.<sup>7</sup>



**Fig. 2.** Gertrude Elion and George Hitchings, 1988 ([https://commons.wikimedia.org/wiki/File:George\\_Hitchings\\_and\\_Gertrude\\_Elion\\_1988b.jpg](https://commons.wikimedia.org/wiki/File:George_Hitchings_and_Gertrude_Elion_1988b.jpg), reproduced under license CC BY 4.0)

She performed menial repetitive tasks, testing pickle juice acidity and mayonnaise colour in her role at Great Atlantic & Pacific Tea Company, better known as A&P supermarkets.<sup>3</sup> She says, "I became restless because the work was so repetitive, and I was no longer learning anything." However, a turning point came for Elion



**Fig. 3.** Elion and Hitchings in the laboratory c.1948 ([https://commons.wikimedia.org/wiki/File:George\\_Hitchings\\_and\\_Gertrude\\_Elion\\_1948.jpg](https://commons.wikimedia.org/wiki/File:George_Hitchings_and_Gertrude_Elion_1948.jpg), reproduced under license CC BY 4.0)

when WWII demanded the manpower of the USA. Laboratories were left understaffed and Gertrude finally had the opportunity to work as a research chemist.<sup>1</sup> In her first role as a researcher at Burroughs Wellcome, she worked under George Hitchings, initiating a collaboration that would last their entire scientific careers (Figs. 2 & 3). Hitchings respected her scientific prowess, and together they developed the method of drug discovery that would eventually earn them the Nobel Prize in Physiology and Medicine. Their success would also help drive the success of Burroughs Wellcome, which would become the modern-day pharmaceutical giant GlaxoSmithKline.<sup>3</sup>

Together with Hitchings, Elion designed a novel approach to drug development. Scrapping the traditional trial and error approach to drug synthesis, they opted for a more strategic line of attack. Their research analysed key biochemical differences between healthy and pathogenic cells, including cancer cells, bacteria, and viruses. This allowed the development of highly targeted drugs that were less harmful to human cells.<sup>3</sup>

The flexibility of her role at Burroughs Wellcome suited Gertrude's passion for learning, allowing her to work across biochemistry, pharmacology, immunology, and virology. Her research mainly focussed on purines, one of the key building blocks of DNA.<sup>8</sup>

In 1967 Gertrude was appointed the Head of the Department of Experimental Therapy, a role in which she led the development of many drugs, including pyrimethamine, trimethoprim, allopurinol, and acyclovir.<sup>2</sup>

### 6-mercaptopurine

The underlying idea of Elion and Hitchings' initial research is that all cells have DNA, and hence require nucleic acid to reproduce. Therefore, since cancerous cells multiply much faster than healthy cells, they require more nucleic acid for DNA synthesis. This biosynthetic process could be hijacked to target disease.<sup>3</sup>

Their research found that the modification of purines, by substituting oxygen atoms with sulfur, can disrupt DNA replication similarly to existing chemotherapy drugs. Elion investigated how modification of purine compounds could most effectively be used to treat cancer. The sulfur-containing purine analogues were non-functional as purines, and hence disrupted formation of leukaemia cells.<sup>1,3</sup>

In 1950, Gertrude's research led to the discovery of 6-mercaptopurine (6-MP), an effective, less toxic drug than existing treatment options (Fig. 4). In experimental trials, the drug cured 80% of children with leukaemia, and was consequently rushed to release. Even acute patients with terminal diagnoses experienced complete remission

of the disease. Although the effects were only temporary, this discovery was a huge victory for cancer treatment.<sup>9</sup>

6-MP competes with purines (guanine and hypoxanthine) for the enzyme hypoxanthine-guanine phosphoribosyl-transferase (HGPRT). Following reaction via HGPRT 6-MP forms thioinosine monophosphate (TIMP), which inhibits the formation of xanthylic acid (XMP) and adenylic acid (AMP) from IMP. Since these compounds are required for DNA replication, the affected cells cannot reproduce.<sup>9</sup>

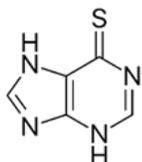


Fig. 4. Structure of 6-mercaptopurine

6-MP also inhibits purine synthesis in cells by inhibiting phosphoribosyl pyrophosphate amidotransferase (PRPP amidotransferase), the rate limiting enzyme of purine biosynthesis.<sup>9</sup>

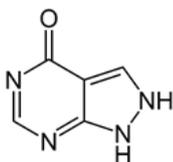


Fig. 5. Structure of allopurinol

In an attempt to make the effects of 6-MP last longer in cancer patients, Elion developed allopurinol (Fig. 5), a drug still used to treat the build-up of uric acid in localised areas of the body, known as gout. Gout is a condition which is often fatal to cancer patients, and its treatment has improved the lifespan of many cancer sufferers and improved the quality of life of many more.<sup>3</sup>

## Azathioprine

Gertrude's pharmacological success continued when in 1957 she synthesised azathioprine (Fig. 6), an analogue of 6-MP. Azathioprine would go on to be marketed as Imuran, the immunosuppressant that would make the first kidney transplants between unrelated donors possible. The drug has also been used to manage a multitude of incurable autoimmune disorders.<sup>3</sup>

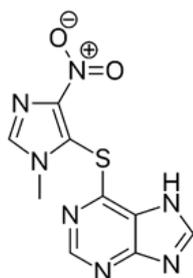


Fig. 6. Structure of azathioprine

Azathioprine is a prodrug, which means that it is not functional itself. However, following absorption into the bloodstream, glutathione almost immediately triggers rapid reductive cleavage of the thioether bond to produce functional 6-MP and 6-thioinosinic acid. The 6-MP

produced then prevents formation of functional white blood cells by interfering with DNA and RNA reproduction.<sup>10</sup>

Azathioprine has improved the lives of more than 500,000 patients since its discovery. It is so important that it now features on the World Health Organisation model list of essential medicines.<sup>11</sup>

## Acyclovir

One of Elion's greatest breakthroughs was the development of an antiviral drug named acyclovir (Fig. 7). At the time, it was generally believed that any effective antiviral treatments would be too toxic for the human body to withstand.<sup>3</sup>

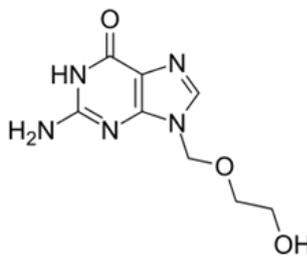


Fig. 7. Structure of acyclovir

Therefore, the development of acyclovir was totally revolutionary in the medical field. The drug, which could attack herpes, Epstein-Barr, chickenpox and shingles, ushered in a new era of antiviral drug discovery, and indirectly allowed the development of a treatment for HIV/AIDS.<sup>3</sup>

Following entry into infected cells, acyclovir is phosphorylated to produce bioactive acyclovir triphosphate. This drug is not toxic to healthy cells because the initiating step is triggered by the presence of viral-coded thymidine kinase. Acyclovir triphosphate prevents DNA replication of viruses by inhibiting the viral DNA polymerase enzyme.<sup>12</sup>

## Legacy

Gertrude Elion thoroughly enjoyed her work, so when she formally retired from Burroughs Wellcome in 1983, she continued as a Scientist Emeritus. In this role she oversaw the development of azidothymidine (AZT), the only antiretroviral medication to successfully fight and prevent HIV/AIDS.<sup>2</sup>

In 1988, Gertrude Elion received the Nobel Prize in Physiology and Medicine alongside Hitchings and her co-worker James Black and in 1991, she was the first woman to be inducted into the National Inventors Hall of Fame.<sup>2</sup>

Despite being one of the few people to receive a Nobel Prize without a PhD, Gertrude received honorary doctorates from George Washington University, Brown University, and the University of Michigan for her scientific contributions.<sup>7</sup>

Perhaps most importantly, Gertrude Elion's name features on 45 patents for life-changing drugs. More than the recognition of esteemed scientific institutions, what meant the most to her were the letters of gratitude she

received from patients who had benefitted from her discoveries. Elion said that these letters were a greater reward than the Nobel Prize.<sup>4</sup>

Her legacy also extends beyond her own discoveries. Gertrude fiercely believed in the investment of resources into future generations of chemists. Burroughs Wellcome established a scholarship for young female scientists in her honour and she was a mentor to many students, making a special effort to regularly meet with them and attend their presentations.<sup>1,13</sup>

Gertrude's illustrious career and intellectual fortune are the product of passion and hard work, but also a series of tragic events. It was both the personal tragedies of Gertrude's life, and the political and economic crises of the early 20<sup>th</sup> century that shaped her professional success, and through which she improved the lives of millions around the world.

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# Wastewater treatment in New Zealand: zeolites as a potential low-cost solution for heavy metal removal

Zahida Zia,\* Adam Hartland and Michael R. Mucalo

School of Science, University of Waikato, Hamilton 3240, New Zealand  
(email: ZZ176@students.waikato.ac.nz)

**Keywords:** *water treatment, heavy metals, zeolites*

## Introduction

Water, which constitutes about 75% of body weight in infants and 55% in adults,<sup>1</sup> is essential for the existence of life on earth. Without drinking water, humans can only survive for five days. Generally, we can describe water as being one of four types;<sup>2</sup> surface water, including lakes, rivers, streams and reservoirs, groundwater which is present in underground bedrocks, soils and sand, wastewater which is water influenced by any human activity, and lastly, stormwater which is generated by precipitation (rain or melting of snow) and which flows over the surface of the earth without penetrating into the ground.<sup>3</sup>

This article is divided into two sections. The first provides an overview of water treatment processes used in New Zealand to treat wastewater while the second discusses a low-cost water treatment option using a local resource (a mineral) with a special focus on removing heavy metals from wastewater. It emphasises the use of zeolites as a low-cost and environmentally friendly option to remove heavy metals from water in New Zealand.

## Water pollution and sources of water pollution

Increases in population have come about from and have been contributors to industrialisation, urbanisation, and deforestation. An increase in industrialisation and agricultural practices has played a key role in the addition of unwanted chemical species into water supplies. For instance, the use of chemicals, fertilisers, and pesticides have caused air, water and land pollution. Runoff of fertiliser from farms, urban runoff from streets, and storm-

water are now categorised as major sources of contaminants which have serious environmental consequences.

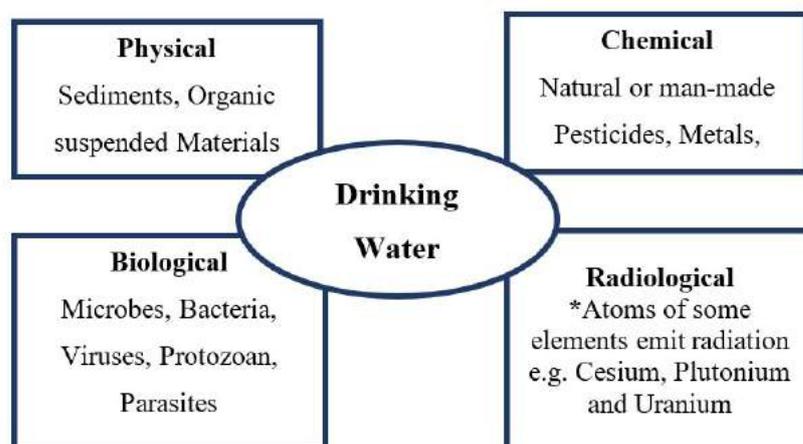
Heavy metals in water represent persistent pollutants which make their way into the environment through different natural and anthropogenic sources such as geological erosion, volcanic eruptions and industrial emissions and discharges. Drinking water contaminants are divided into four categories (Fig. 1) which include physical, chemical, biological and radiological.<sup>3</sup> Clay minerals have been reported as a potential material to remove heavy metals due to their ion-exchange ability. Different clay minerals such as zeolite, vermiculite, perlite, and montmorillonite have been extensively employed to remove heavy metals.

## Water treatment

Many contaminants such as insoluble solids, microbes and chemicals can affect the quality of source water, whether it is surface water or groundwater, rendering it unsafe for health and aesthetically undesirable due to bad taste or odour. It is hence necessary to remove these contaminants by treating water before any use of it which requires a reasonably high standard of cleanliness.

## Water treatment plants in New Zealand

Generally, a treatment plant in New Zealand consists of a series of treatment processes, as shown in Fig. 2. There might be an additional process which could be required for a particular supply or for a particular contaminant and its placement in the "treatment train" would be assigned according to the particular design of the treatment plant.



\*Elements with unbalanced number of neutrons and protons have unstable atoms which can emit ionizing radiations

Fig. 1. Types of drinking water contamination (information sourced from USEPA, 2017 January 19)<sup>3</sup>

## Pre-treatment

One or more pre-treatment steps may be used. These are often unsophisticated processes designed primarily to reduce the load of contaminants reaching the main water treatment processes or to condition contaminants in the water to make their later removal easier. They include settling (e.g., in a reservoir or sedimentation basin to allow particles in the water to sink to the bottom), aeration and chemical pre-oxidation.

A sediment basin is a large impounded area that allows the settlement of particles under gravity and serves to reduce the load of particles reaching the main areas of treatment. This is done by decreasing the speed of water in the large basin.<sup>5</sup>

Source water, i.e. rivers, lakes, etc., is percolated through an infiltration gallery which is a horizontal drain made up of perforated or jointed pipes. It is laid down the surface of the water bed and contains gravel and soil to make an adequate collection of water to remove turbidity, natural organic matter and some microbes such as *Cryptosporidium*.<sup>6</sup>

Oxidising chemicals such as ozone, chlorine and potassium permanganate are usually used to oxidise natural organic matter to make its removal easy. Sometimes they are also used to oxidise dissolved iron and arsenic to precipitate them out in a particle/solids removal process step.<sup>7</sup>

Aeration of water is also used to oxidise contaminants to convert them into their insoluble forms. There are two aeration methods that are generally used. One is the passing or spraying of water through an aeration tower or air bubbling through the actual source of water.

Copper sulfate is used to control the growth of algae in a stagnant water body. Algal blooms can, however, be controlled/prevented more efficaciously by monitoring the factors which cause the increase in algae growth in the first place such as nutrient loads.

## Particle removal

The process of particle removal mainly involves the removal of sand, silt, and clay but it also involves the removal of microbial loads such as protozoa and bacteria by their effective adsorption on large solid particles. A series of processes are used for effective removal of particles from water which includes coagulation/flocculation and filtration.

Coagulation/flocculation is the main process used for the removal of particles/solids. In this method, a coagulant is added to water which causes smaller particles to clump together to form larger particle aggregates so enabling more facile deposition. The coagulant also facilitates the formation of flocs of insoluble chemical salts which further provide potential adsorption surfaces for other metals, microbes and for some nonmetallic particles. These are then removed by filtration of the solids.<sup>8</sup>

Once the coagulation/flocculation step has been executed, the particles are given some time to mature into sufficiently large aggregates so that they eventually precipitate out of the water. This is done to reduce the amount of solids that would otherwise be subject to filtration.<sup>9</sup> A direct filtration step is used after the coagulation/flocculation step if the turbidity of the water is low. In one treatment plant in New Zealand, dissolved air flotation (DAF) is a method that works to float out the larger particles from the clarifier surface rather than allowing them to settle to the bottom.

Filtration is basically the last step of the solids removal process that is executed by means of using filtering aids. Regardless of the filter media type used, contaminants and particles are trapped in such a step, giving a clear water stream. Once the filters are filled with contaminants, they require cleaning, which is necessary to maintain their efficiency over time. In New Zealand water treatment plants, rapid sand, diatomaceous earth, bag, cartridge, slow sand and membrane filtration are used.

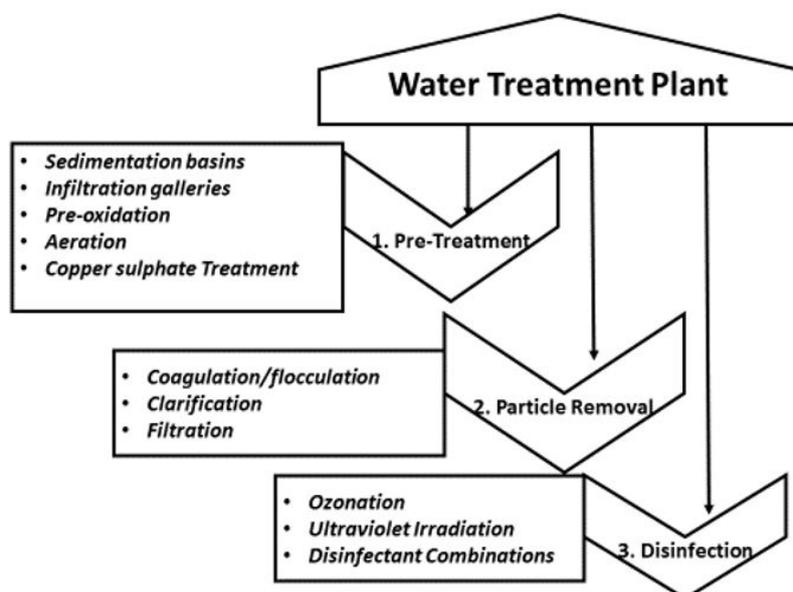


Fig. 2. Series of treatment processes generally involved in wastewater treatment in New Zealand (information sourced from Ministry for the Environment, NZ (MFE)<sup>4</sup> to construct figure)

## Disinfection

The removal, killing or deactivation of disease-causing microbes is called disinfection.<sup>10</sup> Different methods have differing effectiveness. The most commonly used methods in New Zealand for disinfecting water involve the use of chlorine, ozone and UV radiation.

Chlorine is a moderately used oxidiser which serves as a long-term disinfecting agent and this process is called chlorination. The efficiency of this method is determined by pH and is supported in waters at low pH.

Ozone is a strong oxidising agent and provides a rapid deactivation of pathogenic microbes (*Cryptosporidium*, bacteria and viruses) and this is called ozonation. Due to its rapid breakdown, this process produces no residues post treatment.

UV radiation (at a wavelength of 254 nm) is used to destroy the DNA of microorganisms, i.e. bacteria and protozoa). Most viruses, however, cannot be eradicated by this method.

## Heavy metal input in wastewater and its removal

Heavy metals describe a group of elements with high density (greater than 5 g/cm<sup>3</sup>) and include the high atomic weight elements from group (III) to (V) and transition elements. In New Zealand, arsenic (As), lead (Pb), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), nickel (Ni) and zinc (Zn) are of concern as heavy metal contaminants.

There are two major routes that add heavy metals to the aquatic environment: (1) a natural route, including volcanic eruption and the erosion of sediments, and (2) an anthropogenic route, including mining, industrial wastewater discharge, dumping and stormwater runoff. Due to their long-term effects, the concern of heavy metal toxicity was intensified in New Zealand when heavy metals were detected in sediments off Otago Harbour, and in the Hutt River estuary due to discharge of industrial wastewater and in some streams of Coromandel due to uncontrolled mining activities.<sup>11</sup>

In the Waikato river, the level of arsenic has been found to exceed the limit imposed by the World Health Organisation (WHO), as this element is abundant in all geothermal areas and in waterways of the Taupo Volcanic Zone (TVZ).<sup>12</sup> A significant amount of cadmium was reported in Waikato soils due to the use of imported fertilisers, which makes its way eventually to water bodies through soil leaching.<sup>13</sup> In aquatic environments, Pb was reported due to industrial activities emitting lead into the environment which makes its way into aquatic bodies by leaching via rainfall.<sup>14</sup>

Ion exchange resins that are used to remove metal ions such as iron and manganese can also be used for the removal of heavy metals from water. Another method employed is greensand filtration. Greensand (a naturally occurring material) is used to form a layer of insoluble metal oxide which is then further removed by filtration.

The coating of metal oxides on sand grains is regenerated by using potassium permanganate or chlorine. These two methods involve the use of energy and chemicals and there is consequently a need for simpler, low-cost methodologies or technologies to remove heavy metals.

## Zeolites as potential low-cost adsorbents for metal removal

Globally, water demand is predicted to increase significantly over the coming decades. In addition to the large water demand from the agricultural sector which is currently responsible for 70% of water extractions worldwide, large increases in water usage are expected in industry and energy production. These estimates support the often-cited approximation that, globally, it is likely that over 80% of wastewater is released into the environment without adequate treatment. Inadequate wastewater management also has a direct impact on ecosystems, contaminating land and water and polluting the food chain.<sup>15</sup> By paying serious consideration to such environmental problems, it will be crucial to treat wastewater for assuring the quality of surface and groundwater. Additionally, treated wastewater may provide a source for reuse in industrial and agricultural industries. Cost effectiveness is the most important parameter before the application of any method for water treatment. This is especially so if it is to be used on a large scale. Among all available options, use of inherently low-cost materials (such as clay minerals) are hence the best options for water treatment. Use of locally available low-cost natural materials (e.g. zeolites) with a chemical structure which also supports the removal of heavy metals (by adsorption and ion-exchange mechanisms) can provide a feasible option economically. The literature illustrates that these materials could constitute an effective method of water treatment. This is due to enhancement of metal ion removal abilities by the several mechanisms that would exist in any composite made with this and other materials that have the potential for being water treatment matrices.

Zeolites are naturally occurring hydrated aluminosilicates with a porous structure. There are a wide number of crystal structures reported for zeolites. There are 273 zeolite crystal structures registered with the number of cation exchanged zeolites being 409.<sup>16</sup>

## Zeolites in the Taupo Volcanic Zone (TVZ)

In New Zealand, zeolite deposits occur in the TVZ and their geology and mineralogy are well established (Fig. 3).<sup>17</sup> In Ngakuru, located within the TVZ, an extensive deposit of zeolites has been discovered which is less than 50,000 years old.<sup>18</sup> In 1992, the first deposit was discovered at Mangatete Road (Rotorua) which was available for commercial use soon after its discovery. Deposits from this area have been used effectively to soak up oil, chemical spills and animal wastes and have shown excellent adsorption capacities.<sup>18</sup> Zeolites in lower temperature areas such as in Wairakei (a geothermal area in the TVZ) have been known since the 1950s.

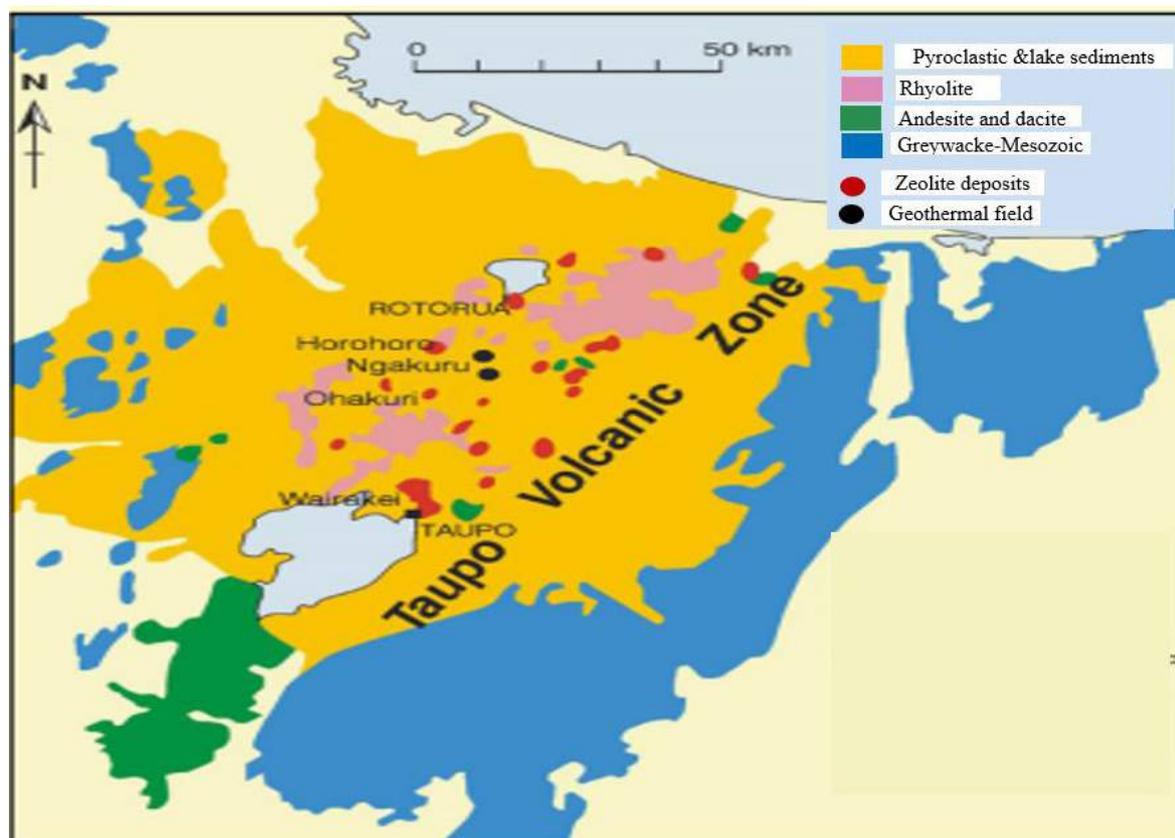


Fig. 3. Zeolite deposits in the Taupo Volcanic Zone (adapted with permission from Blue Pacific Minerals)<sup>17</sup>

### Potential of zeolites for heavy metal removal

A zeolite crystal is composed of three-dimensional frameworks of  $\text{SiO}_4$  and  $\text{AlO}_4$  connected through oxygen bridges.<sup>19</sup> A negative charge is produced by the isomorphous replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in the lattice. Exchangeable cations (e.g. sodium, potassium and calcium) balance out this negative charge.

The zeolites have potential industrial applications such as adsorbents, detergent builders, molecular sieves and ion exchangers.<sup>20, 21</sup> The literature shows that heavy metals from industrial, municipal and agricultural wastewaters have been removed by the application of zeolite.<sup>22</sup> Easy availability and extraction make them low cost adsorbents of great interest due to their high surface area and easy ion exchange ability. It has been shown that ion exchange is the major mechanism for heavy metal removal by zeolites.<sup>23, 24</sup> In a study reporting the efficiency of three aluminosilicate minerals (perlite and vermiculite along with natural zeolites),<sup>25</sup> natural zeolites were reported to be the most efficient agents for lead ion removal from wastewater.

### Modifications of zeolites to remove heavy metals

Clay minerals (e.g. zeolites) have negatively charged surfaces, which hence show low affinity for anions. Inorganic cations, mainly  $\text{Fe(II)}$  ions and other cationic species (e.g. lead, barium and silver) have been used to modify clay minerals for using the modified clays to remove anionic species from water.<sup>26-28</sup> Lead-modified minerals (such as

zeolite, perlite and vermiculite) have been used to remove  $\text{Cr(VI)}$  (in the form of chromate anions). Among these, clay minerals, zeolites and vermiculite show a higher removal efficiency with respect to  $\text{Cr(VI)}$  i.e. 86% and 60% for zeolite and vermiculite respectively.<sup>29</sup> A proposed mechanism to account for this ion removal property suggests that a re-exchange process between the potassium ion of potassium chromate ( $\text{K}_2\text{CrO}_4$ ) and lead takes place initially. In other words, insoluble lead chromate is formed by combination of  $\text{Pb}^{2+}$  and  $\text{CrO}_4^{2-}$  which deposits on the surface of the lead-modified minerals.<sup>30</sup> Therefore, surface modification of minerals helps to increase their ion exchange and sorption ability. Chitosan is a biodegradable polymer which has been reported as an excellent material to remove heavy metals.<sup>31</sup> It can enhance the properties of these aluminosilicate minerals. Chitosan-modified zeolites have been used to extract divalent metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ ) from acidic media (e.g.  $\text{H}_3\text{PO}_4$  solution), which have metal ions present as impurities. Modified zeolites have shown a remarkable removal efficiency of more than 90% for these cations after only 10 minutes of exposure. A study reported the synthesis of hydroxyapatite/zeolite nanocomposites by using a simple sol-gel method. This nanocomposite was used to remove  $\text{Pb(II)}$  and  $\text{Cd(II)}$  from aqueous solutions. Adsorption of cationic species on the surface of this composite was demonstrated to be the removal mechanism for ions in this study.<sup>32</sup> Physical modification is another way to increase the removal efficiency of materials. For example, size reduction of the adsorbent material is considered an important and very basic method for increasing the surface area of an adsorbent which leads to higher adsorption.<sup>33</sup>

## Conclusions

The cost of materials and operations involving the application of these materials are key parameters in deciding the success of water treatment. Many studies have reported the sorption and ion exchange abilities of zeolites for the removal of metal ions from wastewater. These ion removal properties are related to the composition and structure of these minerals. Another way of increasing their adsorption ability can be achieved through mixing these materials to form a composite material for the adsorption applications with other materials (such as hydroxyapatite) which also have heavy metal removal potential. By keeping in view all these aspects, especially in terms of cost, zeolite matrices may be considered as powerfully effective materials for heavy metal removal.

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# Developing a periodic table for earth scientists

Peter Hodder

School of Government, Victoria University of Wellington, New Zealand; and HodderBalog Social and Scientific Research, Wellington New Zealand (email: [peter.hodder@vuw.ac.nz](mailto:peter.hodder@vuw.ac.nz))

**Keywords:** *periodic table, ions, ionic potential, fictional quests, sentiment analysis*

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## Abstract

The development of Mendeleev’s periodic table has been likened to that of a ‘quest’, one of seven types of fictional story proposed by Christopher Booker. Although the stages of these fictional stories have been more recently interpreted by Matthew Jockers as trends in emotions, in true-life stories it is generally necessary to have proxies for the stages of fictional tales and the roles of actors. These may be deduced from analysis of correspondence and historic events or – most recently – through using citation analysis. This paper extends and applies these ideas to the ‘story’ of the development of Bruce Railsback’s periodic table for earth scientists, suggesting that those whose work Railsback cites should be considered ‘companions’ in the quest, while those who cite his work can be considered ‘helpers’. Railsback has been fortunate in that thus far there has been little opposition to his proposed table, i.e., there are no ‘monsters’. However, there may yet be ‘final ordeals’ to overcome, perhaps because of the encyclopedic nature of the data portrayed. The potential usefulness of Railsback’s table is its recognition of the importance of ions rather than elements to geological processes. This has its origins in ionic potential (the ratio of ionic charge to ionic radius) proposed decades ago by Viktor Goldschmidt and Groves Cartledge, and models of how ions are incorporated into the crystal lattices of minerals as initially suggested by Naoki Onuma and subsequently developed more quantitatively. The paper ends by suggesting an alternative form of the periodic table for earth scientists that allows an element to be included more than once – as ions – and uses ionic charge and radius as variables, rather than the atomic number of elements as used in traditional forms of the periodic table.

## Introduction

The earliest periodic table for instructional use is currently considered to be a hand painted version dating back to 1876, thought to have been commissioned by Dimitri Mendeleev himself, displayed in a lecture theatre in the chemistry building of St Petersburg State University in Russia (Fig. 1A).<sup>1</sup> The past 150 years have seen his table expanded to 118 elements, in almost as many versions and derivatives of it as the number of years since its initial publication in 1869. A recent variant of the periodic table is that developed for earth scientists by Bruce Railsback (Fig. 1B).<sup>2</sup> He asserted that natural scientists

“... would like a [periodic] table that contextualizes all the occurrences of matter in its natural environments, rather

than settling for a periodic table that, while theoretically elegant, does little to explain the variety and complexity of matter in nature and has nothing to say about context or environment”.<sup>3</sup>

Railsback’s wish can be considered analogous to the “call” to a fictional quest, one of seven types of stories that have been identified by Christopher Booker.<sup>4</sup> The idea of a quest has previously been used in describing the development of the traditional periodic table,<sup>5</sup> and the stages of a quest and their associated sentiments are shown schematically in Fig. 2.<sup>6</sup>

Railsback’s journey towards *his* quest for an earth scientists’ periodic table is presented as a comparatively brief historical justification and description,<sup>7</sup> in which he refers to 23 previous articles and books, dating from 1928 and peaking in 1997 (Fig. 3A). These references included papers featuring the periodic table (25% of the references) and those in several geological or geochemical environments, as shown in Fig. 3B. The authors of the references in this paper could be considered analogous to the fictional quest’s “companions”;<sup>8</sup> see also Fig. 4. The outcome of Railsback’s initial journey is an impressive chart, densely packed with data and showing the similarity of elemental or ionic behaviour in particular environments as coloured symbols, and including supplementary diagrams, and fragments of text (see Fig. 1B).

## Participation in the quest as revealed by citation analysis

As at mid-2018, Google recorded 108 citations of Railsback’s 2003 paper,<sup>7</sup> the trend over time showing the usual peak in the number of citations a few years after initial publication,<sup>9</sup> and – less usually – sustaining interest by about eight citations annually (Fig. 5). Dahr’s periodic table for biologists is an obvious complement to Railsback’s initiative,<sup>10</sup> although Fig. 5 shows that the number of citations of this paper since its publication is considerably fewer than the number of citations of Railsback’s 2003 paper.<sup>7</sup> One possible explanation for this is that Dahr’s suggestion of “building a bio-periodic table using protein fold as the fundamental unit” does not involve elements or ions directly and so seems to involve a rather different ‘journey’ from that undertaken by Railsback in the development of his periodic table for earth scientists.<sup>11</sup>

None of the papers that cite Railsback’s 2003 paper that are specifically concerned with the periodic table reveal significant objections to the periodic table for earth scientists. The most supportive citing paper declared:

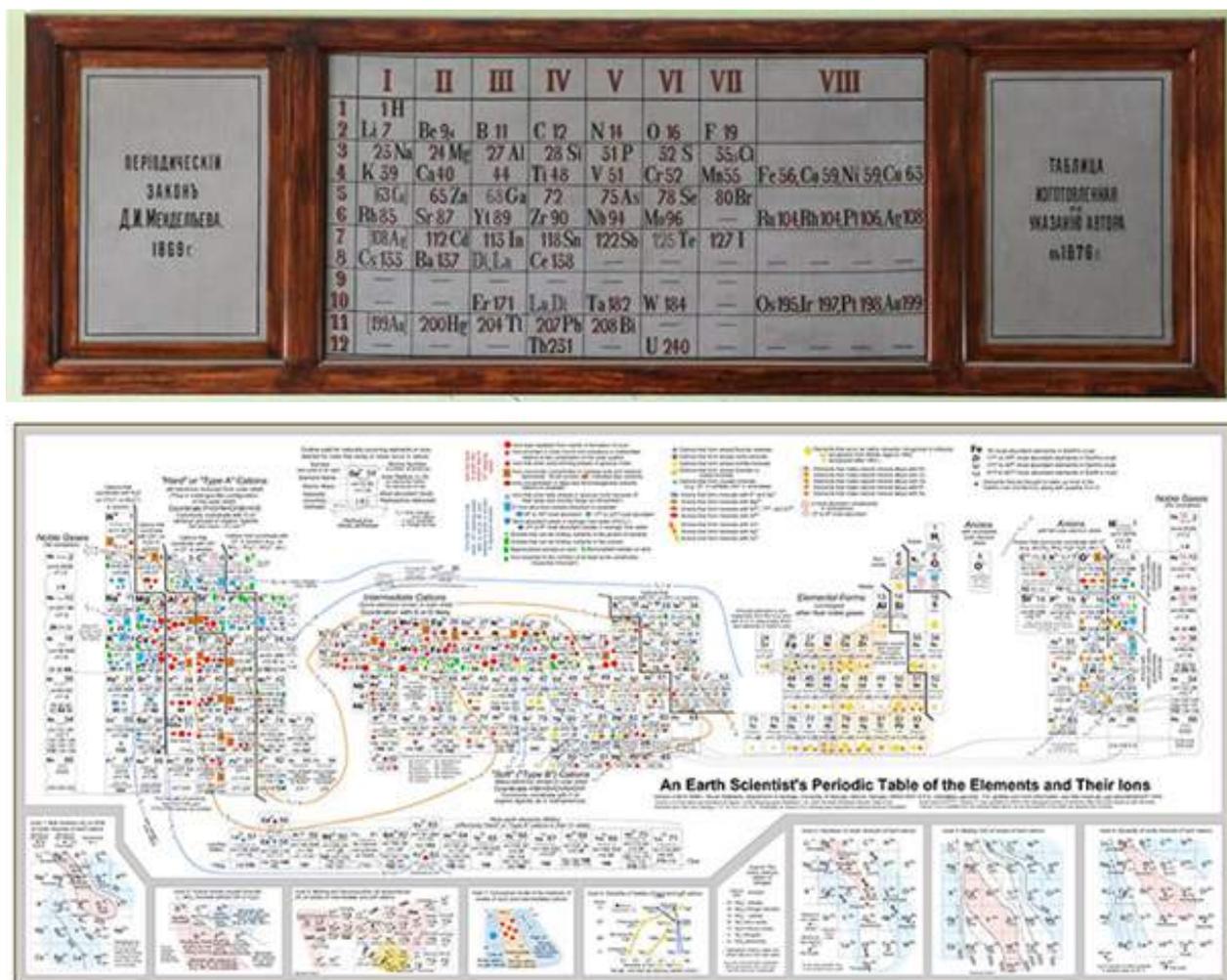


Fig. 1. A comparison in complexity. A. Upper: The hand painted version of the periodic table, 1876.<sup>1</sup> B. Lower: Bruce Railsback's 'An Earth Scientist's Periodic Table of the Elements and Their Ions'<sup>2</sup> - a comprehensive compilation of physical properties and abundances of elements and their ions and isotopes of importance to geoscientists.

Type of plot	Stages of the plot				
<i>The Quest</i>	1, The Call: recognition of need for journey	2, Journey across hostile terrain with companions and helpers, albeit with monsters and temptations to overcome	3, Arrival and frustration	4, The final ordeals – a last series of tests	5, After a 'last thrilling escape from death' the kingdom or life-transforming treasure is won
Sentiment					
Positive	█	█	█	█	█
Neutral	█	█	█	█	█
Negative	█	█	█	█	█

Fig. 2. A. Upper: Stages of a quest from Booker.<sup>4</sup> B. Lower: Schematic variation of sentiment as quest progresses based on Marin Jockers' ideas.<sup>6</sup>

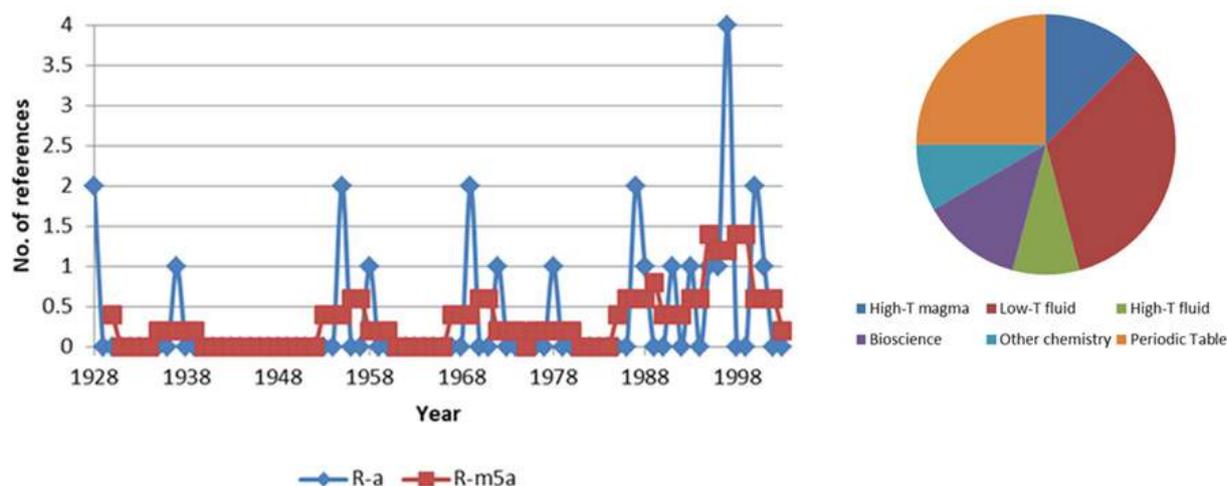
"Within this periodic table, elements are grouped in clusters related to charge and chemistry rather than the traditional division of mass. The chart basically indicates that the chemistry and the charge are related to mineral assemblages. This basic observation is significant and helps the geophysicist relate more to other parameters that may be of significant interest to the geologist such as alteration halos and chemical gradients. It demonstrates the complicated relationship between physics and chemistry, and indicates the potential of using geophysics to map the subsurface more accurately rather than the more common attempt to use it as a utility to directly

detect a geologic feature of interest."<sup>12</sup>

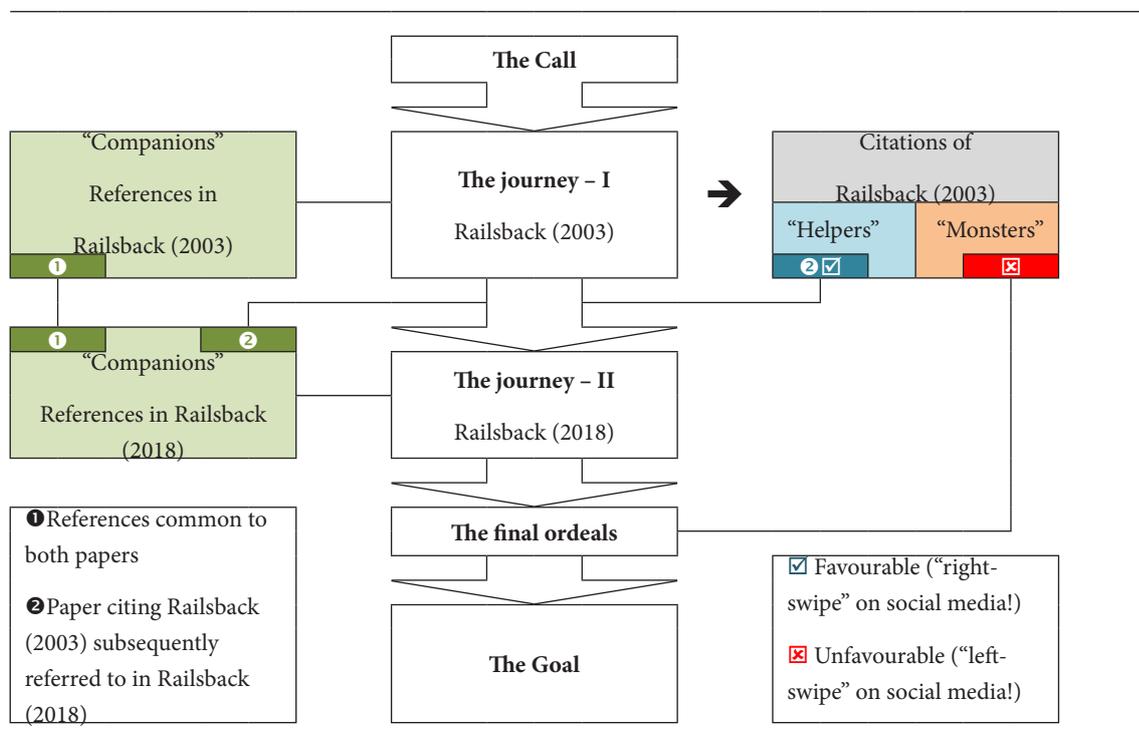
Of the citing papers, the only reservation expressed was:

"In short, while working out of a "synthesis" such a synthesis is never totalizing, or complete. It shapes the established sciences by framing a broad consensus but any aspect of that consensus could break open at a moment's notice under the right conditions."<sup>13</sup>

These papers give visibility to Railsback's ideas and so their authors can be considered analogous to the fictional quest's "helpers";<sup>14</sup> see also Fig. 4.



**Fig. 3.** Dates and themes of references in Railsback, 2003.<sup>7</sup> **A. Left:** Dates of references in Railsback 2003. The blue diamonds and lines are number of references for each year; the red squares and lines are the five-year moving average of dates of references. **B. Right:** Geological environments' of references, viz., high-temperature; low- and high- temperature fluids, typical of weathering and hydrothermal environments, respectively; and studies related to biology, other areas of chemistry, or the development of the periodic table.



**Fig. 4.** References and citations of Railsback's papers in 2003,<sup>7</sup> and 2018,<sup>3</sup> interpreted in terms of the 'companions', 'helpers' and 'monsters' associated with the journey towards and ordeals associated with the achievement of a quest.<sup>4</sup>

Most citations of Railsback (2003),<sup>7</sup> shown by topic in Fig. 6 are in geochemistry papers and relate to the low-temperature environment of weathering and the hydrothermal environment, with a smaller proportion on topics related to magmatic chemistry and general geology. However, some of the citations of the article are by those interested in the periodic table *per se*, with some interest also being shown by biologists.

None of the authors of the 23 papers listed in the references in Railsback (2003),<sup>7</sup> nor any of the five authors whose papers specifically relate to the concept of the periodic table that have been here suggested as Railsback's "companions" above are included among the authors of the 108 papers that subsequently cite Railsback (2003),<sup>7</sup>

i.e. they are not "helpers" as well as "companions". Moreover, from the 37 papers referred to in Railsback's chapter in Scerri's (2018) compilation,<sup>3</sup> only one author – Guillermo Restrepo – is among the authors of the 108 papers that cited Railsback (2003).<sup>7</sup> Another way of expressing this is to say that Restrepo, a "helper" because of his citation of Railsback (2003)<sup>7</sup> in a subsequent paper (*viz.*, Restrepo *et al.* 2006<sup>15</sup>), has joined the journey's "companions" by being referred to by Railsback in a subsequent paper (*viz.*, Railsback 2018).<sup>3</sup>

Despite the results from citation analysis, not all reaction to Railsback's table has been favourable. Some opposition might be expected, analogous to the "monsters"<sup>16</sup> that contribute to the "final ordeals" of the fictional

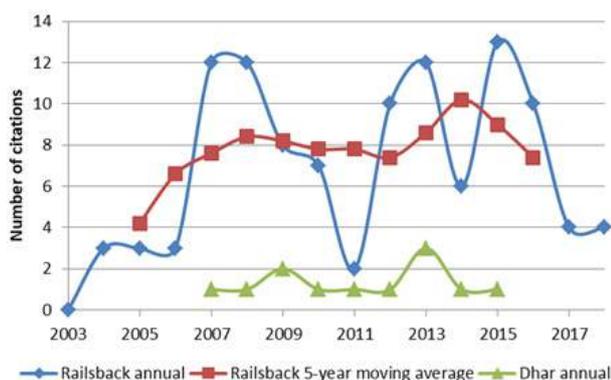


Fig. 5. Citation trend for Railsback, 2003.<sup>7</sup> Annual and five-year moving average of annual citations, showing the expected peak a few years after publication, but - less commonly for many research papers - a sustained interest in its theme thereafter. By comparison, the citation trend for Dhar is more subdued.<sup>10</sup>

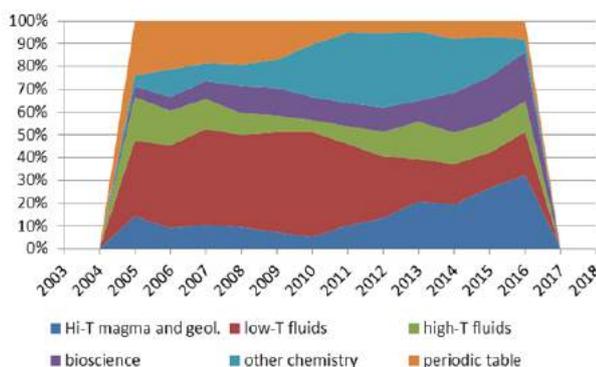


Fig. 6. Five-year moving average of the variation of themes of papers citing Railsback, 2003.<sup>7</sup> Citations are dominated by papers with a focus on low-temperature fluid citations, but the paper attracted continued interest from biologists and an initial flurry of interest from those specifically interested in the periodic table.

quest.<sup>17</sup> To the question “Have different kinds of people responded differently to the new table?”, Railsback himself responded:

“Yes, largely by age. Many (but certainly not all) older people don't like new synthetic theories, but perhaps that's because they don't need them. Some of the harshest criticism of the table has come from senior scientists who said not that the table is wrong but that it only contextualizes information they already knew. I can't argue with that - if someone has already memorized lists and tables, that person may not need a tool that makes sense of those lists for them. It's a newcomer, or person seeking a deeper understanding of why the lists and tables are as they are, who appreciates something like the new table. I suspect old timers who knew the locations of volcanoes and earthquakes didn't think the newfangled theory of plate tectonics told them much - but to those learning geology and to those wanting to know why earthquakes and volcanoes occur where they do, it was an invaluable framework. The new table may not be quite as invaluable, but I think the analogy holds.”<sup>18</sup>

Thus far, the “monsters” seem mild in their activity, but perhaps the story of the earth scientists' periodic table is not yet complete, with the “final ordeals” yet to occur.

These various stages of the quest as they are applied to the development of the periodic table for earth scientists are shown schematically on Fig. 4. This diagram implies a linear approach to the story, but the reality may be more complex, either involving several ‘ordeals’ or reversals of fortune in the progress towards the acceptance of a scientific idea or concept.

It is certainly too early to ascertain whether Railsback's work constitutes a scientific revolution within the ecological development of the periodic table, in the way envisaged by Bray for the adoption of atomic number rather than atomic weight as a defining characteristic for the periodic table during its early history.<sup>19</sup>

The scope and complexity of Railsback's periodic table for earth scientists are reminiscent of how a freshly drawn map of the medieval world – the *Mappa Mundi* – might have looked.<sup>20</sup> Like the *Mappa Mundi*, it is too large for much to be seen when printed within the typical dimensions of a journal's pages.<sup>21</sup> As a consequence, the viewer has to settle either for printing of fragments of the table in order to see the detail,<sup>22</sup> or make the effort to download it either from a data repository<sup>23</sup> or Railsback's website,<sup>24</sup> and then print it at a suitable size.

### Ionic potential - a parameter that defines geochemistry

The characteristics of a chemical element that locate it on the chemist's periodic table could be considered to be the equivalent of the ‘theoretical optimum’ or ‘best point’ in a theory of constraints approach (de Souza *et al.* 2013),<sup>25</sup> as shown in Fig. 7A.<sup>26</sup> For chemists, the ‘best point’ coincides with the most common form in which the element occurs, i.e., the element will be included only once in the table. Occasionally, however, even chemists have developed forms of the table in which an element occurs more than once, an example of which is that suggested for inorganic chemists.<sup>27</sup> Perhaps more cleverly, an interactive periodic table has been developed that at first glance appears traditional, yet when the element is ‘moused over’, the range of oxidation states is revealed.<sup>28</sup> With the greater variety of oxidation states in naturally occurring minerals, and inferred in magmatic, hydrothermal and soil environments, a single ‘best point’ may be inappropriate for earth scientists. Thus, it could be considered that Railsback's periodic table has an extensive ‘good enough zone’ (Fig. 7B).<sup>29</sup> Beyond that there may be too much information: the ‘busyness’ and the amount of information within the representation of a single ion – let alone a whole column, row or section – will surely tax the memory when making comparisons between ions or contemplating wider inferences and implications,<sup>30</sup> and potentially limits the usefulness of Railsback's table.

The feature that appears to unify Railsback's periodic table is the contours of ‘ionic potential’, ( $\phi$ , the ratio of ionic charge,  $z$ , to ionic radius,  $r$ ). The potential usefulness of this parameter was first recognised by Groves Cartledge in 1928.<sup>31</sup> In a subsequent paper he suggested that the ionic potential was correlated with the heats of formation of a wide variety of compounds, stating, “Of

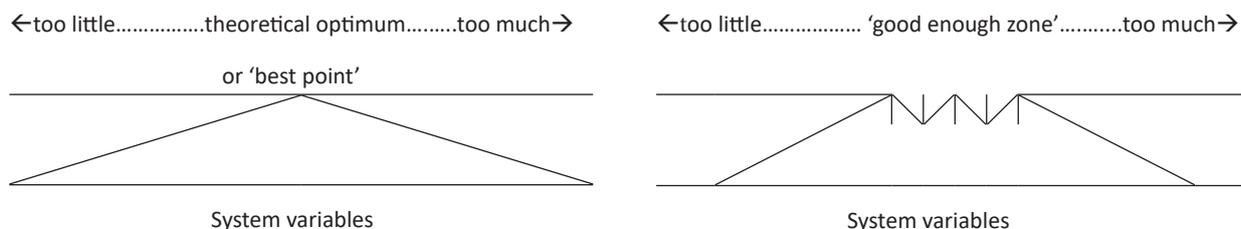


Fig. 7. Differences among the approaches based on: **A. Left:** the ‘theoretical optimum or “best point”, here inferred to be the approach taken by the chemists’ periodic table; and **B. Right:** the ‘zone of good enough’, here inferred to be the approach considered necessary for the earth scientists’ periodic table.<sup>25,26</sup>

various correlations examined, the best results were given by plotting  $\log - \Delta H/z$  against  $\phi$ , where  $z$  is the valence (i.e., ionic charge),  $\phi$  is the ionic potential, and  $\Delta H$  is the “heat of formation for one equivalent [italics are as shown in the original text]”.<sup>32</sup> Ionic potential is also associated with the so-called ‘father of geochemistry’ Viktor Goldschmidt, whose 1937 paper has attracted over 800 citations since its publication.<sup>33</sup> Significant for this discussion is that a paper on the role of the size of a cation in the distribution of an element between magmas and crystallising minerals was promoted fifty years ago by Naoki Onuma and his colleagues<sup>34</sup> has also been widely cited (Fig. 8).

Fig. 9 shows typical recent examples of so-called ‘Onuma diagrams’,<sup>35</sup> in which improved values for the ionic radius and techniques for chemical analysis enable better relationships between distribution or partition coefficients and ionic radii than were originally possible. Broadly similar patterns with ionic radius are apparent in hydrothermal systems, e.g., the solubility of trivalent lanthanide fluorides decreases with increasing ionic radius at temperatures in the range 150-250°C.<sup>36</sup> As a further example,

the various maxima shown in plots of ‘enrichment ratio’ versus ionic potential can be inferred to indicate preferential precipitation of minerals in active hydrothermal systems.<sup>37</sup> Similarly, trends in the solubility of carbonates at low temperatures appear to show a minimum value at an ionic potential ( $\phi$ ) of about 1.7.<sup>38</sup> Thus, a relationship between  $\phi$ ,  $z$  and  $r$  appears applicable to a wide range of geological environments.

For ions of the same charge, then, plots of partition coefficient versus ionic radius have a parabolic shape, with the maximum value of the partition coefficient occurring at an optimum value of the ionic radius, inferred to be the radius of the preferred site in the crystallising mineral. Quantitatively, these types of curves have been partially explained in terms of a lattice strain model (Eq. 1):

$$D_i = D_o \exp \{(-4\pi EN_A / RT) \cdot [(r_o/2) \cdot (r_o - r_i)^2 - (1/3) \cdot (r_o - r_i)^3]\} \quad (\text{Eq. 1})$$

where  $D_i$  is the partition coefficient for the particular ion

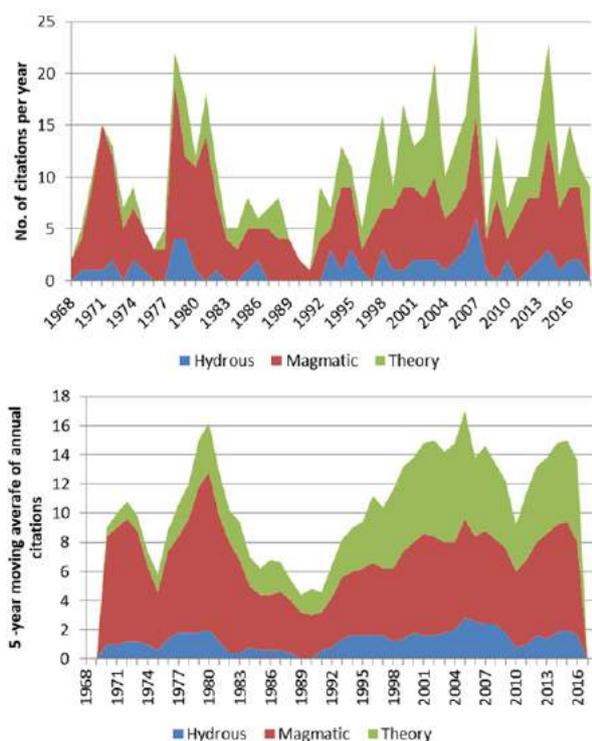


Fig. 8. **A. Upper:** Citation trend for Onuma *et al.*<sup>34</sup> show flurries of activity in 1978, 2007 and 2014. **B. Lower:** Five-year moving average citation trend for Onuma *et al.*<sup>34</sup> in which three dominant flurries of interest are apparent.

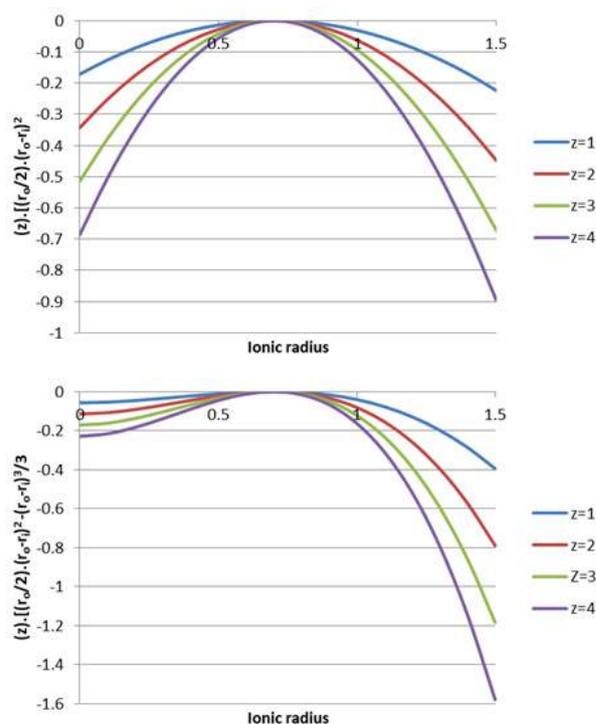


Fig. 9. **A. Upper:** Synthetic Onuma diagram - I.  $(z) \cdot [r_o/2 \cdot (r_o - r_i)^2]$  versus  $r_i$ , (for  $0 < r_i < 1.5$ ), with  $r_o=0.70$ , showing a tightening of parabola for ions of higher charge. This plot excludes the term involving  $r_i^3$  that was added by Brice.<sup>39</sup> **B. Lower:** Synthetic Onuma diagram - II. Plot of  $(z) \cdot [r_o/2 \cdot (r_o - r_i)^2 - (r_o - r_i)^3/3]$ , i.e., all terms involving  $r_i$  from equation 1, versus  $r_i$ , (for  $0 < r_i < 1.5$ ), with  $r_o=0.70$ , which also shows tightening of the quasi-parabola for ions of higher charge.

(i);  $D_o$  is the mineral–melt partition coefficient for the strain-free substitution;  $r_o$  is the optimum radius for the lattice site;  $r_i$  is the ionic radius (which may be larger or smaller than  $r_o$ ),  $E$  is the effective Young's modulus for the lattice site;  $R$  is the gas constant;  $N_A$  is the Avogadro constant; and  $T$  is the temperature.  $D_o$  determines the peak of the parabola with corresponding ideal element radius  $r_o$ , and  $E$  controls the tightness of the parabola.<sup>39</sup> Fig. 9 suggests that this 'tightness' is related to the ionic charge: the divalent ions showing the most widely splayed parabola, and the tetravalent ions showing the tightest parabola. This trend has been attributed to an "increase in effective Young's modulus of the site with increasing charge".<sup>40</sup> Although Eq. 1 was developed for a mineral crystallising from a magma, the same type of relationship can be envisaged to explain the form of the plots for a mineral crystallising from a hydrous system: whether the system is a cool solution (e.g., in depositional /sedimentary environments<sup>41</sup> or during weathering processes), a hydrothermal solution (e.g., ore deposition), or a 'wet' magma.

### Towards a simpler periodic table for earth scientists

Onuma diagrams show a systematic relationship between the components of ionic potential, i.e., between ionic radius and ionic charge. The nature of this relationship also depends on which of hydrated ions, complex anions or insoluble oxides and hydroxides predominates in the particular geological environment, i.e., the presence or absence of these ions or compounds can be attributed to partitioning between these phases and melts or hydrous systems. One such representation is shown in Fig. 10 (with ionic radius on the X-axis, and ionic charge on the Y-axis).<sup>42</sup> A similar diagram with ionic charge on the X-axis and ionic radius on the Y-axis<sup>43</sup> is transformed to a form more akin to a traditional periodic table in Table 1.<sup>44</sup> The naturally occurring ions are arranged in order of increasing ionic charge (from left to right) and increasing ionic radius (from top to bottom). The number shown under each ion is the ionic potential. Ions of comparable charge and radius are shown with ionic potential increasing to the right within the charge 'box'. This gives the table more of the appearance of the traditional 'long' form of the periodic table. The common chemical associations of the periodic table (e.g., vertical groups of alkali metals, alkaline earths, halogens; or the horizontal transition elements) are still apparent.

### Concluding comment

A periodic table based on ionic potential – an influential parameter on chemical and physical processes in geological environments – appears to have some merit. Its overall layout is similar to more traditional versions of the periodic table based on atomic number and – like them – is not overwhelming by its content – unlike Railsback's version. Most importantly, it enables ions of geological importance to be uniquely displayed, i.e., a given element can be shown more than once. That said, as have all its predecessors and its undoubted successors, this table has its limitations:

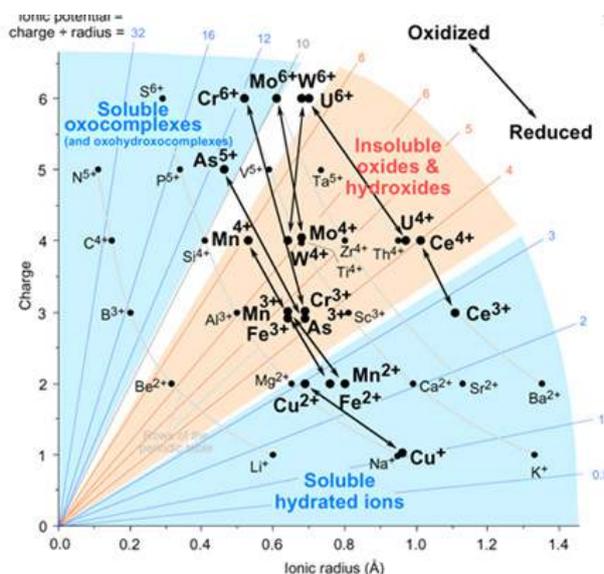


Fig. 10. Ionic radius versus ionic charge from Railsback, 2007<sup>42</sup>

"The attempt to 'humanise' nature has a long and distinguished history. Once a given subject is broken down into parts, each one identified, named and broken into groups – the periodic table, strata of minerals, weight distribution of prizefighters – the whole is given limits and becomes acceptable, or, digestible, almost."<sup>45</sup>

More explicitly, it has been observed that:

"There is no best form of the periodic table since the choice depends on the purpose for which the table is used. Some forms emphasize chemical relations and valence, whereas others stress the electronic configuration of the elements or the dependence of the periods on the shells and sub shells of the atomic structure."<sup>46</sup>

This paper has also explored some sociological aspects of the development of ideas about the periodic table, favouring an approach based on the stages of fictional plots, using aspects of citation analysis to identify types of characters in the 'story'. A limitation to this approach is that in real life – unlike fictional plots – "a story never ends... In any life the neat finish cannot be. It is only the beginning."<sup>47</sup>

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	-2	-1	+1	+2	+3	+4	+5	+6
0.2								
0.3								
0.4								
0.5								
0.6								
0.7								
0.8								
0.9								
1.0								
1.1								
1.2								
1.3								
1.5								
1.6								
1.7								
1.8								
2.0								

Ion	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.5	1.6	1.7	1.8	2.0	
Zn2+	2.27																	
Mn2+	2.27																	
Cu2+	2.30																	
Mg2+	2.33																	
Fe2+	2.39																	
Co2+	2.40																	
Ni2+	2.41																	
Sc3+	3.39																	
Ti3+	3.70																	
Ga3+	3.95																	
Cr3+	3.97																	
Mn3+	4.00																	
Fe3+	4.09																	
As3+	4.17																	
V3+	3.85																	
Al3+	4.44																	
B3+	7.32																	
Be2+	03.39																	
Cu+	1.10																	
Li+	1.11																	
Na+	0.86																	
Hg2+	1.72																	
F-	0.8																	
O2-	1.6																	
Ag+	0.78																	
Au+	0.66																	
Cd2+	1.83																	
Pd2+	2.00																	
Y3+	2.88																	
Tl3+	2.93																	
Eu3+	2.76																	
Ca2+	1.75																	
Ba2+	1.34																	
Sr2+	1.52																	
Pb2+	1.50																	
Ra2+	1.23																	
Eu2+	1.53																	
K+	0.65																	
Tl+	0.61																	
Rb+	0.60																	
Cl-	0.6																	
S2-	1.18																	
Se2-	1.11																	
Br-	0.55																	
Te2-	1.11																	
I-	0.5																	
Cs+	0.55																	

Ion	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.5	1.6	1.7	1.8	2.0	
Mn4+	5.97																	
Ti4+	5.37																	
Mo4+	5.06																	
Zr4+	5.06																	
V4+	5.97																	
Sn4+	4.82																	
Hf4+	4.71																	
U4+	3.88																	
Th4+	3.70																	
Sb3+	3.33																	
Bi3+	2.56																	

Ion	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.5	1.6	1.7	1.8	2.0	
Cr6+	10.3																	
N5+	18.5																	
P5+	9.62																	
As5+	8.33																	
V5+	7.35																	
Nb5+	6.41																	
Ta5+	6.41																	
Sb5+	6.41																	
W6+	8.11																	
Mo6+	8.22																	
U6+	6.90																	
Te6+	8.57																	
S6+	13.9																	
Se6+	10.7																	

Ion	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.5	1.6	1.7	1.8	2.0	
0 <  φ  < 3																		
3 <  φ  < 4																		
4 <  φ  < 7																		
7 <  φ  < 10																		
10 <  φ  < 12																		
φ  > 12																		

Table 1. An alternative periodic table of ions for earth scientists. Only naturally occurring ions are shown; these are arranged in order of increasing ionic charge (from left to right) and increasing ionic radius (from top to bottom), ionic potential being shown for each ion. Some of the usual chemical associations of the periodic table (in particular, the vertical groups of alkali metals, alkaline earths, and halogens) are still apparent, but others (e.g., 2<sup>nd</sup> and 3<sup>rd</sup> row transition elements) are less obvious.

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## Priestley's new airs

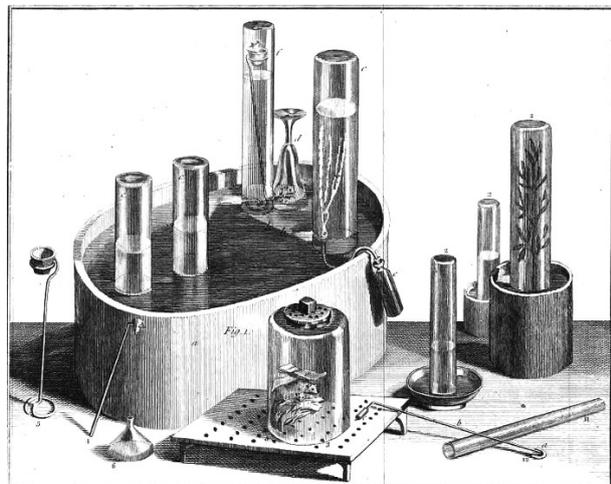
Richard Sorrenson (email: [r.sorrenson@auckland.ac.nz](mailto:r.sorrenson@auckland.ac.nz))

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.

While Davy and Lavoisier made major advances in chemical practice and theory with intricate, expensive and technologically novel instruments like batteries and gazometers, Joseph Priestley had no need for complex or expensive equipment in his investigations into various airs in the 1770s. Instead, he used the well-known pneumatic trough as well as beer glasses to collect various airs, and mice to test the "goodness" of the airs, insisting that chemical instrumentation should be simple and cheap so as to be accessible to all.<sup>1</sup>

Priestley was viewed as a radical in religion and politics during his lifetime. He earned this reputation as a minister in a protestant sect that dissented from the established Anglican church and as a vocal critic of the aristocratic and monarchical government of Great Britain. Paradoxically, however, his lifetime adherence to the phlogiston theory (explained below), long after most chemists had abandoned it, has seen him labelled as a conservative or even reactionary figure in the history of chemistry. However, in his prime investigative years, simple instruments allied with the phlogiston theory were powerful tools for chemical discovery, understanding and innovation.<sup>2</sup>

Priestley cheerfully admitted that his work would never be complete, for "this will ever be the case in the progress of natural science, so long as the works of God are, like himself, infinite and inexhaustible. In completing one discovery we never fail to get an imperfect knowledge of others, of which we could have no idea before; so that we cannot solve one doubt without creating several new ones."<sup>3</sup>



Frontispiece to *Experiments & observations on different kinds of air*, depicting the scientific instruments used by Priestley<sup>3</sup>

How then are beer glasses and mice scientific instruments? In the Frontispiece to *Experiments & Observations*,<sup>3</sup> the beer glass ('d') is depicted upturned on a

raised portion of the pneumatic trough while the mouse is shown in front of the trough inside a cylindrical glass jar sitting on top of a perforated stand. Priestley used mice to test the goodness of the air that had been collected in the beer glass. He would hold "them by the back of the neck, to pass them through the water into the vessel .... If the air be good, the mouse will soon be perfectly at its ease, having suffered nothing by its passing through the water. If the air be supposed to be noxious, it will be proper (if the operator be desirous of preserving the mice for farther use) to keep hold of their tails, that they may be withdrawn as soon as they begin to shew signs of uneasiness; but if the air be thoroughly noxious, and the mouse happens to get a full inspiration, it will be impossible to do this before it be absolutely irrecoverable."<sup>4</sup>

Priestley became very skilled at catching and keeping mice and mixing, heating, combusting and sparking various airs using the pneumatic trough and associated collecting cylindrical glass jars (or beer glasses). In his very long paper to the Royal Society of London in 1772, he laid out the fruits of this labour.<sup>5</sup> Fixed air, which he first began to examine carefully at a local brewery, was not just a product of fermentation, it was also produced by the burning of a candle in common air and when gathered in a jar was uniformly fatal to the mice dragged into it.<sup>6</sup> Living sprigs of plants (as shown to the right of the Frontispiece) reversed the baleful influence of the fixed air and made it as healthful to mice as the common air. Of this he wrote, "I have discovered ... one of the restoratives which nature employs .... It is vegetation."<sup>7</sup>

In a much shorter paper to the Society in 1775, Priestley announced his isolation of a very remarkable new air, derived from heating a mercuric calx, that allowed mice to survive four or five times longer when breathing it compared to the common air; this new air he first called "vital" air (a name that relates to its observed properties) before settling on the more theoretical "dephlogisticated" air.<sup>8</sup> Ever since, as Trevor Levere notes, Priestley has had "bad press" for his devotion to phlogiston and his description of the newly isolated air as "dephlogisticated".

What was the phlogiston theory and why did it work for Priestley? The theory was very well established by the 1770s, having been promulgated in Germany by Georg Stahl in the late 17<sup>th</sup> and early 18<sup>th</sup> centuries. It explained, among other things, how charcoal which was packed with phlogiston refined metal calxes. During refining, the charcoal transferred phlogiston to the calx converting it to a metal; conversely, many phlogiston-rich metals combusted or corroded in the common air which had the property of soaking up the phlogiston that the combusting or corroding metal gave up.<sup>9</sup>

For Priestley, the phlogiston theory not only explained the refining or corroding of metals but, in his experiments with plants, he had a beautiful example of the flow of phlogiston from the fixed air to the vegetable matter of the plants (which then explained why charcoal, which was derived from plants, was so rich in phlogiston). Furthermore, he had found a new air that, in the case of respiration, soaked up tremendously more phlogiston (which the respiration produced) than the common air.

Because of Lavoisier we now see Priestley as misguided; yet, with very simple instruments, he isolated more new airs than had ever before been produced and he expanded the explanatory domain of the dominant theory of his day.<sup>10</sup>

### References and notes

1. See Maurice Crosland, "'Slippery substances': some practical and conceptual problems in the understanding of gases in the Pre-Lavoisian Era," in *Instruments and experimentation in the history of chemistry* (eds Frederick Holmes and Trevor Levere), pp. 79–104, Boston, MA: MIT Press.
2. The best account of these years of Priestley's life is Robert Schofield, *The enlightenment of Joseph Priestley: a study of his life and work from 1733-1773*, Philadelphia, PA: Pennsylvania State University Press, 1997.
3. Joseph Priestley, *Experiments and observations on different kinds of air*, London, 1774-1777, p. vii; hereafter *Experiments & Observations*; available at: <http://www.gutenberg.org/files/29734/29734-h/29734-h.htm>.
4. *Experiments & Observations*, p. 10.
5. Joseph Priestley, "Observations on different kinds of air," *Philosophical Transactions*, 1772, 62: 147–264, p 175; hereafter "Different Kinds of Air;" available at: <https://doi.org/10.1098/rstl.1772.0021>. See John McEvoy, "Gases, God and the balance of nature: a commentary on Priestley (1772) 'Observations on different kinds of air,'" *Philosophical Transactions A*, 2015, 373: 20140229 for an excellent analysis; available at: <https://doi.org/10.1098/rsta.2014.0229>.
6. We would now call fixed air carbon dioxide; "Different Kinds of Air," p. 175.
7. "Different Kinds of Air," p. 166.
8. Joseph Priestley, "An account of further discoveries in air," *Philosophical Transactions*, 1775, 65: 384-394; available at: <https://doi.org/10.1098/rstl.1775.0039>. We would now call a calx an oxide. Lavoisier was to rename this air "oxygen," but recall this name too has a theoretical component – meaning "principle of acidity."
9. In modern terms, phlogiston is somewhat analogous to reaction energy i.e. charcoal contains energy that is available to drive the reaction converting the oxide to the metal.
10. What he called: alkaline, nitrous, dephlogisticated nitrous, marine acid, vitriolic, and dephlogisticated airs; what we would now think of as:  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{O}_2$ .

## Book review: "Something old, something new, something borrowed...": the second edition of *The Periodic Table and Its Significance*

Scerri, E. *The Periodic Table: Its Story and Its Significance* 2<sup>nd</sup> edition. Oxford University Press: Oxford, 2020.

The first eight chapters of the newly published second edition of this book<sup>1</sup> by Eric Scerri appear little changed from those in the first edition.<sup>2</sup> Accordingly, the new edition's highlights, as the author indicates in the Preface, are "the four new chapters – two are completely new, some others have been reworked". Given that the two editions are separated by more than a decade, the revised edition would be expected to have uncovered some new historical materials and made some new interpretations. Indeed, Fig. 1 shows continuing growth in interest in the periodic table as a subject of research, with 93 citations of publications of more recent date than that of the first edition (2007). Although less clearly shown on Fig. 1, an increase in the number of citations of papers written during the world wars of last century is apparent from a subset of the data plotted on Fig. 2. This reminds us of the international and political dimensions of scientific endeavour, which is apparent in other books by Scerri,<sup>3</sup> and which is also evident in Chapter 12 of this one.

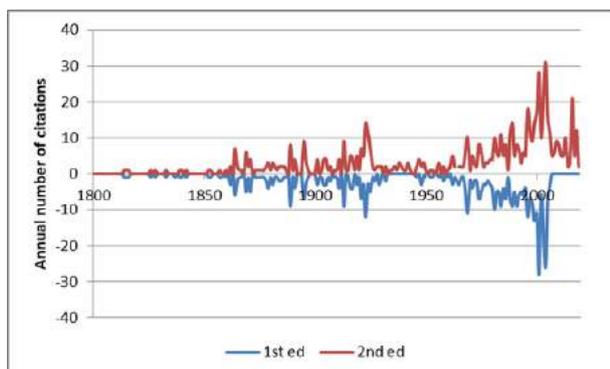
In Chapter 9, two new sections 'Examining the evidence' and 'Anomalous configurations' of one page and four pages respectively contribute to the 'greatly expanded' account of the quantum mechanical account of the periodic table.

The new Chapter 10 ('Astrophysics and Nucleophysics')

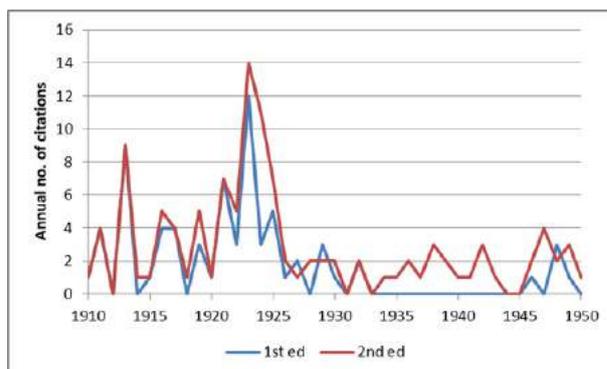
is short, comprising just the first three sections of the former Chapter 10. The first nine 'more chemistry' components of the former Chapter 10 are displaced to the new Chapter 14, and another four to the new Chapter 13 (Fig. 3).

Chapter 11 is certainly new to *this* book, but is derived from the stories of the discovery of seven infra-uranium elements in Scerri's *A Tale of Seven Elements*,<sup>3</sup> with some editing, augmenting and abridging, as shown in Table 1.

By comparison, Chapter 12 'Synthetic elements' is a genuinely new addition to the book. The chapter opens by reminding us that uranium's atomic weight was corrected by Mendeleev himself, and so, despite there being many recent developments, the story is of long duration. The chapter opens by raising complexities related to the techniques involved in synthesis of these elements – now largely the realm of physicists, the naming of these elements – traditionally the right of chemists, as well as priority issues. The complexities extends to just what is an element and how long does its lifetime need to be in order to qualify as one, and the use and value of such discoveries. Such complexities would appear to justify superheavy elements being considered to be a 'wicked' problem,<sup>4</sup> rather than an interdisciplinary one.



**Fig. 1.** Variation of the date of citations for the first (red, shown as negative) and second (blue, shown positive) editions. Overall, there is little difference from 1800 to the date of the first edition (2007). The portion of the plot from 1900 to 1950 is shown more clearly in Fig. 2



**Fig. 2.** Variation of the date of citations for the first (blue) and second (red) editions, 1919-1950

First edition		Second edition			
<b>Chapter 10</b>		<b>Chapter 10</b>	<b>Chapter 13</b>		
<b>ASTROPHYSICS, NUCLEOSYNTHESIS AND MORE CHEMISTRY</b>		<b>ASTROPHYSICS AND NUCLEOSYNTHESIS</b>	<b>FORMS OF THE PERIODIC TABLE</b>		
EVOLUTION OF THE ELEMENTS	→	Evolution of the elements	Differences in Numbers of Columns		
ASTROPHYSICS AND COSMOLOGY: THE CURRENT VIEW	→	Astrophysics and Cosmology: the Current View	What Comes Next?		
STABILITY OF NUCLEI AND COSMIC ABUNDANCE OF ELEMENTS	→	Stability of Nuclei and Cosmic Abundance of Elements	Interesting issues Connected with the Onset of New Blocks of the Table		
MORE CHEMISTRY			Frist Appearance of an f-Electron		
Diagonal Behavior	----	-----	Periodic Tables Other Than Those Literally Table Shaped	-->	Diagonal Behavior
Similarities between Group (n) and Group (n+10)	----	-----	Contributions by Amateurs	-->	Similarities Between Group (n) and Group (n +10)
Early Actinoid Relationships	----	-----	More Specific Tables	-->	Early Actinoid Relationships
Secondary Periodicity	----	-----	Is There an Optimal Periodic Table	-->	Secondary Periodicity
Knight's Move Relationship	----	-----	Elements and Groups of Elements as Natural Kinds	-->	Knight's Move Relationship
First-Member Anomaly	----	-----	Back to Elements as Basic Substances	-->	First Member Anomaly
Other relationships	----	-----	Some Specific Cases	-->	Other Relationships
Ions that Imitate Elements	----	-----	The Placement of Hydrogen in the Periodic System	-->	Ions that Imitate Elements
Superatom Clusters	----	-----	Group 3 Considered Again	-->	Superatom Clusters
VARIETY OF PERIODIC TABLES: IS THERE ONE MOST FUNDAMENTAL PERIODIC TABLE?			A Historical Survey of Evidence and Arguments in Favor of Placing Lu and LR into Group 3		
Back to Elements as Basic Substances			Sum of First Three Ionization Energies		
Elements and Groups of Elements as Natural Kinds			Back to Triads		
The Placement of Hydrogen and Helium in the Periodic System			Reductionist Worries		
IS THERE A BEST FORM OF THE PERIODIC TABLE?			A Final Word on Triads of Elements		
A CONTINUUM OF PERIODIC TABLES	----	-----	A continuum of Periodic Tables	-->	

**Fig. 3.** Commonality of sections in later chapters of first and second editions

Table 1. Content comparison of the second edition's Chapter 11 with *A Tale of Seven Elements*

A TALE OF SEVEN ELEMENTS	Nature of link*	Second edition
		Chapter 11 THE SEVEN LAST INFRA-URANIUM ELEMENTS TO BE DISCOVERED
Chapter 3: Element 91 – Proactinium		Element 91 – Proactinium
[Untitled introduction]	↘	[Untitled introduction]
Crookes   interlude on French researchers   The Curies and Debierne   Back to Crookes	↘	Early history
The search for the mother of actinium and the discovery of brevium	↘	The search for the mother of actinium and the discovery of brevium
Meitner and Hahn's path to Protactinium	⇒	The discovery of proactinium
But why no Nobel Prize for Meitner?   Chemistry of protactinium   Applications	■	
Chapter 4: Element 72 - Hafnium		Element 72 – Hafnium
[Untitled introduction]	↘	[Untitled introduction] Element 72
The role of hafnium in philosophy of chemistry   Hafnium. Properties and applications	■	
Chapter 5: Element 75 - Rhenium		Element 75 – Rhenium
[Untitled introduction]	↘	[Untitled introduction]
Nipponium	■	
Naddack, Tacke and Berg	↗	Noddack, Tacke, and Berg
Applications of rhenium   Modern applications of rhenium   Some contemporary rhenium research   An attempt to rehabilitate nipponium   Interlude	■	
Chapter 6: Element 43 - Technetium		Element 43 – Technetium
[Untitled introduction]	=	[Untitled introduction]
Early claims for Element 43   Very early claims   Ilmenium and neptunium   Davyium   Uralium   Canadium   neo-molybdenum   Moseleyum	■	
The claimed discovery of masurium	=	The claimed discovery of masurium
Van Assche's attempt to rehabilitate the Noddack-Berg claim for element 43	=	Van Assche's attempt to rehabilitate the Noddack-Berg claim for element 43
Finally the "real" element 43 is obtained	=	Finally the "real" element 43 is obtained
The Oklo phenomenon	=	The Oklo phenomenon
Technetium in space and technetium applications   medical imaging   Technetium generators   Chemistry of Tc   Coordination compounds of Tc	⇒	
Chapter 7: Element 87 - Francium		Element 87 - Francium
Quick overview	↘	[Untitled introduction]
The search for Element 87 in more detail   Allison and alabamium   Refutations   Horia Hulubai	■	
Francium	=	Francium
Perey	=	Perey
Uses of francium	■	
Chapter 8: Element 85 – Astatine		Element 85 – Astatine
[Untitled introduction]	=	[Untitled introduction]
Early claims for Element 85	=	Early claims for Element 85
Helvetium and Anglohelvetium	■	
The usually acknowledged discovery of Element 85	=	The usually acknowledged discovery of Element 85
General aspects of astatine	■	
Chapter 9: Element 61 – Promethium		Element 61 – Promethium
[Untitled introduction]	=	[Untitled introduction]
Early claims	↘	Early claims
An Italian claim	=	An Italian claim
Charles James and B. Smith Hopkins	=	Charles James and B. Smith Hopkins
The discovery of the "real element 61"	=	The discovery of the "real element 61"
A little detour on the configurations of atoms   Separation of rare earths   Nuclear batteries	■	

\*Nature of link: ↗ similar, but extended; =, very similar text; ↘, similar, somewhat abridged; ⇒, significantly revised; ■, not used

With a sensitivity to politics and history, as well as sketching the chemistry associated with the physics used in the synthesis, Scerri guides us through 'the real transuranium elements' up to atomic number 100; 'from 101 to 106', highlighting 'the case of nobelium' (element 102) and

touching on the new technique of cold fusion "whereby nuclei are made to collide with one another at slower speeds than were previously used"; the "German elements" 107-112; and finally 'elements 113-118'. Scerri's account is frank about the vicissitudes of international

competitiveness, for example, the ‘farce’ of the naming of seaborgium. The sequence of propositions, retractions, and sanctions reveal the high stakes of the game, and adds real human interest to the science. From a chemist’s perspective the culmination of all this activity is summarised in a sentence of achievement followed by one of aspiration:

“The periodic table has reached an interesting point at which all 118 elements exist either in nature or have been created artificially in special experiments, including a remarkable 26 elements beyond the element uranium. At the time of writing, there are even plans to attempt the creation of yet heavier elements such as 119 and 120, and there are no reasons to think that there should be any immediate end to the sequence of elements that can be formed.”

A world without end? The sections of the chapter that follow this statement discuss possible relativistic effects (inferred to be probably minor) and the intriguing calculations by New Zealander Peter Schwerdtfeger (a distinguished Massey University professor) said by Scerri to suggest “that at certain even higher atomic numbers [than 118] there will come a point at which nuclei will not even have any electrons...”. These ideas, coupled with Scerri’s own speculations, suggest that this chapter – Chapter 12 – could have been better as the last in the book; by comparison, the last chapters of the actual closing chapter – Chapter 14 – are anticlimactic.

Recognising that the appeal of the periodic table goes beyond chemists to include historians and those with an interest in design and representations, the title of Chapter 13 ‘Forms of the periodic table’ foreshadowed expectations of expanding the coverage provided in Chapter 10 of the first edition. In fact, Scerri has done more than this: he explains the constraints imposed on what the periodic table can look like by the chemical periodicity and, in particular, by the introduction of the f-block elements. He takes the reader through three versions of the the medium-longform of the table before observing that amateur engineer Charles Janet’s so-called left-step periodic table “continues to command much attention among periodic table experts [including himself] as well as hobbyists”. He makes passing reference to periodic tables intended to meet the needs of scientists of other disciplines: inorganic chemistry, showing a table which stresses chemical similarities represented by diagonal and knight’s move relationships – ideas picked up again later in the following chapter;<sup>5</sup> earth sciences, showing a table which focuses on ions because of their importance in water-dominated processes such as weathering and hydrothermal alteration and ore genesis;<sup>6</sup> and metallurgy.<sup>7</sup> He also presents a small selection of more fanciful tables, cautioning, “Too many proponents of alternative tables seem to argue about the regularity in their representation and forget that they may be talking about the representation and perhaps not the chemical world itself.”

Chapter 14 also provides the opportunity for Scerri to revisit some long-standing debates, e.g. the placement of hydrogen in the table and the merits of placing Lu

and Lr in Group 3, although the ‘long form’ of the periodic table used as the frontispiece to this edition makes Scerri’s preference for the latter quite clear! Much of the sections ‘A Historical Survey of Evidence and Arguments in Favor of Placing Lu and Lr in Group 3’ and ‘Sum of the First Three Ionization Energies’ are drawn from another of Scerri’s books,<sup>8</sup> and seems to drift away from the expected theme of the chapter. Indeed, by the time the reader reaches the end of this chapter, the impression may be gained that it seems – to use Scerri’s own word with respect to the first edition’s Chapter 10 – “motley”. There is certainly sufficient information available for a complete chapter on the various designs of the table alone, and so perhaps in the next edition, some components of this chapter may be redistributed elsewhere.

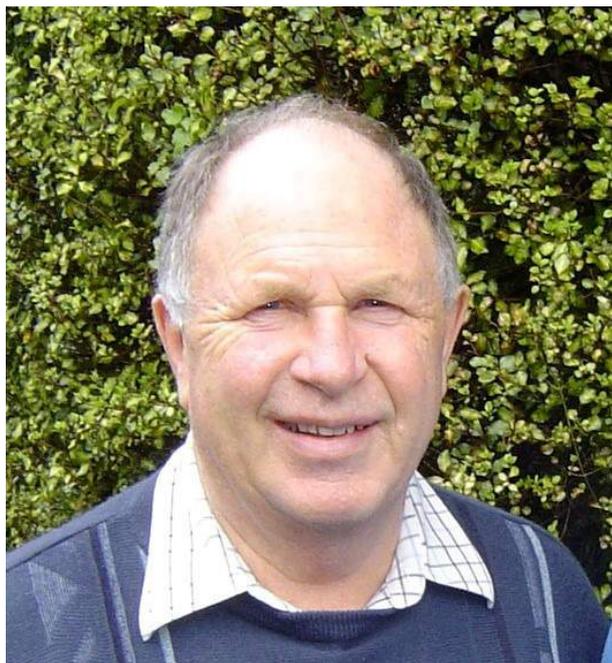
Analysis of the “compilation of all the references that appear in each chapter” reveals that the proportion of Scerri’s works cited in the second edition triples over his research career (Fig. 4). Modesty surely prevents Eric from drawing attention to this, but the graph provides clear evidence of his increasing standing as a doyen of research into the periodic table. With that in mind, and with his pleasing writing style that combines scientific information, historical perspectives and personal reflection, this book will be an ideal starting point for readers new to Eric Scerri. Meanwhile, those more familiar with his scholarship will find enough that is new in this edition to maintain their interest, and may have had the opportunity to attend his plenary presentation at the New Zealand Institute of Chemistry conference held in November 2019 in Christchurch.

**Peter Hodder**  
**School of Government**  
**Victoria University of Wellington**

## References and notes

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2. Scerri, E. *The Periodic Table: Its Story and Its Significance*. Oxford University Press: Oxford, 2007.
3. Scerri, E. *A Tale of Seven Elements*. Oxford University Press: Oxford 2013.
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## Graeme Baxter Russell PhD (Cant.), FNZIC, 1937 - 2019



Graeme Russell, natural products chemist and Fellow of the NZIC, passed away on 18 August 2019. Graeme was an enthusiastic advocate for a functional role for plant secondary metabolites and for the study of the chemistry of New Zealand plants.

Graeme graduated from the University of Canterbury with a BSc (Hons) in Chemistry in 1960 followed by a PhD, supervised by Dr Ron Topsom and entitled "Rearrangement of Disubstituted Diamines", in 1963. Graeme then joined Plant Chemistry Division DSIR in Palmerston North to work with Dr Ray Bailey on the role of plant carbohydrates in causing bloat in cattle grazing clover pastures. In 1965, he was seconded to CSIRO Division of Organic Chemistry in Melbourne to investigate antitumour compounds in Australian plants. This provided valuable experience in contemporary methods for the separation and identification of natural products and contributed to his first significant discovery; a bioactive natural product, tropine-1,2-dithiolane-3-carboxylate, from the bark of the mangrove (*Brugeria sexangula*). While at CSIRO, Graeme became aware of the discovery of insect moulting hormones (ecdysteroids) in podocarps and ferns that later become a focus of his research.

In 1967, Graeme returned to DSIR in Palmerston North to investigate the chemistry of plant-insect interactions in New Zealand, setting up a phytochemistry laboratory with large scale extraction equipment and a Varian T60 proton NMR spectrometer. Graeme took satisfaction in operating the extraction equipment and analytical instrumentation, and in making collection expeditions into the bush, an activity he enjoyed to the end of his career. Collaborations with DSIR entomologists Peter Fenemore and Pritam Singh enabled the isolation of a range of insect-active compounds from podocarps and ferns. This included gram quantities of extremely precious ecdyster-

oids and a range of insect-toxic norditerpene lactones. Graeme presented this work in a keynote address at the 10th IUPAC meeting on the Chemistry of Natural Products in Dunedin in 1976.

In 1972, he travelled on a Royal Society Fellowship to the University of Sussex to investigate ecdysteroid metabolism in the blowfly, using the materials he had isolated to prepare radio-labelled substrates and discover new metabolites.

Graeme returned to Applied Biochemistry Division DSIR in 1975 and was appointed Leader of the Organic Chemistry Group with a greater emphasis on practical research. Working with entomologist Dr Oliver Sutherland, they reported, in 1978, the identification of the isoflavan vestitol from *Lotus pedunculatus* root as a highly active feeding deterrent to the NZ grass grub, *Costelytra zealandica*. This major discovery spurred further research with colleagues to investigate the structure-activity relationship of isoflavonoids from other legumes, with phaseollin isoflavan from bean (*Phaseolus vulgaris*) found to be the most active (ED<sub>50</sub> 20 ng/g in diet).

Graeme's research achievements were recognised by NZIC with the award of the ICI Prize for Excellence in Research in 1978, and a Fellowship in 1979. Despite diversion into administrative responsibilities, Graeme continued with his research and remained a vigorous proponent for the acquisition of contemporary instrumentation, such as the Bruker FT80 NMR machine installed in 1984. In 1984, supported by a DSIR Fellowship and British SERC grant, he furthered his research at the University of Southampton isolating several novel isoflavonoids from kowhai (*Sophora microphylla*) and presenting his research at conferences in Europe and the UK. Back in New Zealand, Graeme became more involved in administration of Biotechnology Division, DSIR. He also developed new international connections through the UNESCO Regional Network for Natural Product Chemistry in SE Asia presenting keynote addresses at Asian Symposia on Medicinal Plants and Spices in Indonesia, Malaysia and Vietnam (1989, 1994, and 1998) and attending annual meetings of the Coordinating Board (of which he was latterly Chairman) as well as local workshops and seminars. He supported UNESCO-sponsored visits of young researchers to New Zealand, publishing on the antifungal isoflavonoids of gorse (*Ulex europaeus*) and bioactives from Philippine plants.

In an era of major change in New Zealand science, Graeme briefly took the role of Director of Biotechnology Division, DSIR prior to its disbandment in 1990. Returning to his research, in 1992 he travelled to the laboratory of Professor Bill Bowers in Tucson, Arizona where he discovered a novel ant repellent from the leaves of kohekohe (*Dryoxylum spectabile*). When Graeme returned to the Horticulture and Food Research Institute, there was inadequate funding support and Graeme took voluntary redundancy in 1993.



Graeme continued as an Honorary Fellow, completing publications and investigating natural products as potential moth-proofing agents for Wool Research (WRONZ). He continued with the UNESCO Natural Product Chemistry Network, presenting a keynote address at the 6<sup>th</sup> Asian Chemical Congress in Manila in 1995, and organising a well-attended Symposium on Natural Product Chemistry in Palmerston North in 1996. Soon the focus of Graeme's research shifted to the phytochemistry of the Southern Beeches (*Nothofagus* spp.). In 1995, a joint proposal with Professor Bowers, Professor Hermann Niemeyer from the University of Chile and others to examine the phytochemistry and insect interactions of *Nothofagus* spp. across their distribution range gained support from the National Geographic Society. Graeme made four trips to Chile, learning Spanish and collecting plant material. A second National Geographic Society grant in 2002 provided the opportunity to work in Professor Niemeyer's

laboratory in Santiago. These investigations resulted in four papers on the phytochemistry and insect herbivory of *Nothofagus* spp.

Graeme enjoyed an active life outside science making the most of international travel opportunities. He was active in the Cub Scouts, becoming District Leader, and was very involved in his church community. Graeme was a keen philatelist, specialising in stamps with a chemistry theme, and winning a gold medal in San Francisco in 2015. Graeme is survived by his wife Anthea, three sons, and eight grandchildren.

**Contributed by Geoff Lane, Peter Reay and Daryl Rowan**

# NZIC Conference 2019, 24-28 Nov, Christchurch



