Chemistry in New Zealand

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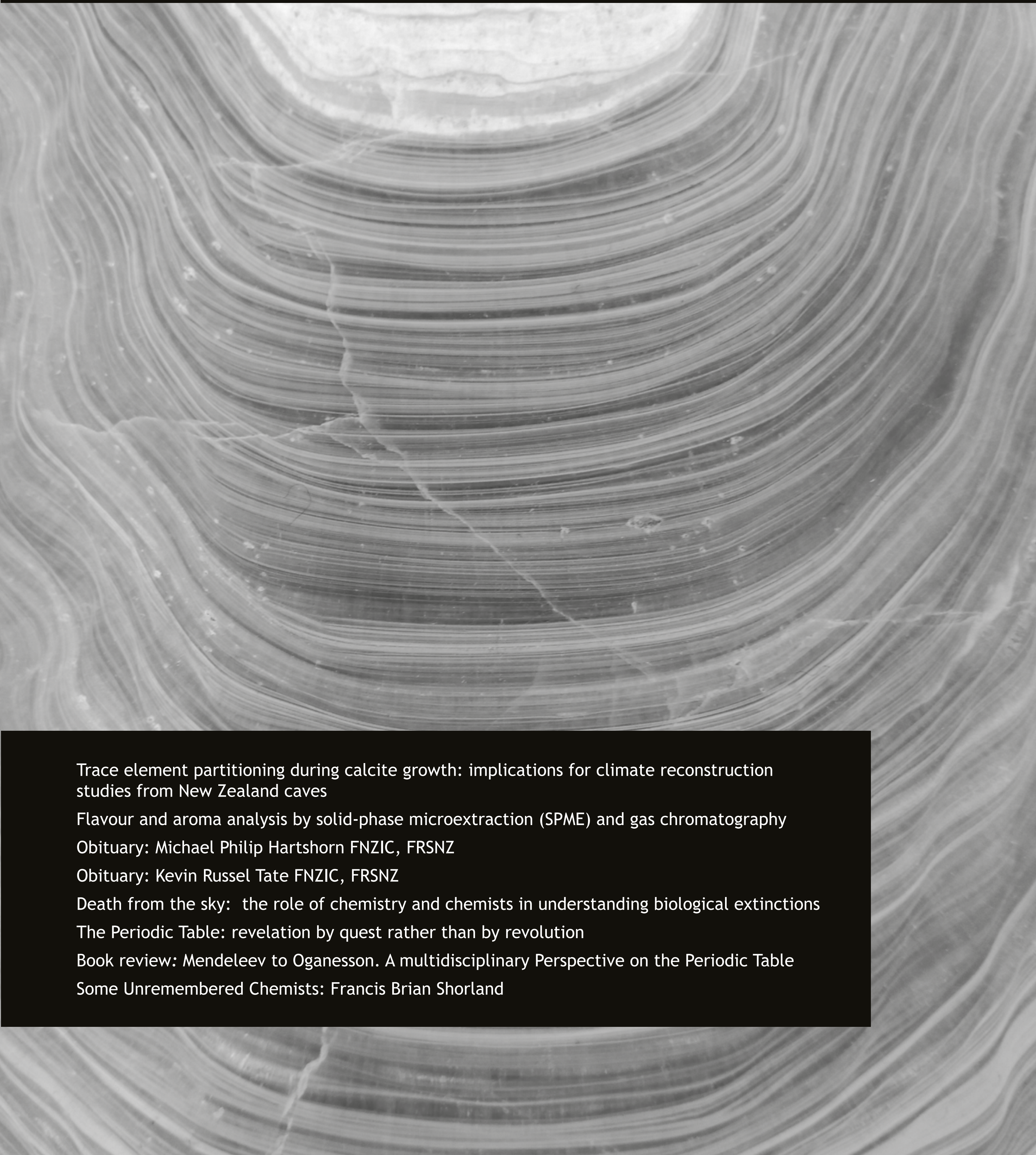

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NZIC Chemistry IN NEW ZEALAND

Volume 82, No.3, July 2018

Articles and features

Other columns

Comment from the President

Welcome to the July issue of *Chemistry in New Zealand*. Hopefully you have all had a chance to go to the new NZIC website and use it to renew your membership. It is hoped that the modern and up-to-date website will become a hub for chemistry information for both members and the public alike. I want to thank Paul Plieger and Joanna Dowle for all their hard work getting the website operational.

In other NZIC news there has been an application to Council to form a new Education Branch of the Institute. As many of you will know, the membership of the Institute has been falling over the years and it is hoped that the formation of the new Education Branch will make membership more attractive to school teachers. This, coupled with the fact that one of the more important roles of the Institute is chemical education, has led to Council thinking that the new branch would be a positive change. The formation of a new branch requires a vote by the whole membership. So later in the year, once the details of the structure of the new branch are finalised, you will all be asked to vote (probably *via* an online form) as to whether or not you approve of the formation of the new Education Branch.

2019 is the 150th anniversary of Dmitri Mendeleev's first report of the periodic table. As I mentioned previously, it was announced by the IUPAC and United Nations that 2019 will be the International Year of the Periodic Table of Chemical Elements (IYPT 2019: https://iupac.org/united-nations-proclaims-international-year-periodic-table-chemical-elements/). A New Zealand committee involving the NZIC, MacDiarmid Institute, IUPAC and RSNZ has now been established to try and organise events for 2019. If you have any great ideas of things that could be done to celebrate IYPT 2019, please let myself or Joanna Dowle know and we can pass on the information to the committee, as this represents a huge opportunity to get chemistry out into the public eye.

There are a couple of chemistry-related conferences, MOF2018 (http://mof2018.com/) and AMN9 (www.amn9.co.nz) that will be held in New Zealand in December 2018 and February 2019 respectively. In addition, the Canterbury branch, led by Sarah Masters, are busy organising the next NZIC conference and are just trying to finalise the dates but the conference will be held in December 2019 so please keep that time free.

Finally, I want to congratulate Distinguished Professor Margaret Brimble CNZM, MNZM who was elected a Fellow of the Royal Society (FRS). This is a richly deserved award, with less than 50 New Zealanders having ever been elected as Fellows and very few chemists having achieved this honour. Professor Brimble has made extensive contributions to organic chemistry including the synthesis of bioactive natural products and peptides, and the development of new small molecule drugs such as trofinetide (NNZ-2566). She is also a Fellow of the NZIC, RSC and RACI and her work has been honoured by numerous awards including the NZIC Easterfield Medal and Chemical Sciences Prize and the Rutherford Medal of the Royal Society Te Aparangi. In addition to this brilliant research, Professor Brimble has also provided strong leadership in our discipline over many years including acting as the President of the IUPAC Organic and Biomolecular Chemistry Division, as an associate editor of the RSC journal *Organic and Biomolecular Chemistry* and as a Marsden Panel Convener. The same week as being elected FRS, Professor Brimble was also awarded the RSC George & Christine Sosnovsky award for cancer therapy. So on behalf of the NZIC I would like to congratulate Professor Brimble on her spectacular success and thank her for showing what can be achieved as a chemist in New Zealand.

James Crowley

NZIC President

New Zealand Institute of Chemistry

supporting chemical sciences

July News

AUCKLAND

The University of Auckland

Welcome

We have welcomed Michael Groom as our new Group Services Manager. Michael joins us from the Department of Exercise Sciences where he just completed his term as Business Operations Manager. We look forward to working with you, Michael.

Farewell

We recently said farewell to Professor Lynda Pitcaithly, who has moved to a new position at the Liggins Institute. Lynda was our first Group Services Manager. Lynda was a very positive influence, both in her outlook and her impact on the School. She played a key role in such activities as preparation of our three year plans and monthly budget planning, as well as managing the Group Services team. We wish her well in her new role.

Events

Chemistry Olympiad

The Chemistry Olympiad camp finished on 4 May and the team was selected. Team members were Stephen Ma from Auckland Grammar School, Stefan Ivanov from Westlake Boys on the shore, Callun Loomes from Auckland Grammar School and Russell Boey from St Andrews College in Christchurch. There was a lot of excitement in the group who travelled first to Bratislava and then to Prague for the international competition. This was the 50th anniversary of the Olympiad which originated in Bratislava. The students, accompanied by Sheila Woodgate, Jan Giffney, and Buck Rogers (from St Peter's College Epsom) worked really hard before mid-July in order to prepare for the 5 hour theory and 5 hour practical exam. We would like to thank Katrina Graaf and her team for helping us out with the practical training.

International Day of Light, Historic Science Fair

Cather ***Simpson*** and the Photon Factory coordinated an event on 13 May for the International Day of Light (the actual day to celebrate the invention of the laser was on 16 May). The event included an all-day science fair with fantastic demonstrations of 3D photoprinting, photonic crystals in nature, natural radioactivity, fluorescence, and many other light-related phenomena, together with a panel discussion by women scientists including Dr *Erin* ***Leitao*** and Dr *Michel* ***Nieuwoudt***, Cinnamon Latimer, Ankita Gangotra, chaired by Cather. School children from all over the city attended. A big thanks to Cather, Andy Wang, Rakesh Arul and Rachel Ou as well as a number of other volunteers who made the event possible.

Inaugural lecture by Professor Brent Copp

On 16 May, Professor *Brent* ***Copp*** gave his inaugural lecture entitled, *From natural products to zombie drugs: chemicals with biological effects*. Natural products are molecules produced by living organisms. These so-called secondary metabolites are thought to improve the survival fitness of the producer. These same natural products, or derivatives, have also been utilised by humanity for millennia, providing positive benefits as medicines (examples include morphine and penicillin) and negative effects such as misused drugs (which include cocaine and heroin). Brent's lecture was well attended and entertaining.

Research Showcase

On 6 June, the School of Chemical Sciences held its 10th Annual Research Showcase. This event provided an excellent opportunity for PhD students to showcase their research and network with the New Zealand chemistry community. The exciting, one-day event featured two minute 1st year PhD talks, 8 senior PhD student talks, a poster session, competitions, a high-profile keynote lecture by *Carla* ***Meledandri***, and was followed with a reception to bring together students, staff, industry, and government researchers. Watch this space for photos from the event and an announcement of the prize winners!

ANZNMF 2018

The 2018 Australia and New Zealand Nano and Microfluidics (ANZNMF) meeting took place from 27 – 29 June at the University of Auckland. The conference covered all areas of microfluidic and nanofluidics, from theory, fundamentals and engineering developments, through to bionanotechnology and the latest innovative technologies – so there is good alignment with some research in the School of Chemical Sciences. On 27 June there was a student workshop aimed at developing skills for graduate student researchers. The 28th and 29th were research sessions, with keynote speakers Professor Sandra Troian (CalTech) and our own Professor *Jadranka* ***Travas-Sejdic***.

Visitors

On 7 March, Dr Peter Canfield from the University of Sydney gave a seminar on *The last fundamental form of isolable conformational isomerism demonstrated in a B(F)OB(F)-quinoxalinoporphyrin.*

On 28 March, Professor Scott McIndoe from the University of Victoria (Canada), gave a colloquium entitled, *Catalytic reaction mechanism elucidation via real time analysis*.

On 29 March, Professor Vasantha Rupasinghe from Dalhousie University, Nova Scotia, Canada, gave a seminar entitled, *Flavonoids and biological activity: exploring the value-added opportunities for cool climate fruits.* Professor Elliot Gilbert from the Australian Centre for Neutron Scattering also gave a seminar on *Small angle X-ray and neutron scattering: natural tools for food science and technology research.*

Dr Koro de la Caba and Dr Pedro Guerrero from the BIOMAT research group in Spain were hosted for a three week visit to the Biocide Toolbox and School of Chemical Sciences in March. On 16 March they gave a joint seminar entitled, *A sustainable approach towards the production of biopolymeric materials.*

On 24 April, Professor Wei Zhang from Dalian University of Technology, China, presented a seminar on *Magnetic induction hyperthermia for cancer treatment.*

On 30 April, Dr Buddy Ratner from the University of Washington, USA, gave a seminar entitled, *Plasma deposited thin films: biomaterials applications.*

On 8 May, Dr Jonathan Kitchen, newly appointed lecturer at the Institute for Natural and Mathematical Sciences, Massey University, Auckland, gave an NZIC seminar on *Responsive metallosupramolecular materials.*

Congratulations

A big congratulations to Distinguished Professor *Margaret* ***Brimble*** who was elected as a Fellow of the Royal Society. Margaret was also awarded the Royal Society of Chemistry 2018 George and Christine Sosnovsky Award in Cancer Therapy for developing a novel innovative chemistry platform to generate fully-synthetic, self-adjuvanting cancer vaccines for the treatment of different cancers.

We congratulate *Margaret* ***Brimble***, *Jon* ***Sperry***, and *Paul* ***Harris*** who have been invited to submit full standard proposals to the Marsden Fund along with their collaborators, and *Paul* ***Hume*** and *Ivanhoe* ***Leung*** who have been invited to submit full Fast-Start proposals.

Congratulations to *Megan* ***Jamieson*** (PhD student in *Margaret* ***Brimble***'s group) for the publication of a review on the isolation and synthesis of a new family of sesterterpenoids isolated around the Pacific rim. The review was featured on the front cover of *Natural Product Reports* (impact factor = 11) and was a collaborative effort with Professor Chris Bray from Queen Mary University London. Harry Shirley (former postdoc in Brimble group) was also a co-author.

Congratulations to *Benjamin* ***Frogley***, *Lakshika* ***Perera*** and *James* ***Wright*** who had their paper entitled, *Syntheses of amino-substituted iridabenzofurans and subsequent selective N-functionalisation*" nominated as a "Very Important Paper" (VIP) and highlighted on the front cover of *Chemistry – A European Journal*, **2018**, *24*, 4304–4309. Benjamin also had one of his papers (*Chem. Eu. J.* **2018**, *24*, 2025 –2038; DOI:10.1002/chem.201704888) featured on a Frontispiece in the same journal.

Distinguished Professor *Margaret* ***Brimble*** and her PhD student *Shengping* ***Zhang*** with *Paul* ***Harris*** and *Ivanhoe* ***Leung***, and colleagues, have just had their work published as a "VIP" in leading chemistry journal *Angewandte Chemie*. Together, they completed the first ever synthesis of callyaerin A, a challenging natural product with strong potential as an agent for combatting tuberculosis.

Congratulations to the Food Waste Diversion Trial team, who were awarded the Vice-Chancellor's Excellence Award – Environmental Sustainability Award. *Anoma* ***Ratnayake*** played a key organisational role in this trial, and other SCS contributors were *Courtney* ***Davy***, *Mansa* ***Nair***, *Shaheena* ***Shaheem***, and *Kristel Mae* ***Castillo***.

Congratulations to our 200 School of Chemical Sciences graduates who graduated on 11 May, including 13 PhD graduates, 18 MSc and MProf students, 17 BSc Hons and 37 PGDip Sci or PGDip Forensic graduates. The School of Chemical Sciences held a morning tea to celebrate graduation which included a short prize giving to award the LH Briggs prize for the most distinguished research worker who has submitted a thesis for the degree of PhD from the School of Chemical Sciences during the calendar year. The winner was *Benjamin* ***Frogley*** (Supervisor: Professor *James* ***Wright***). Benjamin has made several fundamental discoveries in the chemistry of metallaaromatics, specifically those that contain iridium.

Food Waste Diversion Trial team – winners of the Vice-Chancellor's Excellence Award for Environmental Sustainability

Benjamin Frogley receiving the LH Briggs prize from Gordon Miskelly

Benjamin's PhD research has already resulted in several world-class publications. The runner-up this year was *WanTing* ***Chen*** (Supervisor: Associate Professor *Geoff* ***Waterhouse***). WanTing's research aimed to develop and understand new low-cost methods to get fuels such as hydrogen from sunlight. Her research has already been cited 440 times, which indicates the international interest in her results.

PhD candidates who successfully presented and defended their PhD theses were *Daniel M.* ***Ayine-Tora*** **-** thesis title: *In silico design and discovery of antifungal, anticancer and malaria drug candidates* (supervised by *Jóhannes* ***Reynisson***) and *Zhao* ***Li*** (jointly supervised by Associate Professor *Yacine* ***Hemar***, Dr Don Otter from University of Wisconsin-Madison and Dr Ken Scott who is retired from the School of Biological Sciences).

Auckland University of Technology

New faces

We have welcomed a new PhD student, Navneet Kaur, who will be working with Dr *Cameron* ***Weber*** and a new MPhil student, Sabeena, who will both be working with Dr *Jack* ***Chen***.

Two French interns have joined us to work with Dr *Jack* ***Chen***. William Poletti is visiting us from École Nationale Supérieure de Chimie de Rennes, Rennes and Yasmine Fares is from National Polytechnic Institute of Chemical Engineering and Technologie (INPENSIACET), Toulouse.

Events and invited talks

Professor *Allan* ***Blackman*** was thrilled to be asked to appear on stage with Professor Richard Dawkins in the Aotea Centre (Auckland) and the Isaac Theatre Royal (Christchurch) in May. Both shows were sold out, with Professor Dawkins giving his views on both science and religion to appreciative audiences.

Emma ***Matthewman***, *Paul* ***Jun*** (University of Auckland) and Dr *Cameron* ***Weber*** had a productive visit to the SAXS beamline at the Australian Synchrotron. These experiments will provide insight into the relationship between the structure and concentration of diluents, and the nanostructure of ionic liquids, which will affect the use of nanostructured ionic liquids as solvents and as soft materials.

Ruth ***Cink*** travelled to the University of Hong Kong to perform experiments in the lab of Professor David Lee Phillips. Time-resolved spectroscopic data were collected for the Brasch group's photoactive HNO donor molecules, giving insights into the ultrafast photochemical events that occur upon their excitation. Her

Richard Dawkins, Allan Blackman and Mikey Havoc at the Isaac Theatre Royal

Cameron Weber, Paul Jun and Emma Matthewman at the SAXS beamline of the Australian Synchrotron

Ruth Cink (sitting in the centre) together with Professor David Phillips' research group travel was funded by the Dodd-Walls Centre and the Photon Factory.

Congratulations

Dr *Jack* ***Chen*** and his collaborators were successful in the concept stage of the MBIE Smart Ideas scheme with his project invited to the full proposal stage.

Dr *Cameron* ***Weber*** had his Marsden Fast Start project invited to the full proposal stage.

Marwa ***Omar*** completed her MSc degree and *Lynn* ***Lisboa*** her BSc(Hons) degree with Professor *Nicola* ***Brasch***.

Ruth ***Cink***, PhD student with Professor *Nicola* ***Brasch***, won the best poster prize at the School of Science Graduate Research Showcase.

A paper by *Ruth* ***Cink*** and Professor *Nicola* ***Brasch*** in collaboration with Professor *Cather* ***Simpson***, University of Auckland, and researchers from Kent State University, USA, has been featured on the cover page of the *European Journal of Organic Chemistry*. The paper describes the preparation of photoactive HNO donors incorporating the (3-hydroxy-2-naphthalenyl)methyl phototrigger.

CANTERBURY

Events

NZIC Annual BBQ

The annual BBQ for University and Polytech undergraduate and post-graduate students was held at the University of Canterbury Club on 14 March. There was an excellent turnout from the Canterbury Branch membership and also from new students. The sun shone to make it an excellent occasion.

NZIC Public Lecture

Building and Designing in the World's Finest Workshop was the title of the public lecture given by Professor Scott McIndoe of the University of Victoria, BC, Canada on 22 *March.* Scott is the 2018 Erskine Visiting Teaching Fellow and is a chemistry professor at the University of Victoria, BC, Canada. He spent 4 months of his 2016/7 sabbatical at Autodesk's Pier 9 workshop in San Francisco, home to an amazing array of modern manufacturing tools including waterjets, laser cutters, 3D printers and more. The audience found out more about the largely science-inspired things he made while he was an Artist in Residence there, including a 3D periodic table, a solar analemma chandelier, a black hole table and a laser sword.

NZIC members enjoying the sunshine at the annual BBQ

Carol Robinson deep in discussion with Professor Richard Hartshorn (University of Canterbury)

NZIC Sponsored Event

On 16 March Dame Carol Robinson, Professor of Chemistry at the University of Oxford, UK, gave a public talk at the University of Canterbury entitled, *What's really in your medicine cabinet?* The event was sponsored by the Royal Society Te Apārangi and the UC Biomolecular Interaction Centre (BIC). Her talk is available on our YouTube channel at: http://bit.ly/2GRFJuR, and Dame Carol was also interviewed on RNZ: http://bit.ly/2DmQrTm

The Canterbury Branch of NZIC hosted a *meet the speaker* reception at the University of Canterbury Club following her public lecture.

New appointments

Welcome to Professor Rudi Marquez! Rudi recently joined the School of Physical and Chemical Sciences at the University of Canterbury as the new Head of School. Rudi comes to Canterbury via Mexico, Scotland and China, and is an experienced higher education leader where in his previous role he was employed at the Xi'an Jiaotong-Liverpool University (XJTLU) as the Head of the Department of Chemistry and the Chair of the Faculty of Science leading three departments including chemistry, environmental sciences and biological sciences. Rudi is also one of the co-founders and acting directors of his own organisation, Tissue Repair Technologies (TRT). Rudi's research interests are at the interface between synthetic organic chemistry, medicinal chemistry, and molecular and cell biology with a particular emphasis on diabetes, parasitology and water quality. Rudi has held a number of fellowships, including an Engineering and Physical Sciences Research Council (EPSRC) Leadership Fellowship and the Japan Society for the Promotion of Science Fellowship. Rudi is a Fellow of the Royal Society of Chemistry (FRSC).

Ernest Rutherford Building Opening

The Ernest Rutherford building was officially opened by Prime Minister Jacinda Ardern on 16 February.

Seminars

Two recent seminars were well attended by the NZIC membership: *Cellulose nanocrystal - a promising sustainable nanomaterial for advanced engineering applications* presented by Professor Michael K.C. Tam, University of Waterloo and *Tuning the complexity of palladium(II) cages* presented by Dr *Dan* ***Preston***, University of Canterbury.

Congratulations

Congratulations to *Sarah* ***Masters*** from the School of Physical and Chemical Sciences at the University of Canterbury on being made a Fellow of the Higher Education Academy. HEA Fellowship is an internationally recognised mark of professional expertise for those who teach and support learning in higher education. It is increasingly recognised by international institutions, and Sarah is amongst the first academics from the University of Canterbury to gain FHEA status.

MANAWATU

The ***Telfer*** Group has welcomed three new students. Nisansala Bandara (PhD), Bernhard Auer (PhD) and Tim Craig (MSc) are working on various aspects of metal-organic frameworks.

The ***Filichev*** Group has welcomed two new students - Harikrishnan Kurup (PhD) and Coline Bretecher (Intern).

The NZIC Student Evening was held on 18 April. Attendees were informed of the functions of the NZIC and the benefits of joining the society. Brodie Matheson and Sam Powick of Massey University and Daisy Wilkie of UCOL received 300 Level Chemistry Top Scorer prizes. Sidney Woodhouse won an NZIC travel grant of $500 for attending the International Conference on Coordination Chemistry being held in Sendai, Japan.

The NZIC sponsored a Manawatu Branch prize for the best talk at the Institute of Fundamental Sciences Post Graduate Symposium held in June.

Winners of the 300 Level Prize for Chemistry along with Catherine Whitby

Sydney Woodhouse (L) receiving the NZIC travel grant from Rebecca Severinsen

Shane ***Telfer*** gave a departmental seminar on *Multicomponent metal-organic frameworks* at Monash University, Melbourne in Jan 2018. In March, he conducted a week-long speaking tour in China, visiting Fujian Institute of Research on the Structure of Matter in Fuzhou, Hangzhou University, Nanjing University and then Fudan and Jiao Tong Universities in Shanghai.

Catherine ***Whitby*** delivered a seminar on *Women in nanoscience* at the Space and Science Festival in Wellington on May 19.

Several seminars have been held at Massey University over the past few months:

Professor Jim Skea presented *Climate change: stormy weather ahead* and Michael K.C. Tam gave the talk entitled, *Phosphorylated cellulose nanocrystal-modified chitosan complex for the stabilisation and nutrient encapsulation in Pickering emulsions* on 23 March.

Shane ***Telfer*** spoke on *Multicomponent metal-organic frameworks* on 28 March.

The NZIC President, *James* ***Crowley***, gave seminars titled, *Adventures in supramolecular chemistry: self-assembly of metallosupramolecular cages and the synthesis of non-interlocked molecular machines* followed by *Rise of the nano-machines: mechanically interlocked molecules and synthetic molecular machines* on 11 April.

Haritina Mogosanu spoke on *How single cells, telescopes and volcanos are keeping New Zealand at the forefront of astrobiology - New Zealand's leading role in the global astrobiology effort* on 18 April.

Yang (Richard) Fong presented *Fighting ancient disease with modern tools - how?* on 23 May.

OTAGO

Congratulations to Jacob Ward, Brianna Nally and Geoffrey Weal who received prizes in the latest NZIC Otago Student Essay competition and had their articles published in the April 2018 issue of *Chemistry in New Zealand*. Jacob won first prize with *From South America to Willy Wonka – a brief outline of the production and composition of chocolate*, while Brianna and Geoff wrote about *A day in the life of an Outreach student"* for 2nd place.

The Branch co-hosted a poster evening with ChemClub on 20 April. The event was well supported ensuring a great evening. The judges' poster prize was awarded to Robert Smith from the Department of Chemistry with his poster *Expedient access to chromones: application towards the synthesis of biologically relevant molecules*. For the first year, a people's choice award was also on offer, and it was the poster *Using evolution to discover carbon dioxide reducing catalysts* by Geoffrey Weal that attracted the greatest attention and earned him the award.

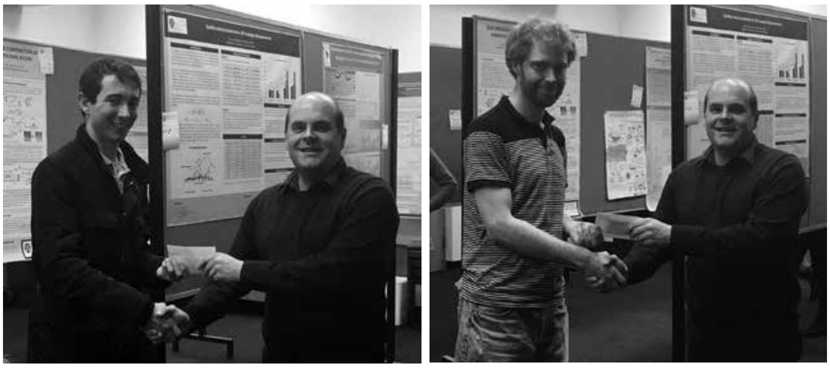
University of Otago, School of Pharmacy

Anna ***Cooper*** (supervisors *Andrea* ***Vernall***, *Joel* ***Tyndall*** and *Sarah* ***Hook***) graduated with her PhD from the School of Pharmacy (medicinal chemistry project), and her PhD thesis was put on the Division of Health Sciences exceptional theses list.

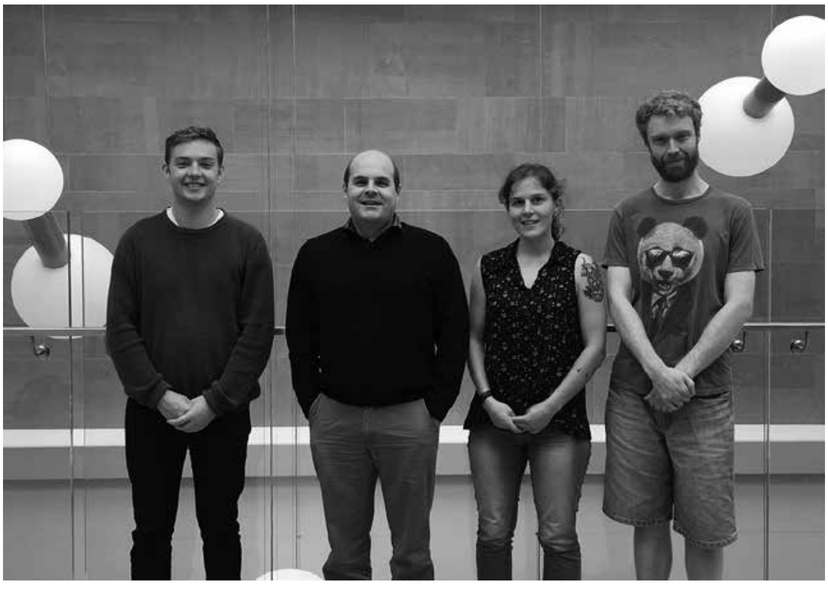
University of Otago, Department of Chemistry

Dr *Jaydee* ***Cabral*** presented *Biomaterials for cell therapy* at the NZ Biomaterials Symposium in Auckland in April; and at the Biomaterials and Regenerative Medicine Symposium in Dunedin in April.

Dr *Jaydee* ***Cabral*** and Associate Professor *Srdjan* ***Vlajkovic*** (University



Robert Smith (L) and Geoffrey Weal (R) receive their poster prizes from Nigel Lucas



NZIC Otago Student essay winners, L-R: Jacob Ward, Nigel Lucas (Branch Chair), Brianna Nally, Geoffrey Weal of Auckland, Department of Physiology) along with their team won first place in the Brain & Technology Symposium Funding Competition on 10 April and were awarded $25,000 for their research proposal entitled, *Drug delivery to the inner ear*.

Charlie ***Ruffman*** (PhD student with *Anna* ***Garden***) was awarded a $1,000 travel award from the Otago Energy Research Centre for his upcoming travel to Finland, Iceland and Denmark. *Ray* ***Yang*** (former student of *Anna* ***Garden***) left the Garden group to begin a PhD at Massey University with Professor *Joachim* ***Brand***.

Professor *Sally* ***Brooker*** presented an invited talk at the Society of Pure and Applied Coordination Chemistry (SPACC) symposium in Auckland late last year – she particularly enjoyed the opportunity to catch up with members of the NZ chemistry community. In December 2017 her PhD student *Fabrice* ***Karabulut***, and postdocs Dr *Santiago* ***Rodríguez-Jiménez*** and Dr *Humphrey* ***Feltham***, participated in the master class on advanced electrochemical techniques workshop run by Professor Alan Bond at Monash University, for invaluable training relevant to their current projects on hydrogen production catalysed by transition metal complexes. Fabrice also attended the MacDiarmid Institute Future Leaders Program on commercialisation and industry. He had an opportunity to meet representatives of various industries and was subsequently called for an interview and then offered a position in a well-regarded Auckland firm after completion of his PhD.

Sally ***Brooker*** also participated in the Gordon Research Conference on Renewable Energy and Solar Fuels conference earlier this year. She made the most of the opportunity to discuss the next phase of her collaboration on photocatalytic hydrogen production with Professor Garry Hanan (Montreal), and to line up some speakers for the Solar Fuels workshop she is planning for 7-8 February 2019 at Otago University (prior to AMN9 in Wellington). Sally then spoke at the Pacific Climate Change Conference in Wellington and enjoyed the MacDiarmid dinner with plenary lecturer Professor Dan Nocera (Harvard) in February. Thanks to the support of the MacDiarmid Institute, specifically the MacDiarmid Emerging Scientists Association (MESA), Santi was able to attend Professor Nocera's talk at Victoria University that week, and to discuss with him face to face exciting topics such as climate change and future energy challenges. *Sriram* ***Sundaresan*** (MSc from University College Dublin, Ireland), has taken up a MacDiarmid Institute funded PhD scholarship, joining Brookers Bunch in February. Professor *Annie* ***Powell*** (now an Honorary Research Professor at the University of Otago) and Professor *Ali* ***Malik*** (Karlsruhe Institute of Technology) visited in February.

In March, Santi took the opportunity to improve his pitching skills by participating in a fantastic MacDiarmid Institute workshop organised by Daniel Batten. Humphrey made visits to the groups of Professor *Alison* ***Downard*** (Canterbury) in March, and Professor *Jandranka* ***Travas-Sejdic*** and Associate Professor *David* ***Barker*** (Auckland) in April, to progress our MacDiarmid-funded collaborative project on surface attachment of hydrogen production catalysts.

Professor *Silvia* ***Giordani*** (Turin) had a busy few weeks with us during April and May on a William Evans fellowship, hosted by *Sally* ***Brooker*** and *Carla* ***Meledandri***. Silvia gave three very well received department seminars in pharmacology, pharmacy and chemistry, a 400-level module on carbon nanomaterials, consolidated her existing collaboration with Sally, and established a number of new collaborations. Our collaborator Dr *Paul* ***Jerabek*** (Massey Albany) visited us for a week, hosted by *Sally* ***Brooker*** and *Anna* ***Garden*** to work closely

L-R: Professor Sarah Hook, PhD graduate Anna Cooper, Dr Andrea Vernall, Associate Professor Joel Tyndall (all from School of Pharmacy, University of Otago)

Jaydee Cabral (front left) and Srdjan Vlajkovic (back right) and their winning team at the Brain & Technology Symposium Funding Competition with us, and in particular with PhD student *Luca* ***Bondí***. PhD student *Fola* ***Akogun*** is just back from his first solo visit to our collaborator Professor *Geoff* ***Jameson*** (Massey), collecting a new set of pressure NMR data.

In news from the group of Professor *Keith* ***Gordon***, firstly, congratulations to *Jono* ***Barnsley*** for the successful submission of this thesis titled, *Spectroscopy of some donor acceptor dyes*. The Gordon group has been busy with a series of visitors and new students starting. First off was a seven week visit by Jaana Koskela, from the University of Helsinki, to study the polymorphic changes in indomethacin using mid and low frequency Raman with *Joshua* ***Sutton*** and Dr *Sara* ***Miller***. This follows a successful visit last year by Tiina Lipiäinen, who has since gone on to publish this work and has her PhD defence later this month. Immediately after Jaana's visit Bjarke Laugesen arrived for three weeks to study how the low frequency vibrational density of states in amorphous drugs change across the glass transition temperature under Jono and Sara's guidance. In addition to these longer visits, Ben Boyd, from Monash University, visited for a couple of days to work with Joshua on testing the use of low frequency Raman to monitor the digestion of drugs in milk in a flow through system, successfully replicating the results of experiments originally requiring the use of a synchrotron.

The Gordon group has welcomed *Piumika* ***Samanali***, who has got off to a flying start with her PhD, continuing the study of preservatives in traditional Māori fibres in collaboration with Catherine Smith and Bronwyn Lowe. *Elliot* ***Tay***, *Sam* ***McIntyre*** and *Lachlan* ***Gaudin*** also joined the group as Honours students and for CHEM390 respectively. Elliot is studying the unique pigments in parrot feather, to try and understand the interplay between chemical structure and environment that results in the wide range of observed colours. Sam will be looking to study apricots and variations within them, while Lachlan will be attempting to probe the degree of order and spatial distribution within polymer blends for solar cells.

The Gordon group has also been busy preparing for a variety of conferences, with *Ruth Eloisa* ***Sales***, *Joe* ***Mapley*** and *Joshua* ***Sutton*** attending the International Conference of Raman Spectroscopy in August. Ruth will be presenting a talk entitled, *From lab to lake: spectroscopic analysis of New Zealand 'Lake Snow'*, while Joe and Joshua are presenting the posters, *A computational and spectroscopic analysis of β-indandione substituted zinc porphyrins* and *Raman spectroscopy from low frequency to overtones – insight into the electronic structure of self-assembling materials* respectively. *Georgina* ***Shillito*** will attend the Gordon Research Conference in August and will be presenting

Professors Annie Powell and Ali Malik (Karlsruhe) at Riverstone Castle. Photo credit: Sally.

New Brookers Bunch PhD student Sriram Sundaresan

Professor Silvia Giordani (Turin), here on an Otago University William Evans fellowship, was the inaugural occupant of the new Visiting Professor office in the Mellor building a poster of her recent work on the *Interplay of ILCT and MLCT states in Re(I) and Pt(II) phen-TPA complexes*.

Finally, congratulations go to *Joe* ***Mapley*** for getting his first paper accepted into *J. Phys. Chem. A* (*A computational and spectroscopic analysis of β-indandione substituted zinc porphyrins*) and to *Georgina* ***Shillito*** for getting her paper entitled, *Dramatic alteration of* ^{3}*ILCT lifetimes using ancillary ligands in* $[Re(L)(CO)_3(phen\text{-}TPA)]^{n+}$ *complexes: an integrated spectroscopic and theoretical study* accepted into the *J. Am. Chem. Soc*. *Jeremy* ***Rooney*** is finishing writing up his thesis.

WAIKATO

University of Waikato

Mohammad Soleimani Zohr Shiri has begun a PhD with *Michael* ***Mucalo*** and *Bill* ***Henderson*** on the little-studied topic of colloids of selected precious metals. He is originally from Iran but has been based in Norway.

Hill Laboratories

Jonno Hill, son of company founders Roger and Anne Hill, has been appointed as the new CEO of Hill Laboratories. Jonno will take over from departing CEO Dr Matt Glenn, who led the company for four years including through the process of consolidating four Hamilton sites into one city location, and opening two asbestos testing laboratories in Auckland and Wellington. Jonno says that the company has flourished under Matt's leadership: "Under Matt's watch our leadership and management grew into a strong team, ably leading the company to where it is now".

Jonno has a PhD in synthetic organic chemistry from the University of Canterbury. He has worked in the business for the past 13 years, beginning as a technologist and later becoming an analytical technology team leader, section manager, and divisional manager. Most recently he was general manager of technology on the executive leadership team. Roger Hill remains active at Hill Laboratories, providing both strategic leadership and a considerable amount of technical knowledge, whilst Anne Hill also retains an ongoing important role as payroll manager.

Scion

Science Leader *Florian* ***Graichen,*** recently back from delivering an award-winning presentation at MaD2018 (Manufacturing and Design NZ), is now travelling as an invited speaker to the World PLA Congress (Munich). *Florian* will give a talk at the Technische Universitat Bergakademie Freiberg while he is in Germany and he plans to catch up with Prof. Dr Henning Zeider, who is a collaborator with Scion on the 3D printing of bio-based polymers.

L-R: Dr Paul Jerabek (Massey Albany), Prof Silvia Giordani (Turin), Prof Sally Brooker, Dr Anna Garden and Luca Bondí

Research Leader *Warren* ***Grigsby*** will be hosting Drs Gerd Unkelbach and Susanne Zibek from Fraunhofer Institute for Interfacial Engineering and Biotechnology and Center for Chemical-Biotechnological Processes (Germany) as part of reciprocal visits funded through an RSNZ Catalyst grant on a NZ-based bark biorefinery. This interaction will be followed up later in the year when *Florian* ***Graichen*** and *Laura* ***Raymond*** will travel with Warren to Germany to carry out pilot scale evaluations of supercritical carbon dioxide extraction.

Research Leader *Dawn* ***Smith*** and *Marie Joo* ***Le Guen*** have both been preparing to present to MBIE officials on their respective MBIE-funded projects. Dawn's ExtrusionPlus programme is nearing its end and she will be reporting on outcome impacts of the project which have included science taken into industry with products such as the *Biospife* and bio-based 3D printing filament. Marie's Smart Idea, which combines 3D printing and functional surfaces, has just reached the end of its first year, and she will report on the progress to date in 3D flow modelling and photoinitiated resin chemistry.

Gerty ***Gielen*** has commissioned a biodegradation plant capable of simultaneously testing up to 60 samples, allowing research into the chemical breakdown products of degradable and compostable polymers. Along with this new capability, *Eva* ***Gaugler*** and *Lou* ***Sherman*** are investigating analytical chemistry approaches to determine the nature and amounts of intentional and non-intentional substances migrating from packaging into food.

Over 100 industry and science delegates that attended the Plastics NZ conference in Rotorua (16-18 May) toured Scion laboratories and pilot scale facilities. Scientists across a range of disciplines from analytical chemistry, polymer and materials science, and packaging were on hand to talk with delegates and give them a heads up on some of the latest developments in new materials.

Scion has recently welcomed two new employees. *Roya* ***Rezanavaz***, formerly of the University of Canterbury, works on the use of 3D printing porous materials as stationary phases in chromatography columns and Kim Pritchard, formerly of the University of Waikato, has been appointed as a Science Advisor.

Scion is hosting four international students, three from Germany and one from France. One is working with *Marie Joo* ***Le Guen*** on 4D printed polymers and the other three are working with *Marc* ***Gaugler*** and *Samir* ***Shah*** on bio-based polymer projects.

WELLINGTON

In May, the Wellington Branch was treated to a lunchtime seminar given by Gavin Dunbar (Antarctic Research Centre) on iron fertilisation of sea water leading to plankton blooms, focussing on observations and experiments in the Ross Sea.

VUW

The May graduation ceremony saw undergraduate and research students awarded their degrees including a number of chemistry PhDs: *Graham* ***Fairweather*** (supervisors *Kate* ***McGrath*** and *Justin* ***Hodgkiss***), *Putri* ***Fraser*** (supervisors *Robin* ***Fulton*** and *Jim* ***Johnston***), *Muhammad Ali* ***Hashmi*** (supervisors *Matthias* ***Lein*** and *Rob* ***Keyzers***), *Alex* ***Hunt-Painter*** (supervisors *Mattie* ***Timmer*** and *Bridget* ***Stocker***) and *Taitusi* ***Taufa*** (supervisors *Peter* ***Northcote*** and *Rob* ***Keyzers***). Congratulations to all!

Members of the New Materials and Technologies research group attended the 20th annual TechConnect World Innovation Conference and Expo, held in Anaheim, California, 14-16 May. Professor *Jim* ***Johnston*** brought with him Research Fellow Dr *Michelle* ***Cook***, PhD students *Emma* ***Wrigglesworth*** and Matilda Hayward, and Master's student Sami Aljohani. CEO of start-up company Inhibit Coatings and previous group member, Dr Eldon Tate, also attended. The conference brought together researchers in fundamental and applied science and engineering as well as those involved in research and management from a wide range of international companies who were presenting their current products and looking for new products, processes and technologies. Representatives from government and private funding organisations with deep pockets also attended.

Jim and Eldon were both invited speakers, and the four VUW representatives gave oral presentations. Jim's talks were entitled, *Silver-wool textiles - development pathway and challenges, New generation durable, effective antimicrobial composites of natural fibres and polymers* and *Nanostructured calcium silicate phase change materials for thermal buffering in packaging and construction applications.* Eldon talked about *Antimicrobial and antifouling coatings for industrial applications.* The other presentations were *Combining a fluroalkylsiloxane and ion implantation for hydrophilic/hydrophobic patterning* given by Michelle, *Discovery of the dichroic effect in cuprous oxide particles for the development of novel composite materials that change colour with direction of light source* given by Emma, *Optimising the properties of polymer composites: low weight/ high strength composites for commercial applications* given by Matilda and *Composite wool-natural product antimicrobial textiles* given by Sami.

All of the presentations were very well received and the conference was very beneficial for the students' studies. The participants also had a really good time checking out L.A., including a memorable day at Disneyland.

VUW delegates at the 20th annual TechConnect World Innovation Conference and Expo, Anaheim, Californi

Trace element partitioning during calcite growth: implications for climate reconstruction studies from New Zealand caves

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Keywords: *environmental geochemistry, trace elements, speleothems, climate proxies*

Ingrid Lindeman completed her BSc, majoring in chemistry, in June 2017 at the University of Waikato and subsequently spent two months working with the speleothem research unit at the Johannes-Gutenberg University (JGU), Mainz, Germany. Ingrid has recently started her MSc project under the supervision of Dr Adam Hartland at the University of Waikato, where she will be investigating the dissociation of metal-ligand complexes during calcite precipitation under cave analogue conditions, building on the work carried out at JGU. She is a 2018 William Georgetti Scholarship recipient, and her research will contribute to the Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) project known as QUEST (QUantitative paleoEnvironments from SpeleoThems).

Introduction

Over the past half-century, a significant amount of research into the geochemistry of $CaCO_3$ cave formations such as stalagmites, stalactites and flow stones (speleothems) has been carried out.[1-8] Researchers across Aotearoa New Zealand have been heavily involved in this field of research, making important contributions to speleothem science. This is unsurprising given the vast number of caves scattered throughout New Zealand's landscapes (Fig. 1), with cavers and tourists travelling from across the world to explore and experience these unique subterranean features.[2,6] However, it is now apparent that such caves may not only contribute to New Zealand's tourism industry, but they may also hold within them secrets of New Zealand's past.[2,6]

Speleothems are known to contain important information on past events and past climatic conditions throughout the world. Not only are major events such as bush-fires and volcanic eruptions recorded within them, but they are also indicators of past climatic conditions including temperature and rain fall.[2,9] With increasing attention on climate change research, there has been a major focus on the importance of establishing past climatic conditions for comparative purposes. Terrestrial records of past climate are therefore being heavily studied so that the magnitude of current climatic events can be put into perspective. The major advantage of speleothems over other terrestrial records such as lake sediment cores is the age of these records and the high temporal resolution that they provide (sub-annual resolution in some cases).[2,10-11] More importantly, their growth layers can be precisely dated using uranium-thorium disequilibrium and uranium-lead dating methods.[2,12] In addition, their ubiquitous geographical coverage from all

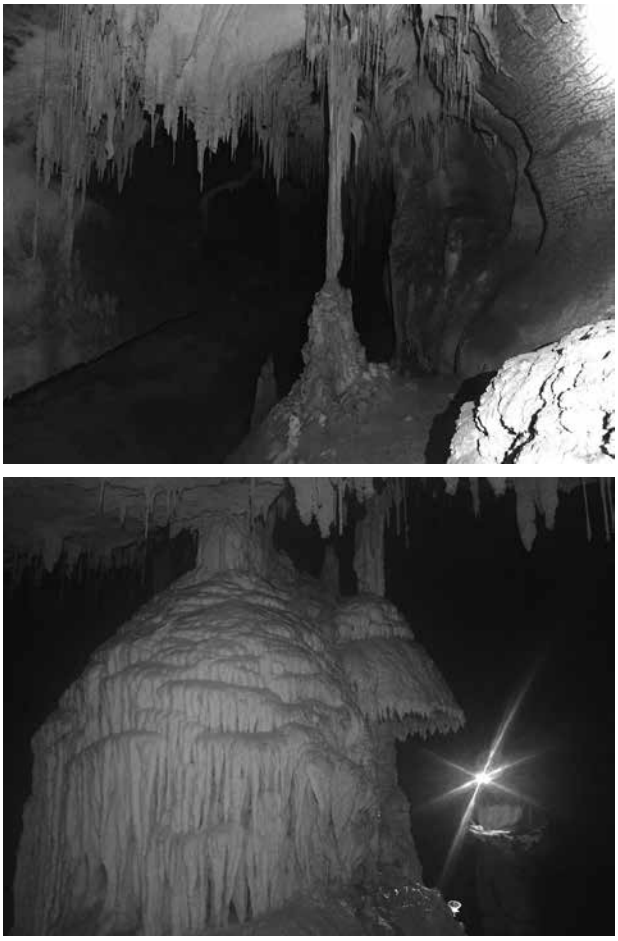

Fig. 1. Stalagmite and stalactite formations in Waipuna cave, Waitomo, where researchers from the University of Waikato measure dripwater pH, conductance and trace element composition. Speleothem samples have also been taken from this cave. Photos courtesy of Cynthia Nava.

climate zones make speleothem samples a fundamental tool for terrestrial paleoclimate reconstruction and for understanding climate-system mechanisms.[2]

Speleothems are formed via the precipitation of calcium carbonate (usually in the form of calcite or aragonite) from cave drip waters.[2] High carbon dioxide partial pressures (pCO_2) occur in the soil above cave systems, as a result of the decomposition of organic matter and root respiration. This results in an acidic solution that dissolves carbonate minerals (dolomite and/or calcite) present in karstic regions as it percolates through the carbonate host rock from the soil above, enriching the water in Ca^{2+} and HCO_3^-.[2] When the water eventually reaches an area of lower pCO_2 (such as in cavities or a cave), degassing of CO_2 from the supersaturated solution results in the deposition of $CaCO_3$ according to Eq. 1:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad \text{(Eq. 1)}$$

In this way speleothems arise from the deposition of calcite from cave dripwaters.[2] As the speed of this process is dependent on water availability and factors such as initial dripwater supersaturation and Ca^{2+} concentration, the carbonate is frequently deposited in distinguishable growth layers (laminae) with a sub-annual to a millennial scale resolution (Fig. 2). Each of these layers will contain information indicative of the environmental conditions affecting water movement and content when the layer formed.[2,6,11]

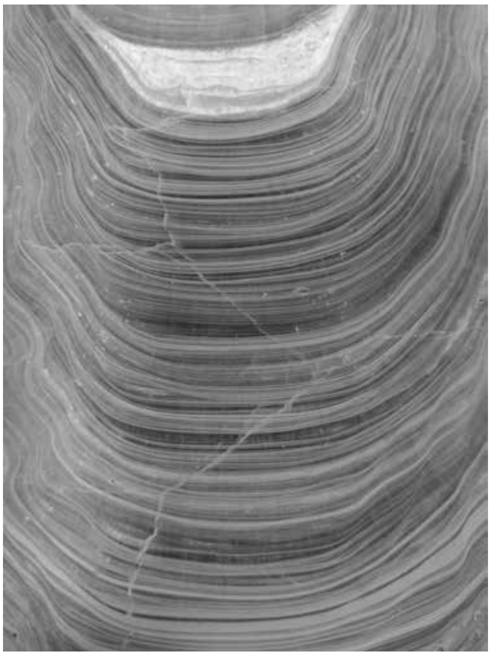

Fig. 2. Example of visible growth laminae seen in a cross section of a New Zealand speleothem.

Climate proxies in speleothems

$\delta^{13}C$ and $\delta^{18}O$ stable isotopes

Defining the nature of climate events for spatial and temporal comparison of records requires robust proxies. The stable isotopes of carbon and oxygen have been widely applied for such purposes in speleothems, as these parameters have been shown to be affected by rainfall above ground and temperature. Various studies of speleothem ^{13}C and $\delta^{18}O$ have indicated past periods of aridity and high rainfall, supplementing information from other paleoclimate archives such as ice-cores.[13] For instance, an abrupt cold period experienced in the North Atlantic region 8,200 years ago known as the 8.2 kiloyear (ky) event has been well documented in Greenland ice-cores, and recently $\delta^{18}O$ data from a sub-annually resolved stalagmite record from central China has shown that this event was also experienced in the East-Asian monsoon region. The $\delta^{18}O$ data was able to show a significant period of aridity was experienced in this region, coinciding with the onset of the 8.2 ky event, that lasted 150 years. This in turn demonstrated the existence of teleconnections in the climate system that transmits climate change from the North Atlantic to other regions.[13] Rainfall variability has also been recorded in an Ethiopian stalagmite in the form of changes in stable isotope composition.[14] Baker *et al.* (2010) employed a hydrological model and high resolution $\delta^{18}O$ measurements of the annually laminated speleothem to show that decadal scale variability in rainfall in the Ethiopian region occurred throughout the Holocene.[14] Low and high frequency climatic fluctuations on the northern Iberian Peninsula during the last glacial maximum have also been recorded in stalagmite $\delta^{18}O$ and $\delta^{13}C$ values, providing an important link between the millennial climate variability well characterised in the North Atlantic and Greenland, and the correlative abrupt climate changes observed in high accumulation rate marine cores in the western Mediterranean.[10] These are just a few of the many examples where speleothem $\delta^{18}O$ and $\delta^{13}C$ data has been used to qualitatively reconstruct past climatic events, which illustrate the power of speleothems to provide vital information for paleoclimate reconstructions.

Despite the ability of $\delta^{13}C$ and $\delta^{18}O$ values in speleothem to reveal information such as that discussed above, the interpretation of $\delta^{13}C$ and $\delta^{18}O$ data is difficult due to a multitude of other factors affecting $\delta^{13}C$ and $\delta^{18}O$ values.[2,7,15-16] Complex processes that occur in the soil, epikarst and during the flow of water down into the cave render the unambiguous interpretation of stable isotope data very difficult:[17] $\delta^{13}C$ and $\delta^{18}O$ proxies are not as robust and reliable as needed. Thus, past rainfall can only be measured qualitatively not quantitatively using these proxies and further research into other available speleothem proxies, such as trace elements content, has been undertaken in an attempt to find a method of analysis that allows a less ambiguous interpretation of past climatic conditions.

Trace elements

The development of techniques such as Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) have allowed quantitation of trace elements in both speleothems and cave dripwaters. This, coupled with the fact that trace elements are known to respond to environmental variables, means that trace elements have become a focus of speleothem scientists for their possible use as climate proxies. Trace element incorporation at the speleothem surface is understood to respond to a number of factors, including temperature, the growth rate of calcite and characteristics of the drip solution. Thus trace element data has the potential to yield valuable information about past climate.

Significant amounts of research into the partitioning behaviour of the alkaline earth metals Mg, Sr and to a lesser extent Ba into calcite has been undertaken. Liu *et al.* (2013) used Mg/Ca data from their speleothem to support the $\delta^{18}O$ evidence for aridity in the East-Asian monsoon region during the 8.2 ky event.[13] Similarly, Zhou *et al*. (2011) used Mg/Ca, Sr/Ca and Ba/Ca ratios from stalagmite SZ2 (from Suozi Cave in Sichuan province, Central China) to demonstrate changes in past climate and environment during the Marine Isotope Stage (MIS).[18] They suggest temperature to be the dominant control on the Mg/Ca ratios observed, and tentatively suggest prior calcite precipitation (PCP) and surface soil and atmospheric dust activities to be the main influences on the Sr/Ca and Ba/Ca ratios observed. Fewer studies have investigated the incorporation of transition metals into speleothem calcite than for the alkali earth metals but data for some trace metals in cave dripwaters have been reported in the literature, including Ni, V, Cu and Co.[19-21] Hartland *et al.* (2014) demonstrated the potential for trace transition metals in speleothems to record changes in organic ligand concentration and composition in cave dripwaters, and suggest this information could be used to make inferences about the state of surface ecosystems overlying the caves of interest.[20]

Again, these are only a few of the vast number of studies of such proxies in speleothem samples. However, despite this long history of research in trace element partitioning into speleothem calcite, many uncertainties remain regarding the controls on trace element incorporation into speleothem calcite and, just like for stable isotopes, further information is required for these proxies to provide data that can be interpreted unambiguously. One particular factor that should be considered is the presence of organic ligands in cave dripwater. Hartland *et al.* (2012) demonstrated the widespread occurrence of colloidal and particulate natural organic matter (NOM)–metal transport in cave dripwaters during their studies of three international caves.[19] This highlighted the importance of taking the presence of organic matter into consideration when interpreting trace element data in speleothems during climate reconstruction studies.[19]

Non-traditional stable isotope fractionation

The analysis of various non-traditional stable isotopes in speleothems has also recently been investigated by speleothem scientists. Owen *et al.* (2016) reported the first comprehensive study of Ca isotope cycling in a natural cave system, with measurements of bedrock, cave dripwater and recently formed carbonate in Hesheng Cave, China, and coupled these measurements to data from a stalagmite with growth layers spanning the 8.2 ky event.[7] They found that Ca isotope ratios responded to changing climate: $\delta^{44}/^{42}Ca$ increased at the onset of the 8.2 ky event (supported by changes in $\delta^{18}O$ and Mg/Ca data) and remained high for 80 years. They proposed this was a result of increased PCP occurring as a result of the period of aridity known to have occurred in central china during the 8.2 ky event.[7] During periods of aridity, the aquifers present in the overlying bedrock have a lower volume of water, and thus a greater volume of air. In these spaces, PCP is likely to occur as CO_2 evolves from solution. Here, isotopic fractionation of elements such as Ca can occur, and thus the isotopic signal recorded in the speleothems below will be affected.[2]

In a laboratory experiment, Mavromatis *et al.* (2017) investigated the effects of organic ligands on the isotopic fractionation of Mg during low-temperature precipitation of calcite.[22] Of the six ligands investigated, they found that only citric acid caused any significant change in the Mg isotopic fractionation factor. They therefore concluded that the presence of organic ligands in Earth's precipitation environments is not a significant factor affecting Mg isotope fractionation, which has important implications for the analysis of Mg isotopes in speleothems. Experiments investigating the isotopic fractionation of trace elements during calcite precipitation have been carried out in a laboratory environment for Ba, Mg, Sr, Zn, Cu, Cd, Mn, Co and Ni,[23] however the application of the finding to speleothems needs to be investigated further.

Implications for speleothem studies in New Zealand

Cave dripwater studies

Speleothem scientists in NZ have been carrying out research into the dripwater hydrochemistry of both local and international caves using various techniques from the fields of geochemistry (stable metal isotope analysis) and environmental chemistry (diffusive gradients in thin films, (DGT)) in recent years. These techniques have the potential to help speleothem scientists gain a better understanding of the processes occurring in dripwaters in the soils and epikarst overlying cave systems, and to help distinguish between the effects of PCP and metal-ligand interactions on trace element content in cave dripwaters (and thus speleothems). This research has a strong focus on transition metals such as Cu and Mn, and preliminary findings have indicated that such elements may have a significant role in enabling scientists to reconstruct past rainfall volumes from speleothem archives.[24] The use of DGT gels in cave dripwater studies is of particular interest, as they allow the lability of metal-ligand complexes to be studied. Thus, the use of this technique will help researchers to better understand the effects of NOM in cave dripwaters on trace metal partitioning behaviour in natural systems.

Laboratory cave analogue experiments

Despite the extensive analysis of natural speleothems and cave drip waters undertaken during the past half-century, and the significant progress made in the ability of climate researchers to interpret the resulting data, incorporation of trace elements is known to be influenced by a large number of factors as discussed above. Thus, in order to fully interpret and understand speleothem records, there is a need for further research into the kinetic and thermodynamic processes affecting trace element incorporation into calcite. Laboratory experiments represent one possible approach to this, and several laboratory cave analogue experiments have been carried out to study the effects of various factors on trace element incorporation.

There have been several laboratory studies dealing with trace element incorporation into calcite with the aim of establishing partition coefficients for various trace elements. Day and Henderson (2013) studied the partitioning behaviour of Li, Na, Mg, Co, Sr, Cd, Ba and U into calcite at various temperatures (7, 15, 25 and 35°C), using an experimental setup that closely mimicked natural processes.[25] They were able to develop temperature dependent expressions for the partition coefficients of these trace elements, and suggested that due to the different responses of each trace element to both temperature and the fraction of calcium remaining in the solution, that combined analyses of these trace elements in natural cave systems would be useful for the assessment of past cave conditions. They found that high $Cd/Ca_{stalagmite}$ values, in particular, were indicative of low amounts of PCP in cave systems. Huang and Fairchild (2001) also carried out a series of experiments using a karst analogue setup.[26] They also determined partition coefficients for Mg and Sr, and suggested that magnesium partition coefficients (D(Mg)) may allow the determination of $Mg/Ca_{solution}$ in enclosed caves that have a fairly constant temperature. They found that the partition coefficient values for strontium, (D(Sr)), in contrast, should be interpreted with caution due to the growth rate dependence of D(Sr).[26]

The use of a completely sealed cave analogue setup with controlled temperature, pCO_2, humidity and solution composition has been reported in the literature by Dreybrodt *et al.* (2016) and Hansen *et al.* (2017) and represents a major improvement in calcite growth laboratory experiments (Fig. 3).[16-17] By conducting experiments within a sealed environment, they were able to study in detail the carbon isotope exchange between dissolved inorganic carbon (DIC) in a thin solution film composed of water and calcium carbonate, and gaseous CO_2. By providing a sealed 'cave like' environment, they were able to flush the box with N_2 and then establish a defined pCO_2 level within the box (500-1000 pCO_2), using CO_2 of known isotopic composition. These experiments allowed the development of a novel, complete reaction diffusion model describing the carbon isotope exchange between gaseous carbon dioxide and dissolved DIC. This represents a considerable advancement in the understanding of the processes affecting $\delta^{13}C$ values that are measured for natural cave formations and thus in establishing $\delta^{13}C$ as a more robust proxy for paleoclimate reconstruction.

Fig. 3. The 'climate-controlled calcite precipitation box' used by Dreybrodt *et al.* (2016) and Hansen *et al.* (2017) during their carbon isotope exchange experiments.[16-17] The box is open in this picture, with most insulation removed, as no experiments were being undertaken at this time. Any adjustments to the experimental setup inside that are required during an experiment must be undertaken using the gloves at the front of the box to ensure the integrity of the seal so that no atmospheric disturbances to the experiment occur.

Researchers at the University of Waikato are in the process of constructing a similar 'climate-controlled cave analogue' box in which experiments will be undertaken in order to help establish the processes affecting the behaviour of trace metals at the water-calcite interface. A schematic of the experimental setup inside the climate-controlled box is given in Fig. 4.

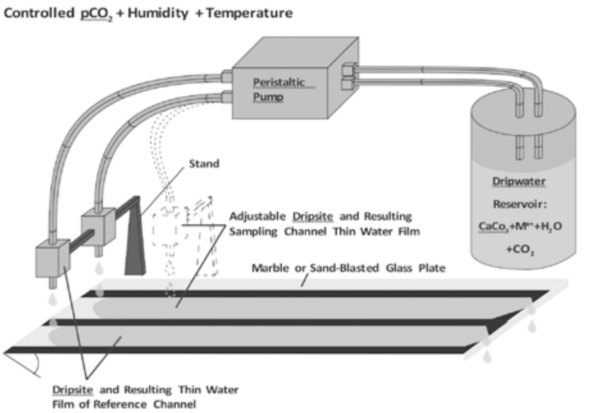

Fig. 4. A schematic representation of calcite growth experiments that are currently being undertaken at the University of Waikato. This experimental setup will be contained within an insulated box that allows tight control over pCO_2, humidity and temperature. Diagram courtesy of Matthias Magiera.

Water with dissolved calcium carbonate and CO_2 from the reservoir, spiked with trace metals of interest, is dripped via a peristaltic pump onto an angled plate, where a thin water film (0.1 mm in thickness) is established. The temperature, pCO_2 and humidity levels inside the box are well controlled and logged. As calcite precipitates from the solution due to CO_2 degassing from the solutions, trace metals are incorporated in the calcite at rates determined by factors such as calcite growth rate and temperature. The distance of flow along the channels is able to be adjusted so that the effect of prior calcite precipitation and growth rate on trace metal incorporation can be established and investigated. This setup allows for comparison of trace metal content of both the precipitated calcite and the solution content at varying time intervals so that partition coefficients may be determined for each element at various temperatures, residence times and distances of flow. Further experiments will be undertaken using this system to further investigate the effects of organic ligands present in cave drip-waters on the trace element incorporation into calcite. The temperature dependence of these effects will also be investigated.

The use of this type of cave analogue system will allow investigations into the effects of temperature, drip rate, solution composition and growth rate on the incorporation of a wide variety of trace metals into calcite, and the isotopic fractionation of these elements. The insights that these laboratory experiments will provide into calcite growth behaviour may then be applied to the data collected from natural caves systems, such as Waipuna cave, and help to establish trace metals in speleothems as robust and reliable proxies that may be used in a multi-proxy approach for paleoclimate reconstructions.

Summary and future research

Although a significant amount of research has been done both in the field and in the laboratory to try to enable researchers to quantitatively reconstruct past climatic conditions from speleothems, the complex geochemical processes that occur above and within caves have made the unambiguous interpretation of stable isotope and trace element data unachievable so far. Further research must be carried out in order to make speleothem data analysis more reliable. This is especially crucial for a quantitative interpretation of speleothem proxy data. Research at the University of Waikato is continuing in order to decipher the controls on trace metal partitioning into calcite using a cave analogue climate-control box. Partition coefficient data for various trace elements will be determined at various temperatures, organic ligand concentrations and growth rates. This research will help to determine the viability of the use of trace elements in speleothems as robust and reliable proxies for paleoclimate reconstructions and provide important insights into the mechanisms behind trace metal incorporation and speciation within speleothem calcite. Ultimately, this may help us to better understand our current climatic conditions and climate variability so that we are better able to assess the impacts of current climate change events.

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Flavour and aroma analysis by solid-phase microextraction (SPME) and gas chromatography

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Keywords: *analytical chemistry, honey, wine*

Bruce holds a PhD in marine natural products chemistry. Previously involved in insect chemical ecology, he is currently an R & D chemist at RJ Hill Laboratories where he works in a range of areas including pesticide residue testing, honey and wine analyses and robotic sample preparation.

Introduction

Solid-phase extraction (SPE) is commonly used in analytical chemistry to prepare samples for instrumental analyses.[1] Generally it is a cleanup step between solvent extraction and injection of extracts onto a chromatography column. It functions by selectively retaining compounds on the solid phase to pre-concentrate those of interest (analytes), or separate them from interfering compounds co-extracted from the sample (the matrix). Once the analytes are eluted from the solid phase, they are injected onto an instrument such as a high-performance liquid chromatograph (HPLC), or gas chromatograph (GC). Most solid phases use silica or polymeric particles derivatised with functional groups that give them polar or non-polar characteristics, ion-exchange, or π-π interaction capacity. The solid phases are packed into small columns eluted with solvent. Solid-phase microextraction (SPME) is a subset of SPE and was invented by Janusz Pawliszyn and coworkers in the early 1990s.[2] It uses sorbents immobilised by coating them onto a fused silica fibre (Fig. 1), and was originally designed for direct injection into a GC injector, avoiding the injection of extraction solvents. Analytes collected by the fibre are desorbed by heating in the GC injector. SPME is commonly used for headspace extractions, with the fibre passed through the septum of a sealed vial into the headspace above a solid or liquid sample. The volatile compounds in the headspace are retained on the fibre, which is then withdrawn from the vial, and inserted into the hot GC injector where they are transferred to the GC column, for separation and identification (Fig. 2). This makes it ideal for flavour and aroma analysis of food, as it allows clean extraction of volatiles, leaving behind the often complex food matrix.

Principles of SPME

For a headspace SPME experiment, an equilibrium concentration of analyte in the fibre coating is eventually reached.[3] Once equilibrium is reached the concentration of analyte collected by the SPME fibre can be described by Eq. 1.[4]

$$n \approx K_{fs} V_f C_0 \qquad \text{(Eq. 1)}$$

Where: n is the mass of analyte absorbed by the fibre

- C_0 is the initial concentration of analyte in the sample
- V_f is the volume of the fibre coating
- K_{fs} is the partition coefficient for the analyte between the fibre and the sample

Eq. 1 assumes that the sample volume is much greater than the volume of the sorbtive layer on the SPME fibre. This means that the amount of each aroma compound is

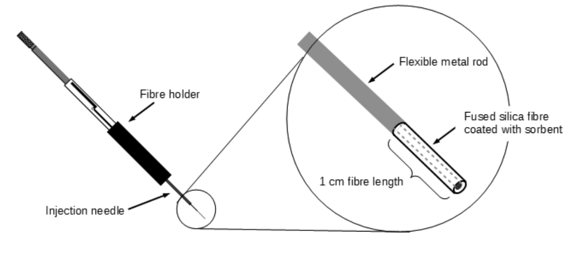


Fig. 1. SPME fibre assembly, with close-up showing sorbent coating on a typical 1 cm long fused silica fibre. The metal rod and fibre are housed within a hollow needle for injection through a septum, then extended from the needle, for sorption of sample, or desorption in a GC inlet.

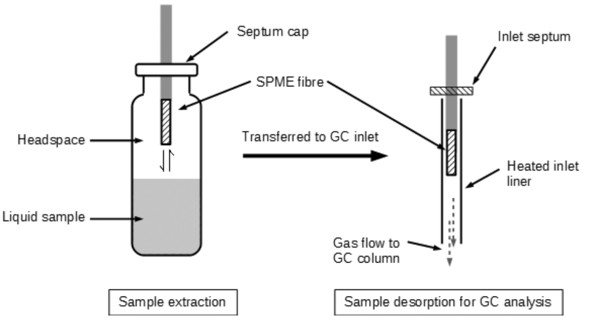


Fig. 2. SPME headspace extraction, followed by desorption in a hot GC inlet.

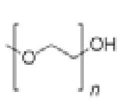
directly proportional to the amount in the food sample being tested, so quantitation is possible. Often solid samples are dissolved or dispersed in water before SPME. To increase the value of the partition coefficient K_{fs} , salts (such as NaCl) can be added, to reduce the solubility of analytes in the liquid and force them into the headspace and subsequently the fibre. Warming the sample, or stirring, can help increase K_{fs} and give greater recoveries of aroma compounds, while acidic or basic compounds may require pH adjustment to reduce their water solubility, by pushing their acid-base equilibria towards neutral species.[5] Optimising these parameters is an important part of developing an SPME method, to give maximum sensitivity. Practically, the time taken to reach equilibrium can be inconveniently long, so shorter, non-equilibrium extractions are used in many commercial laboratory methods. To obtain accurate quantitative results using SPME extractions before reaching equilibrium, extraction time has to be tightly controlled, or internal standards with a similar K_{fs} value to the analytes can be added. If a mass spectrometer is used as the detector, deuterated analogues of the aroma compounds are ideal as internal standards, as they compensate for K_{fs} variations resulting from differing extraction temperatures or times or differing matrix retention of analytes.

SPME fibre coatings

Several types of SPME sorbent coatings are available commercially, either liquid polymers or polymers with a solid sorbent embedded. These have different selectivities for volatile compounds, therefore choosing the appropriate fibre type has a large influence on the amount of analyte recovered from the sample. Polydimethylsiloxane (PDMS, **1**) was one of the earlier polymer coatings to be developed and is similar to a non-polar GC column coating. It retains non-polar analytes strongly, such as terpenoids (e.g. limonene from citrus), that are highly soluble in the liquid coating (like dissolves like principle). Carbowax and polyacrylate coatings are polar and preferentially absorb polar compounds, for example organic alcohols and acids. Carbowax is a polyethylene glycol (**2**), which has also been used as a GC column coating, and can retain polar compounds by hydrogen-bonding, while polyacrylate (**3**) is less polar, with a methyl ester group. Two solid sorbents, embedded in PDMS, are Carboxen, and divinylbenzene. Carboxen is a carbon molecular sieve, and strongly adsorbs compounds with molecular weights between *m/z* 30 and 225, so is very effective at trapping highly volatile aroma compounds (e.g. floral aromas of honeys).[6] Divinylbenzene polymeric particles have mesoporous molecular sieve properties and adsorb higher molecular weight compounds (*m/z* 60-275).[7]

Divinylbenzene/PDMS fibres have been used for the analysis of phthalates in water, originating from contact with plastic bottles,[8] and we have used these fibres for analysis of phthalates and bisphenol A in wine. An advantage of these solid adsorbents is that they extract volatile compounds with a wide range of polarities.

1



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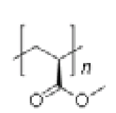


3

Applications of SPME

In a commercial testing laboratory, or if undertaking a study of many samples, manually transferring the fibre from the extraction vial to the GC injector can become tedious. The advent of robotic x-y-z autosamplers (Fig. 3) has allowed automated SPME with accurate heating and agitation (equivalent to stirring) of the sample, and accurate extraction times, giving highly reproducible results from non-equilibrium SPME.

In our laboratory, we have studied honey aroma profiles with the aim of differentiating the floral origin of New Zealand honeys.[6] Aroma is one of the sensory characteristics that distinguishes unifloral honeys, and contributes to their unique flavours. Traditionally, labeling of unifloral honeys has relied on pollen counting (melissopalynology), identifying the unique shapes of pollen grains, which requires a high level of training and skill. In our SPME experiments, we found warming honeys in a headspace vial, without adding water or NaCl, gave high enough recoveries of aroma compounds, if extracted with a Carboxen/PDMS fibre, to identify them by full-scan GC-MS. This allowed collection of mass spectra of each compound, so they could be compared with mass spectral libraries (such as NIST) to identify the volatile compounds. Examples of full-scan chromatograms are shown in Fig. 4, illustrating both the large number of volatiles extracted, and obvious visual differences between honeys. Avoiding water or NaCl meant that SPME was acting as an analytical "nose", with extracted odour concentrations similar to those above a warmed honey. Some monofloral honeys were found to contain distinctive compounds, such as pohutukawa and southern rata (both in the genus *Metrosideros*), which had high levels of dimethyl sulfide and dimethyl sulfoxide, both with low sensory thresholds, and thyme honey, with thymol.[6] Viper's bugloss honey uniquely contained *p*-benzoquinone, while beech honeydew honey had high relative levels of phenol,[6] illustrating the diversity in chemical structures present, from organosulfur compounds, to monoterpenes and those based on a benzene ring. Many

Fig. 3. Robotic x-y-z autosampler mounted on a GC-MS, used for automated SPME extraction and injection into the instrument. The SPME fibre assembly is shown during the desorption step with the fibre in the GC injector.

compounds were common to several unifloral honeys, and statistical methods such as principle component analysis (PCA), were needed to separate honeys into clusters, based on their SPME-GC-MS results (Fig. 5). SPME has also been used successfully by other laboratories for honey aroma analysis, from Spain to Brazil.[9,10]

Another field where SPME-GC-MS is useful is in wine aroma analyses.[11] Wine develops a highly complex aroma during fermentation with some compounds originating from the fruit, and some developing due to the action of yeasts.[12] In white wines fruit aromas and flavours impart important quality characteristics, with fatty acid esters (e.g. ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl decanoate) and acetates (e.g. isoamyl acetate, isobutyl acetate, phenylethyl acetate) forming during fermentation.

Methoxypyrazines originate from grape skins and stalks, and have capsicum or herbaceous aromas. They are found in higher concentration in wines from cooler regions,[12] with New Zealand Sauvignon Blancs having higher levels than those from Australia.[13] At Hill Laboratories we use SPME-GC-MS/MS to quantitatively analyse the methoxypyrazines 3-isobutyl-2- methoxypyrazine (IBMP, **4**), 3-sec-butyl-2-methoxypyrazine (SBMP, **5**) and 3-isopropyl-2-methoxypyrazine (IPMP, **6**) in wine. Tandem mass spectrometry (MS/MS) is needed to obtain clean chromatographic peaks and reach the detection limits needed, as the sensory thresholds are extremely low (1 -2 ng/L, or parts per trillion, in water).[13] MS/MS is more sensitive and selective than single quadrupole mass spectrometry, due to target ions being further fragmented in a collision cell, producing daughter ions which depend on the molecular structure of the parent. As long as the analyte is known (this is a targeted technique),

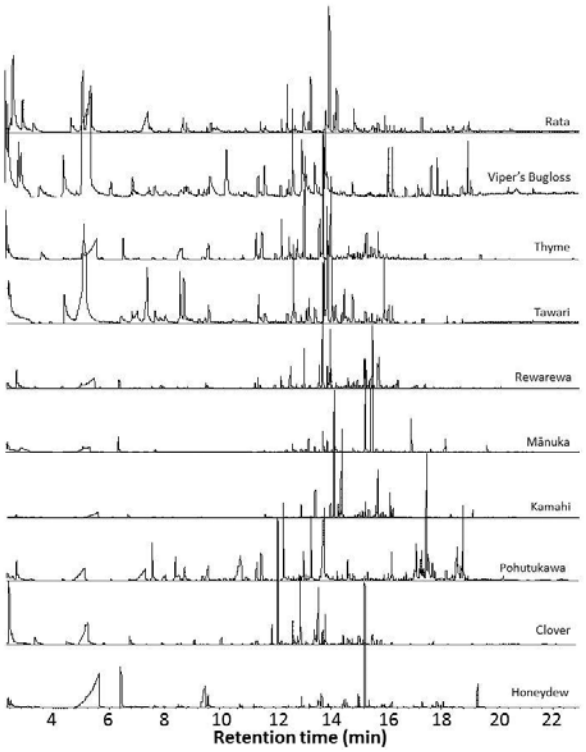
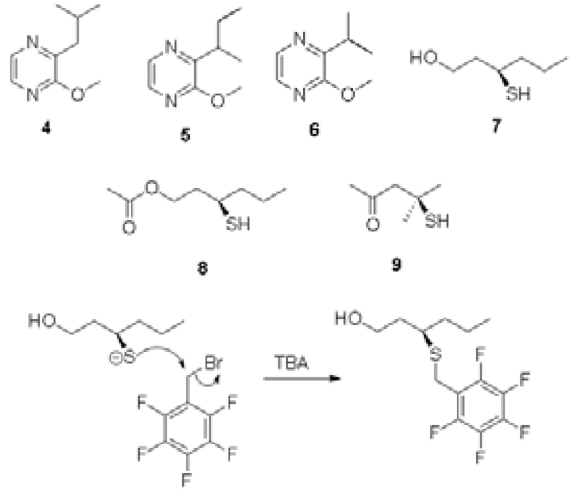


Fig. 4. Full scan GC-MS chromatograms of ten New Zealand unifloral honeys (total ion count traces shown).



Scheme 1

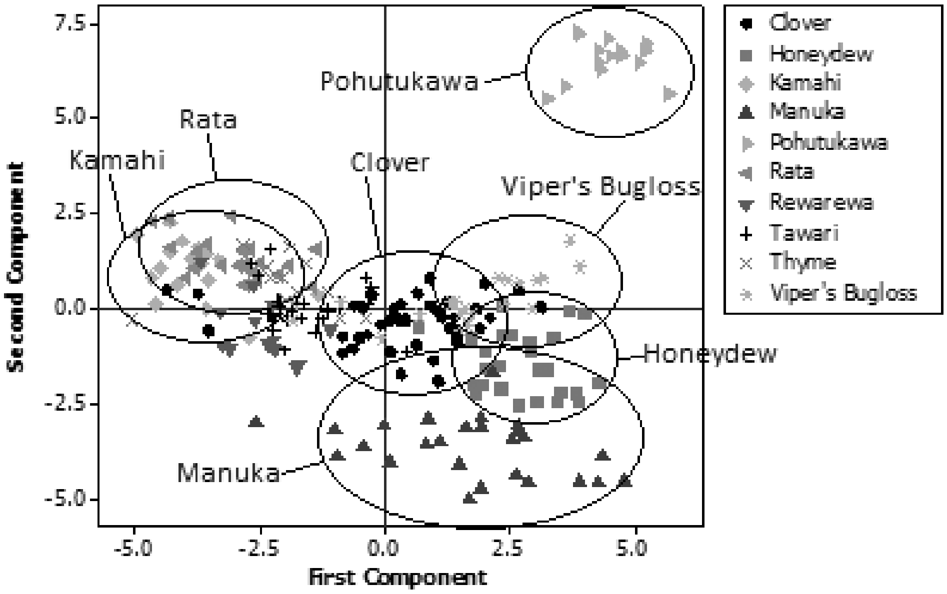


Fig. 5. Score plot showing results of PCA, for 234 New Zealand honeys, with floral origins identified by pollen counting.

MS/MS allows aroma compounds such as methoxypyrazines to "pulled" out of the complex chromatogram of wine volatiles. Optimisation of our SPME method resulted in adding NaCl to the wine, to "salt out" the analytes along with increasing the pH, to de-protonate the basic pyrazine nitrogens, and make them less water soluble.[14] A deuterated internal standard compensates for extraction variability since extraction times are used that are well short of equilibrium being reached.

Other wine compounds that can be detected by SPME-GC-MS are thiols. While most sulfur compounds cause flavour defects (e.g. ethylmercaptan, dimethyl disulfide), varietal thiols (3-mercaptohexan-1-ol (3-MH, **7**), 3-mercaptohexyl acetate (3-MHA, **8**) and 4-methyl-4-mercaptopentan-2-one (4-MMP, **9**) have passionfruit, grapefruit or boxwood aromas.[12,15] These thiols are present in relatively high levels (3-MH 100 – 20000 ng/L, 3-MHA 5 – 2500 ng/L) in Marlborough Sauvignon Blancs, and help make them distinctively fruity and successful worldwide.[16] The original method used to analyse for thiols involved CH_2Cl_2 extraction of 500 mL of wine, back extraction/derivatisation using *p*-hydroxymercuribenzoate, anion exchange SPE cleanup (trapping the thiol-hydroxymercuribenzoate complex then releasing it with cysteine), and finally re-extraction into CH_2Cl_2 and concentration to 25 µL to allow GC-MS analysis with clean chromatograms and sensitivity in the parts-per-trillion range, which is the sensory thresholds for these compounds (3-MH 60 ng/L, 3-MHA 4 ng/L, 4-MMP 0.8 ng/L).[17] Use of HS-SPME can give enough pre-concentration on the fibre to detect down to these levels using modern GC-MS/MS instruments, and saves the large amount of solvent and time needed for the liquid extraction method (and the use of hazardous *p*-hydroxymercuribenzoate). As a rapid and gentle technique, SPME also avoids loss of thiols due to oxidation to form disulfides, or hydrolysis of 3-MHA to 3-MH under basic conditions as used in the *p*-hydroxymercuribenzoate method.[18] With automation, SPME has made thiol analysis possible in our commercial laboratory, and in turn contributed to studies on the effects of viticultural practices on the aroma compounds in the resulting wine,[19] and the role these compounds play in influencing wine sensory characterisitics.[20] In the latter study, the mean concentrations of 3-MH and 3-MHA in New Zealand Sauvignon Blancs were approximately four and ten times greater, respectively, than the levels found in French and Austrian wines, and these high levels of thiols were associated with perceived notes of gooseberry and boxwood.[20] Wine thiols are relatively polar (analogous to alcohols), and poorly released from wine into the headspace above it, therefore more polar SPME fibres, or one with a combination of Carboxen and divinylbenzene molecular sieves (Carboxen/divinylbenzene/PDMS) can be used to give higher extraction recoveries.[21] Other methods use on-fibre derivatisation to give more non-polar analytes, and drive the extraction equilibria in favour of the fibre. For this scheme, the fibre (divinylbenzene/PDMS) is exposed to the vapour of the derivatisation reagent (pentafluorobenzyl bromide) and an alkali (tributylamine) in a separate vial, then transferred into the headspace of a vial with the wine sample.[22] The pentafluorobenzyl derivatives (***Scheme 1***) have a higher molecular weight, which means they can be differentiated by MS from the many lower molecular weight aroma compounds in wine, giving cleaner chromatograms with fewer interferences.

Conclusions

Headspace SPME has proven to be a useful technique for analysing volatile flavour and aroma compounds in a commercial analytical chemistry laboratory. The main benefits have been the relative lack of sample preparation, compared with solvent extraction and SPE cleanup, and automation of extraction provided by x-y-z autosamplers placed on top of analytical instruments. The solventless injection of the SPME fibre into the GC inlet also reduces fouling, as only volatile compounds are extracted and then desorbed, without the non-volatile matrix typically present in solvent extracts, which is left behind in the headspace vial. The pre-concentration of aroma compounds on the SPME fibre, along with highly sensitive GC-MS/MS instruments, has meant trace level analyses are possible, down to the often very low levels that the human nose perceives, enabling studies to be carried out relating aroma chemistry to food quality characteristics and geographical origins, in foods such as wine and honey.

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Michael Philip Hartshorn FNZIC, FRSNZ, 1936 — 2017

Michael arrived in Christchurch in 1960 to take up a lectureship at Canterbury University, fresh from completing his PhD at Oxford. His research there, under the supervision of Professor Sir Ewart Jones, dealt with conformational and stereo-electronic effects on the bromination of ketones. The thesis title was "Steroid Hormone Analogues" and the research was published in a paper with Sir Ewart, entitled, "Some tricyclic analogues of steroid sex hormones". Twelve years after his arrival in Christchurch, Michael was appointed Professor, becoming Emeritus Professor on his retirement in 1997.

Michael's research was always focussed on the details of the transformation that occurs in a complex chemical reaction. His initial work at Canterbury was strongly influenced by a collaboration with David Kirk, who arrived at Canterbury shortly after Michael and came with a background in the British pharmaceutical industry, having been involved in steroid chemistry at the time of the development of the steroid contraceptive.

Michael and David together established a solid base for research into steroid chemistry at Canterbury before David left three years later for a position at Westfield College, London, where he soon became Professor. Their collaboration resulted in a book "Steroid Reaction Mechanisms", and their work reflected a long standing bias at Canterbury on organic reaction mechanisms, initially established by Professors Jack Packer and Jack Vaughan.

In the ensuing years Michael developed collaborations with more than a dozen Canterbury colleagues and was involved in the publication of more than 260 scientific papers.

Michael had a notable clarity of presentation in both his lectures and his papers. His lecture notes were detailed and complete to such an extent that they could be offered to younger colleagues as a model. His ability to present results very clearly for publication was a particular strength, and his often very detailed supervision of more than one hundred postgraduate and undergraduate students invariably resulted in them having the pleasure of seeing their own research in the current literature.

Michael met Jackie Joll, an MSc student in zoology, soon after arriving in Christchurch and they married in January 1963. At this time Michael moved from a small Warren and Mahoney-designed apartment in central Christchurch to a villa in Merivale with space for a cricket net. Michael was a keen tennis player, but this morphed into cricket with the successive arrival of their four sons. The boys evidently caught their father's and mother's ability and determination – they had little choice! Their subsequent successes in sport and in their professional careers is a tribute to Michael and Jackie's parenting and the boys' own innate abilities.

Michael organised and focussed his time on desired outcomes, always arriving at work early and leaving while there was still daylight to see his sons develop their cricket and ball skills (and presumably complete their homework). At different times he was involved with the staff club at Ilam, the Canterbury branch of the New Zealand Institute of Chemistry, high school governance, the Professorial Board and the University Council, and in the emerging teaching of biochemistry and biophysics.

Michael was elected to Fellowship of the New Zealand Institute of Chemistry and to the Royal Society of New Zealand. He was awarded the Easterfield Medal of the NZIC and the Hector Medal of the Royal Society of New Zealand. He spent sabbatical leaves at Cornell University and at the University of Lund, Sweden.

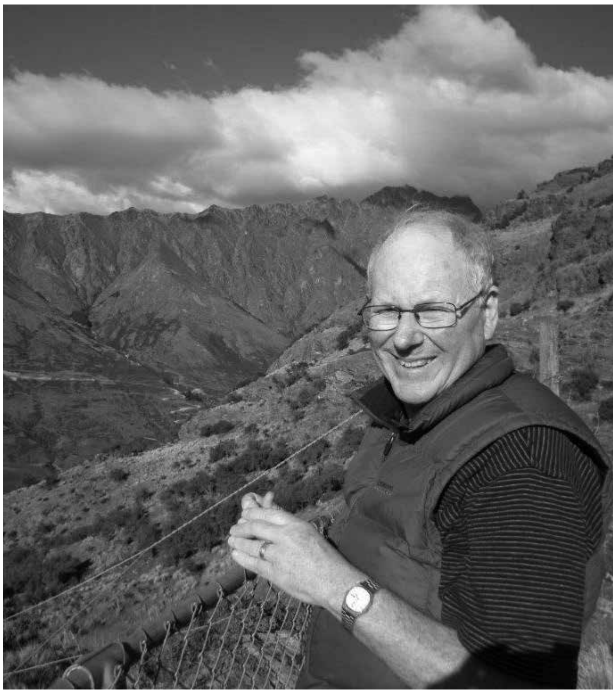
Like his own postgraduate mentor, Michael was well organised and focussed. By nature he often hid his own strong opinions amid concern for colleagues and friends. Michael cared.

James Coxon & Leon Phillips
School of Physical & Chemical Sciences
University of Canterbury

Dr Vincent Grey

Dr Vincent Grey, former Director of The Coal Research Institute and FNZIC member since the 1960s died on Thursday June 14. An obituary will appear in the October issue of *Chemistry in New Zealand*.

Kevin Russel Tate FNZIC, FRSNZ, 1943 – 2018



New Zealand and the international scientific community have been saddened by the tragic loss on 22 January 2018 of Kevin Tate.

Kevin began his scientific career teaching chemistry at Victoria University of Wellington before becoming a soil scientist at the New Zealand Soil Bureau, DSIR, in 1968. Following a number of years leading major research programmes on greenhouse gas exchange with the terrestrial biosphere, Kevin retired in 2005 but continued working at Manaaki Whenua – Landcare Research - as a Research Associate. In retirement he applied his research to the development of mitigation technologies for greenhouse gas emissions from agriculture.

Kevin was the essence of a great scientist, as well as a mentor, with a strong commitment to family, and a lifelong Christian faith. His vast intellect, and his dedication and passion for research led to major breakthroughs in our understanding of the complexities of the importance of carbon in plants and soils. He kept NZ soil science at the leading edge through his research on soil organic matter.

Throughout his career Kevin received many accolades and awards. He was elected to Fellowship of the New Zealand Institute of Chemistry in 1980. He was the recipient of all of the major awards from the New Zealand Soil Science Society (NZSSS). He gave the Norman Taylor Memorial Lecture in 1988. He was an inaugural Fellow of the NZSSS in 1995 and received the M.L. Leamy Award in 2002 for the most meritorious publication by a New Zealander on soil science between 2000 and 2002. In 2011, Kevin was awarded the NZSSS's Grange Medal, the top recognition for making an "outstanding contribution to New Zealand soil science".

Elected a Fellow of the Royal Society Te Aparangi in 1995, Kevin was active in the Academy of the Royal Society Te Aparangi, serving on many of its committees. In particular, he served many times on the Fellowship Selection Committee where he highlighted the contribution to 'science excellence' by Crown Research Institutes. In 2005, he was awarded the prestigious Marsden Medal by the New Zealand Association of Scientists for research into ecosystem processes and climate change – a testament to his outstanding professional achievement.

While Kevin was much 'medalled' with prestigious awards, at the other end of the scale he also worked to mentor and encourage the younger generation of scientists, as well as working with school children to show them the 'excitement of science', ready to engage and offer balanced opinion and advice. Between 2008 and 2011 Kevin was the Chief Judge at the Fonterra Manawatū Science & Technology Fair.

Kevin's work continued with renewed enthusiasm after his official retirement, when he was excited to have the opportunity and freedom to start new projects. This research resulted in the development of biofilters to mitigate methane produced from dairy farm waste ponds. Most recently, he worked extremely hard editing the book *Microbial biomass – a paradigm shift in terrestrial biogeochemistry* (World Scientific Publishing, 2017), which celebrates 50 years of research in soil biology. Publication of the book last year represents Kevin's pinnacle of scientific achievement.

Kevin's skills and experience allowed him to communicate the findings from his research through his impressive list of scientific publications. But, much more than that, Kevin was highly respected by science managers and policy makers, and he was able to transform New Zealand's approach to accounting for changes in carbon stored in plant and soil. This work formed the basis for government policy that earned New Zealand the reputation for its world-leading approach to the mitigation of the impacts of climate change.

The scientific community, colleagues and friends grieve the loss of Kevin, but we are encouraged that his enormous contribution has provided us with a legacy to better understand how we use our land-based resources to feed the world's growing population, protect our environment and ensure the wellbeing of all people.

Contributed by Manaaki Whenua Landcare Research,
Royal Society Te Aparangi,
Warren Tate and Heather Tate

Death from the sky: the role of chemistry and chemists in understanding biological extinctions

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Keywords: *biological extinction, K-T boundary, meteorites*

Introduction

Biologists have long debated the cause or causes of extinctions of flora and fauna which are dispersed throughout the fossil record, interrupting – but not stopping – the overall increasing diversity of life on the planet.[1] The duration of each of the five major so-called "mass" extinctions (Ordovician, 444 million years ago; late Devonian, 375; end of Permian 251; end Triassic, 200; and Cretaceous – with which this article is primarily concerned, 66 million years ago) was comparatively short, and its effect on biota quite variable:

> "Mass extinctions, great or small, are not all the same. Some were sudden, some more gradual; some affected only selected taxa [i.e., life-forms], while others devastated all inhabitants of certain environments. Some seem almost arbitrary, wiping out some species while leaving others virtually intact, eliminating the dinosaurs for example, but doing little damage to the mammals. Some coincide with large changes in the environment, but other major shifts of the earth environment seem to have had little impact. Mass extinctions also have things in common. Many affected life on land and in the sea, although rarely in equal measure. As a rule, tropical faunas appear to be more vulnerable than those of higher latitudes, because they are more specialized. Curiously also, plants have been more resistant to extinction than animals and, as a result, the evolution of plant life has been more gradual than that of animal life. Also some animal groups, such as trilobites [which existed from 521 to 251 million years ago] and cephalopods [which existed from 500 to 65 million years ago], have been much more prone to crises than others."[2]

Most of the explanations of extinctions made by geologists and paleontologists were in terms of comparatively slow evolutionary changes to life-forms, coupled with changes in the distribution of continents which, in turn, triggered volcanism and/or disrupted climate. In essence, geologists continued to apply the uniformitarian thinking (epitomised by the idea that "the present is the key to the past",[3] which has its origins with Charles Lyell and the Scottish Enlightenment) that has been a central tenet of their science for several centuries.

Against this background, the suggestion by Alvarez *et al.*[4] of an asteroid-induced life-snuffing event from the sky that killed the dinosaurs at the end of the Cretaceous (about 66 million years ago) was bound to be controversial. The idea was certainly novel, and although one of the co-authors – Walter Alvarez (Luis' son) – was a geologist, the other two co-authors were chemists, and the lead author – Luis Alvarez – was a Nobel laureate in physics.[5] Geologists with long memories, recalling the role that geophysics (and later, geochemistry) played in the plate tectonics 'revolution',[6] must surely have wondered whether history was poised to repeat itself and that progress in another long-standing area of contention would be achieved through the ideas of scholars outside their discipline.

Fig. 1. *Left:* Woodside Creek in Marlborough was the first site at which iridium and other platinum group elements anomalies at the K-T boundary in New Zealand were recognised; the site has been extensively sampled. Most of the drill holes were made by Canadian geologists in 1977 in order to obtain samples for chemical analysis. [Photo: Chris Hollis GNS Science] *Right:* Professor R.R. Brooks [Photo: Massey University]

This paper considers the chemical evidence for an extra-terrestrial cause or contribution to terrestrial extinctions, and uses citation analysis as a means of assessing the extent to which geologists have been converted to that view.

Chemistry and biological extinctions

Central to the Alvarez *et al.* hypothesis was the recognition of high amounts of iridium (which is rare on earth but not in meteorites; see Table 1) in sediments at the boundary between the Cretaceous and Tertiary/Paleogene periods, 65 million years ago (often referred to as the K-T boundary) at a small number of sites around the world. It did not take long for those sites to include localities in New Zealand - Woodside Creek, in Marlborough, being the first K-T boundary site in New Zealand at which an iridium anomaly was identified (Fig. 1).[7] This was followed within a couple of years by other localities nearby.[8]

A leader in this research was Professor Robert Brooks of Massey University, who "had collected one of the best meteorite collections in New Zealand, and with his research students and colleagues, produced a great deal of analytical information about them".[9] In fact, only nine meteorites have been found in New Zealand, with only two observed during their fall (Table 2).[10]

Table 1. New Zealand meteorites*

Year	Name	Location	Mass (kg)	Chemistry	
				Descriptive	***Class****
1863	Wairarapa Valley	Near Wellington	6.0	Chondrite, with high siderophile content and metamorphosed	H6
1879	Makarewa	Southland	2.3	A low-iron chondrite, metamorphosed	L6
1908	Mokoia†	Taranaki	4.5	Carbonaceous chondrite with Mg/Si ratio close to that of the sun (Finder: W.Syme)	CV3
1915	Waingaromia‡	Near Tolaga Bay	9.2	Principally Fe-Ni metal, which crystallised from a melt	Iron III AB
1925	Morven	Canterbury	7.1	Chondrite with sub-solar Mg/Si but high-iron content and metamorphosed	H4/5
1952	View Hill	Canterbury	33.6	Principally Fe-Ni metal, which crystallised from a melt	Iron III AB
1960	Dunedin§		5.1	Chondrite with low metal and low iron contents	LL3
1976	Dunganville¶	Near Greymouth	54.0	Principally Fe-Ni metal, which crystallised from a melt	Iron III AB
1976	Kimbolton‡	Manawatu	7.5	Chondrite with high iron content	H4
2004	Ellerslie†,**	In Auckland	1.3	Chondrite (Finders: B & P Archer)	L5

*From the *Meteoritical Bulletin* Database (https://www.lpi.usra.edu/meteor/metbull.php)except for Ellerslie; further details of the chemical classes are also given on this website. 'Siderophiles' are meteorites containing abundant iron and nickel as metals. Chondrites are 'stony' (i.e., contain silicate minerals rather than metals) meteorites which could be considered small asteroids; they account for about 86% of meteorites found on Earth.

† This meteorite is one of only two in New Zealand whose fall was observed (see text).

‡ Found during farming activities.

§ Small fragment of a meteorite found in geological museum of University of Otago; labelled 'Morven', but is said to be chemically distinct from the Morven meteorite in Canterbury.

¶ Found in a creek bed while prospecting for gold.

** A meteorite with the same name is also recorded in Australia.

Table 2. Distribution of selected elements below, at and above the K-T boundary in Marlborough, NZ

Element*	Chondritic meteorite†	Cretaceous (K)	At K-T boundary				Tertiary (T)	
		Below K-T boundary at Woodside Creek‡	*Woodside Creek (mean)‡*		*Flaxbourne River (average of values 0-1 cm either side of boundary)†*		*Above K-T boundary at Woodside Creek‡*	
	CH	CK	CB1	CB1/CK¶	CB2	CB2/CK¶	CT	CT/CK§
Au	0.16**	<1	42	42.00	-	-	<1	1
Sb	0.162	0.2††	-	-	4.0	20.00	0.2††	1
As	1.93	81	48	0.59	20	0.25	25	0.31
Cu	124	28	162	5.79	163	5.82	23	0.82
Zn	312	171	612	3.58	530	3.10	154	0.90
Ir	481	<1	70	70.00	14	14.00	<1	1
Co	502	26	125	4.81	210	8.08	18	0.69
Cr	2,640	19	203	10.68	91	4.79	19	1
Ni	11,000	39	275	7.05	175	4.49	32	0.82
Fe	19.0	1.38	4.05	2.93	1.64	1.19	0.89	0.64

*Concentrations of elements (*CE*) in μg/g except for Fe, which is in %

† Chondrite and Flaxbourne River compositional data from Strong *et al* 1987 (see reference 8)

‡ Woodside Creek and sediments below and above the K-T boundary compositional data (*CB1*, *CK* and *CT*, respectively) from Brooks *et al* 1984 (reference 7)

¶ This ratio is the 'enrichment' at the KT boundary relative to underlying rocks

§ The ratio of the composition of sediments above the KT-boundary (*CT*) to that below (*CK*) is expected to differ from 1.0 if there have been different processes occurring to form the older and younger rocks.

** From chondrite composition data in Jones (1968) (see reference 22)

†† From Earth's crust composition data in Mason and Moore (1982) (see reference 22)

As expected, witnessing the fall of a meteorite attracts rather more media attention than merely finding one. Of the Mokoia meteorite in 1908, the *Wanganui Herald* reported that a Mr Syme

> "… with three other men had been working on the railway near a creek [about half a mile (0.8 km) from Mokoia station, some seven miles (11.2 km) south of Hawera] when they heard a crackling noise overhead, like a volley from rifles. The next development was the sound of a piece of material falling over onto Mr C.J. Hawkins' estate into a pine plantation, about half a mile east of the station. Another piece, as far as could be observed, fell among some deep bush on a steep bank above a creek, about 200 yards from the bridge. A third piece was heard falling shortly afterwards, like a piece of rock, the explosion, which must have occurred at a great height, having distributed the pieces. The third portion fell into the creek with a splashing, hissing sound, like that produced by the immersion in water, of hot iron. The other workman, T. Ibbotson, also saw the phenomenon, and saw a flash, like a tongue of flame, and what he took to be steam, in a white film. The noise was heard distinctly by a number of people in Mokoia, who also saw the flash." [11]

The newspaper's report also noted that the curator of the Wanganui Museum (Mr Marriner) had collected two fragments – one weighing 4.5 pounds (2.0 kg), the other weighing 3.5 pounds (1.6 kg) – of an estimated total weight of 12 pounds (5.4 kg) of the pieces that fell on Hawkins' farm. Marriner described them as "greyish black stones with whitish markings", advising readers that they would be displayed in the Wanganui Museum the following day; he also provided a brief report to the New Zealand Institute.[12] A fragment of the meteorite is held at Puke Ariki Museum, New Plymouth (Fig. 2).[13] Interestingly, a few months previously, the same newspaper had speculated that the Earth might "blow to pieces" analogously to that proposed as the means by which the asteroids were formed by the explosion of a planet between Mars and Jupiter.[14] Clearly, the editor of the *Wanganui Herald* had not envisaged that it might be the behaviour of asteroids themselves that could lead to "questioning the soundness of the tacit assumption that the earth is everlasting", as is implied by recent media reporting on the prospect of a 79 billion kg asteroid impacting Earth in September 2135.[15]

Fig. 2. Marriner's "whitish markings" on "greyish black stones" are apparent on the 75 gram fragment of the Mokoia meteorite held at Puke Ariki in New Plymouth. (Photo: Puke Ariki)

In 2004, a meteorite fell through the roof of a house in the Auckland suburb of Ellerslie. Despite its being intriguing in showing a "tiny protruding shard of green gemstone olivine", it was reported that the meteorite would not be broken up for analysis,[16] and it is held at the Auckland Museum.[17]

Both the Mokoia and Ellerslie meteorites are chondrites, the chemical composition of which broadly resembles that of the sun,[18] and which contain iridium and other highly siderophile elements (notably Re, Os, Ru, Pt, Rh, Pd and Au).[19] Although iridium was the element in meteorites that gripped the public's interest[20] and the marketers' imagination,[21] the chemical anomalies at the K-T boundary were found in other elements as well as iridium, as is apparent in Table 2.[22]

The concentrations of some elements at the K-T boundary were higher than in the materials below and above them, and this was attributed to the contribution to the surface materials of an extraterrestrial component, widely inferred to be from an asteroid, but not excluding the possibility of a comet. The numerous attempts to determine the extraterrestrial component of the K-T boundary deposits, initially using simple mixing models, produced widely varying estimates depending on the inferred composition of the impacting body (often referred to as a 'bolide') and the composition of the materials into which it impacted. Such calculations were made even more difficult until there was general acceptance of Chicxulub as a likely site of impact.[23] Recent measurements suggest that the depth of material excavated is up to 700 m;[24] this provides a very large amount of material – considered to be dominated by limestone (dominantly calcite, $CaCO_3$), dolomite ($MgCO_3$) and marl (a mixture of clay, dolomite and calcite)[25] – available to be shattered by the impact and then dispersed around the globe as 'dust'. However, samples from drilling to depths of about 1000m in the region of the crater revealed the heterogeneous character of Cretaceous rocks near Chicxulub, which suggested a complex mixture of Laurentian and Gondwanan crustal materials,[26] implying that simple mixing models of meteoritic and terrestrial materials may be inadequate to fully determine the extraterrestrial component.

The material at the K-T boundary was considered likely to be augmented by the contribution of smoke and debris from fires triggered by the impact. As far away as Marlborough is from Chicxulub, 0.1-0.2 ppm of the fullerene C_{60}[27] was found in the soot at the two K-T boundary sites in Marlborough,[28] later extended to nine sites worldwide.[29] The analogy of the atmospheric effects from impact to those from erupting volcanoes was not long in being recognised. Dust from significant volcanic eruptions has long been known to interfere with the planet's weather and climate. The classic example is the eruption of Tambora in 1815,[30] which gave Europe its "year without a summer",[31] during which the orange colour of the European skies (which was allegedly caused by the discharge of sulfate aerosols during the eruption) is said to have influenced paintings by the artist J.M.W. Turner.[32] The gases emitted during volcanic eruptions include sulfur dioxide and nitrogen oxides, which can be oxidised to sulfurous/sulfuric acid, and nitrous/nitic acids respectively (Table 3).[33] These acids are components of 'acid rain', the effect of which on forest ecosystems can be severe,[34] especially when the atmosphere contains the larger amounts of sulfur dioxide that are derived from the burning of coal as opposed to being emitted from volcanoes.

Wood contains significantly less sulfur than coal,[35] so the chemical effects on the atmosphere of impact-initiated wildfires may be expected to be less than from that deduced from scenarios involving industrial pollution.

Also during the "year without a summer", the temperature fell significantly – but variably: western and central Europe were persistently cold, with temperatures about 2-4°C below average; while in eastern Europe, western Russia and parts of Scandinavia temperatures were higher than average.[36]The eruption of Pinatubo in the Philippines in 1991 had a similar short-term cooling effect of about 0.5°C.[37] More chilling – both literally and figuratively, however, was the analogy to the atmosphere in the aftermath of a nuclear war. In this so-called 'nuclear winter' a plunge of temperature to -15°C to -25°C was suggested.[38] Such low temperatures would surely suppress photosynthesis and potentially disrupt food chains – albeit unevenly – across the planet's biota. However, the effects of a single war or a single impact might only last a year or so, and might not be sufficient to cause a large-scale extinction event. An obvious solution is to suggest more than one impact at the K-T boundary, perhaps from a shower of comets, an idea suggested in 2003,[39] but which has recently been reactivated.[40] Moreover, and perhaps inevitably, as the impact hypothesis gains ground (see next section), the suggestion has been made that impacts are just a normal geological occurrence.[41]

Chemists and biological extinctions

The Geological Society of America responded to the challenge posed by the 1980 paper by Alvarez *et al.* by organising a 'productive multidisciplinary conference' on the 'geological implications of large asteroids and comets on the Earth' in 1982.[42] Unsurprisingly, chemistry and physics dominated the 48 papers selected for inclusion in a publication resulting from the conference: chemistry because of the initial focus on anomalous concentrations of iridium and other siderophile elements; and physics, because of the opportunity to discuss the physics of impact of meteorites and comets. Biologists were also well represented, as might have been expected in order to defend the use of biogeography in the explanation of faunal and floral extinctions, but few papers were included on 'traditional' geology. In the decades since, three more volumes of 'Special Papers' were published: In 1996, comprising 39 papers;[43] 2002, comprising 56 papers;[44] and 2014, comprising 24 papers,[45] distributed by prominent discipline in Fig. 3.

The distribution of papers by discipline in these volumes suggest that over time geologists and biologists have 'reclaimed' biological extinctions, in part by incorporating

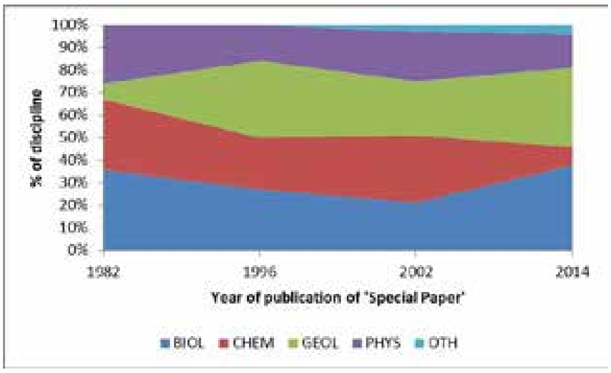

Fig. 3. Variation of discipline emphasis in the Geological Society of America Special Papers. *Legend:* **BIOL**, Biology (including paleontology and faunal systematics); **CHEM**, Chemistry (including atmospheric and isotopic chemistry); **GEOL** (geology, other disciplines may be included, but are subordinate); **PHYS**, physics (including astronomy); **OTH**, Other (e.g., historian, media analyst).

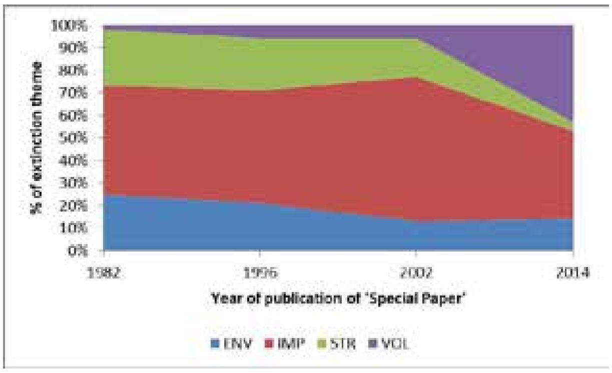

Fig. 4. Variation of emphasis on causes of extinction in the Geological Society of America Special Papers. *Legend:* **ENV**, Gradual environmental changes; **IMP**, Extraterrestrial impact (generally meteorite or comet); **STR**, paper emphasises stratigraphic and time relationships, but not definitive about cause; **VOL**, Volcanic trigger of short-term environmental change

Table 3. Chemical reactions during the formation of acid rain*

Acid reactions involving O_3	Acid reactions involving sulfur	Acid reactions involving nitrogen
$O_3 \rightarrow O_2 + O$	S (from coal etc.) + $O_2 \rightarrow SO_2$	$N_2 + O_2 \rightarrow 2NO$
$O + H_2O \rightarrow OH^{\cdot}$ (hydroxyl radical)	$2SO_2 + O_2 \rightarrow 2SO_3^{2-}$	$2NO + O_2 \rightarrow 2NO_2$
$OH^{\cdot} + SO_2 \rightarrow HSO_3$	$SO_3^{2-} + H_2O \rightarrow H_2SO_4$	$4NO_2 + O_2 = 2H_2O \rightarrow 4HNO_3$
$HSO_3 + OH. \rightarrow H_2SO_4$		$O_2 + NO_2 \rightarrow NO_3 + O_2$
$OH. + NO_2 \rightarrow HNO_3$	$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow H^+ + HSO_3^-$	$NO_3 + NO_2 \rightarrow N_2O_5$
$HSO_3 + O_2 \rightarrow SO_3^{2-} + HO^{\cdot}_2$ (peroxy radical)	$HSO_3^- + H_2O \rightarrow SO_4^{2-} + H^+ + O_2$	$N_2O_5 + H_2O \rightarrow 2HNO_3$

*From Singh and Agrawal 2008 (reference 33) the aspects of impacts that chemists brought to the topic (in particular, the recognition of iridium anomalies at the K-T boundary, the identification of spherules and their chemical composition in the boundary deposits, noting the presence and potential significance of fullerenes at the K-T boundary, etc.). Accordingly, the number of papers that emphasise chemistry and physics has declined. It is noteworthy that in the last two volumes the editors chose to include a very small number of papers that focused on non-scientific aspects of extinction, notably aspects of human history and mythology related to impacts and the response of the media (OTH in Fig. 3).

Although the emphasis in the 1982 compilation of conference papers was on the possibility of an extraterrestrial cause of the Cretaceous-Tertiary (K-T) extinction, contrary views were also included. Fig. 4 shows that this diversity of views was maintained in the 1996 and 2002 compilations, although an impact being less directly associated with biological extinction retained some support. As examples, environmental causes of extinction could be triggered by an impact;[46] or an impact might be sufficiently large to trigger volcanic eruptions which in turn disrupts climate which stresses the environment and causes extinction.[47] In the 2014 compilation of conference papers there are relatively few papers that emphasise stratigraphic relationships (suggesting that the editors preferred contributors to have a view rather than being 'fence-sitters'). However, there are a number of papers that maintain that volcanism and its associated short-term climatic effects is a cause of biological extinctions.[48] If real – and not simply reflecting the selection bias of the editors of the Special Papers – the trend of Fig. 4 seems destined to pit volcanism against impact as the preferred cause of extinctions.

Citation analysis

Most papers that scientists publish have a relatively short shelf-life, reaching a peak in the number of times they are cited within a few years of publication and then decreasing rapidly.[49] A typical plot is shown as the inset to Fig. 5.[50] Alvarez *et al.*'s paper of 1980 is an exception: since publication the paper has been cited more than 4,500 times[51] and its annual number of citations continues to increase, although the rate of its being cited has decreased since 1990 (Fig. 5). This quantitative trend in citations is consistent with a prescient observation made in 1994:

"The mass extinction debates began slowly in 1979, but then quickened and broadened. By 1983 they had become a promising case for study… The debates have expanded to entrain a variety of formerly isolated disci-

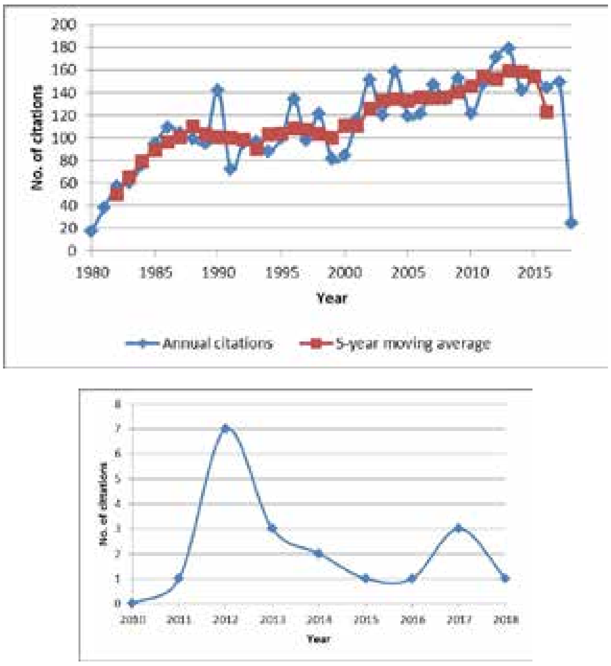

Fig. 5. Variation of citations of Alvarez *et al* (1980) (reference 4) from 1980 to 2018. As expected, citations increase initially, but have not declined after the initial peak in 1990. Indeed, there is a slow increase throughout the subsequent period. *Inset:* Typical plot of citations of a scientific article with time (reference 50).

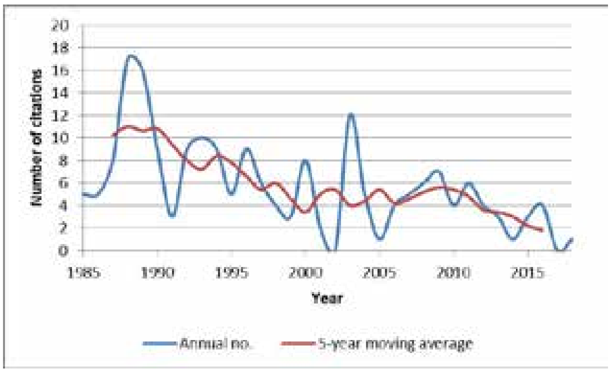

***Fig. 6.*:** Annual and 5-year moving average of number of citations for the totals for Papers #1 (reference 7), #2, #3 and #4 (all in reference 8).

Table 4. Positivity towards extraterrestrial impact as the mechanism for K-T extinctions as revealed in the references to and the citations of Brooks *et al* (reference 7)

Perception	References		Citations	
	No.	***%***	***No.***	***%***
Positive	7	54%	33	60%
Neutral	2	15%	11	20%
Negative	4	31%	11	20%
All	13	100%	55	100%

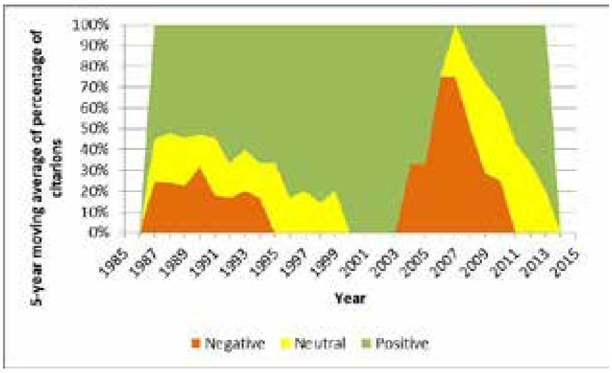

Fig. 7. Distribution of papers (on a 5-year moving average of citation percentages basis) that cite Brooks *et al* (1984) (reference 7) that are negative, neutral or positive towards the K-T extinction being attributed to an impact of an extraterrestrial bolide. Until the early 2000s, there is a relative increase in positivity; the later 'blip' of negativity may be attributed to papers by Russian and Chinese scientists who have belatedly entered this field of research.

plines, forced unprecedented interdisciplinary collaborations, rejuvenated long-quiescent fields, given rise to significant bodies of new knowledge, and fostered the appearance of provocative theories within and across several disciplines, including both corollaries and alternatives to the impact hypothesis."[52]

Even the papers relating to iridium anomalies in New Zealand[7, 8] have an unusual citation profile, with the initial peak followed by several subordinate ones (Fig. 6). A possible explanation is that these papers have been cited by other authors largely as examples to demonstrate the global extent of the distribution of extraterrestrial debris.

Probably for that reason, many of the citations of and references in the earliest paper on the New Zealand geochemical anomalies at the K-T boundary[7] are generally favourably disposed to the extinction hypothesis (Table 4), and that positivity increases with time, apart from a flurry of more recent papers by Russian and Chinese scientists (Fig. 7).

Although the representation of Fig. 6 as percentages of relatively small numbers may exaggerate this effect and/or it may be reflective cultural or institutional differences, [53] plots showing a decrease in positivity towards the present after an earlier maximum are also found for articles about the mechanism for extinction of the dinosaurs in news and research items in *Nature* and in newspapers, as is shown in Fig. 8.[54]

Conclusion — Revolution or evolution?

Considering that about six decades elapsed between the first ideas of a 'mobile' earth were proposed and the acceptance by geologists of the theory of plate tectonics, a universal acceptance of a mechanism for biological extinctions is likely to take time. It is noteworthy that it was geophysicists – on the margins of geology – who provided the first techniques and the evidence for plate tectonics. The initial reluctance by a generally conservative geological community to accept these ideas is epitomised by one of its earliest proponents expressing his views as an "essay in geopoetry".[55] And yet, within a decade of the theory's introduction most geologists supported it. Indeed, as already mentioned,[6] the rapidity of the change in thinking was widely held to meet the characteristics of a scientific revolution.[56] By comparison the development of an impact-centred paradigm for explaining biological extinctions has taken much longer: the citation curves presented here suggest a more evolutionary approach, more akin to that which has been proposed for the development of the periodic table.[57] If that is the case, it is only fitting that chemists (and physicists) should have had an active part in the evolutionary development of the impact-centred paradigm.

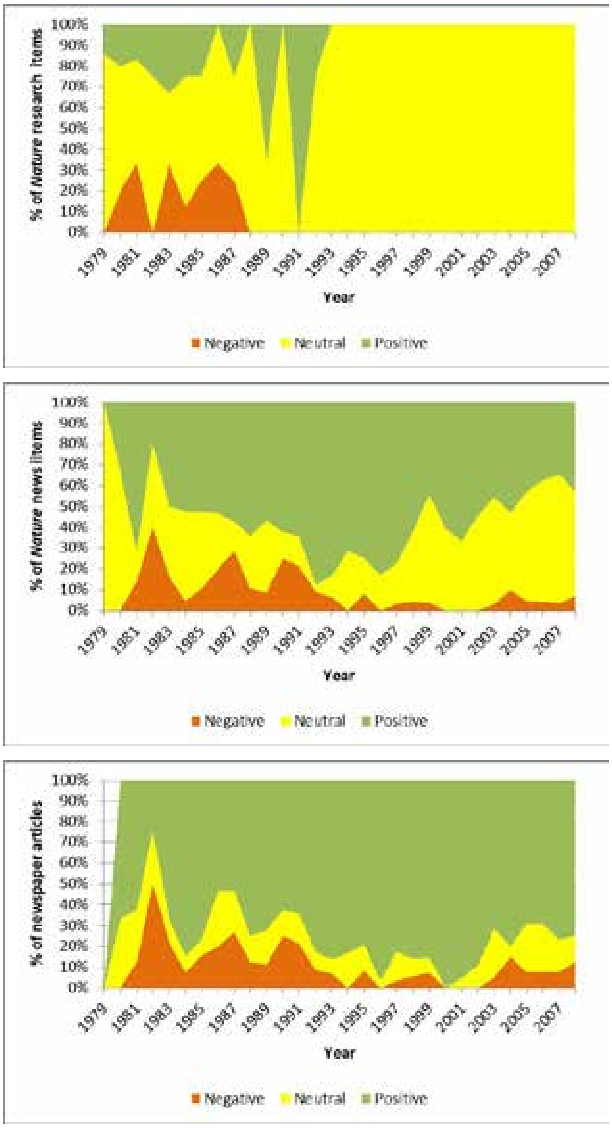

Fig. 8. Annual distribution of articles that are negative, neutral or positive towards the extinction of the dinosaurs at the K-T boundary being attributed to an impact of an extraterrestrial bolide. **Upper:** "Research" section items in *Nature*, 1979-2008. **Middle:** "News" section items in *Nature*, 1979 -2008. **Lower:** Aggregate of articles in the *New York Times* and the *Washington Post* (United States), the *Guardian* (united Kingdom), and the *Globe and Mirror* (Canada), 1979-2008. [Redrawn from data extracted from Figs. 2, 3 and 8 of reference 54.]

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20. Iridium received publicity when a 1.5-mm diameter pellet made of 10% iridium and 90% platinum which contained less than two milligrams of ricin and was 'fired' from a furled umbrella and killed Bulgarian writer Georgi Markov in London in 1976. While it was a Communist nation, Bulgaria denied it was responsible for the assassination, but admitted it in 1991 (Evans, C. *The Casebook of Forensic Detection*. Wiley: New York, 1996, 246-248.)

21. Iridium Communications, a US-based company which operates a system of communication satellites, at least has an extraterrestrial dimension to its activities which could justify the use of the element's name in its branding. Few other users of 'iridium' in their branding would seem justified in making such a claim, e.g., Fisher & Paykel's 'E522BRM (Iridium Right Door)' refrigerator.

22. In Table 2, Au-content in chondrite is from: Jones, R.S. Gold in meteorites and in the earth's crust. *Geological Survey Circular 603* **1968**, 2; Sb-content in the Earth's crust is from: Mason, B.; Moore, C.B. *Principles of Geochemistry*, 4th ed. Wiley: New York, 1982.

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28. Heymann, D.S.; Felipe Chibante, L.P.; Brooks, R.R.; Wolbach, W.S. Smalley, R.E. Fullerenes in the Cretaceous-Tertiary boundary layer. *Science 265* (5172) **1994**, 645-647.

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31. Wood. G. D'A. Tambora. *The Eruption that Changed the World*. Princeton University Press: Princeton, NJ, 2014, p. 293. A more populist treatment of the climatic effects of the Tambora eruption is: Klingaman, W.K.; Klingaman, N.P. *The Year Without Summer: 1816 and the Volcano That Darkened the World and Changed History*. St. Martin's Press: New York, 2013; an earlier book in the same genre, but relating to the 1883 eruption of Krakatoa, is: Winchester, S. *Krakatoa: The Day the World Exploded*. HarperCollins: London, 1993.

32. Brönnimann, S.; Krämer, D. *Tambora and the "Year Without a Summer" of 1816: A Perspective on Earth and Human Systems Science*. Institute of Geography: University of Bern, Switzerland, 2016, p. 10: "Though fascinated by volcanic eruptions [e.g., his painting of the eruption of Vesuvius], Turner was most likely not aware that he painted "volcanic skies" for many years [e.g., his 1838 painting of "Fighting Temeraire"] after having been inspired by colourful sunsets in 1817–1818". A more often cited example of the eruption's influence on Turner's art is his "Chichester Canal"; see: Delgado, J.E.A. 1816, The year without a summer (25 July 2016). http://geekcast.josearredondoart.net/2016/07/22/1816-the-year-without-summer/ (accessed 23 March 2018)

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The Periodic Table: revelation by quest rather than by revolution

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Abstract

The concept of major scientific advances occurring as a short-term 'revolutionary' change in thinking interspersed by long periods of so-called 'normal' science seems to be losing ground to more ecological models, which are more inimical of the twists and turns of life. From this idea it is a short step to charting science's progress against stages used in fictional storytelling, which after all is life-based. This paper explores the development of the Periodic Table in terms of the achievement of a fictional 'quest', and finds the stages of such a story are well represented. While Mendeleev or perhaps Meyer might be considered by some to be the hero of the quest, its first stage – the call – is represented by the Karlsruhe conference in 1860, with an international cast of 'companions' and 'helpers' who contributed to the Table's early development. The 'journey' may have been frustrated by lack of appropriate data and understanding of concepts, but the 'arrival' phase is clearly marked by the award of the Davy medal jointly to Mendeleev and Meyer in 1882. Throughout these stages there are lesser, although still significant contributions made by "little people" of science to the overall progress of the Table. The end of the journey is not the end of the quest: the discovery of new elements – "new ordeals" – and their incorporation into an increasing range of types and styles of Periodic Table, which – akin to the 'life-renewing goal" of the fictional quest – continue.

Introduction

Scientific revolutions

About fifty years ago Thomas Kuhn suggested that science proceeds by periods of so-called normal science, interrupted by revolutionary times where existing theories are supplanted rapidly by new ones better able to explain new observations.[1] Since then the histories of development of several fields of science have been interpreted in this way, most notably astronomy in the Age of Enlightenment and the succeeding Romantic period[1-3] and – more recently – the development of cell genetics in the 1950s[4] and the theory of plate tectonics in the 1960s.[5-7] Towards the end of Kuhn's 'revolution' book, he observes that 'revolutions' in thinking are not confined to science, but are evident in other fields of human endeavour, such as art,[1] of which an often cited example is the development of perspective in drawing.[8]

Kuhn's research started in 1954, so he would certainly have been aware of at least some of the events of what has subsequently been termed by James[9] as the 'terrible twentieth century', although Kuhn makes no explicit reference to being influenced by these events. The first edition of his book was published in 1962; the second just after the time of widespread civil unrest in the western world, including campus uprisings at universities in America and Europe and the Soviet invasion of Czechoslovakia.[10] Such *socio-political* revolutions have been described as progressing through five stages, viz., Anticipation, Dream, Frustration, Nightmare, Downfall and Destruction,[11] of which only the first three appear to be associated with scientific revolutions.

Whether *scientific* revolutions really do occur continues to be debated. Chapman's recent commentary[12] on the 'Astronomical Renaissance' – which would include the time period covered by Kuhn's Copernican revolution – observes:

> "The Astronomical Renaissance was not the offspring of heroic battles between blind traditionalists and 'enlightened' progressives, a scenario beloved by those who see intellectual development in terms of 'conflict' and revolution'. Absolutely crucially it was not the outcome of a battle between the church and science; far too many churchmen and devout laity, both Catholic and Protestant, made far too many original scientific discoveries for that ever to be the case. Whatever brought about the Astronomical and Scientific Renaissance was not a conflict; it was a *quest* – perhaps the most far-reaching quest in the history of human thought

The notion of 'quest' will be considered subsequently in this paper.

The Periodic Table

Although Scerri[13] notes that no-one of whom he is aware – including Kuhn – "has argued that the development of the periodic system did represent a scientific revolution", he is, nevertheless, forthright in his criticism of the idea:

> "The history of the periodic system appears to be the supreme counterexample to Thomas Kuhn's thesis, whereby scientific developments proceed in a sudden revolutionary fashion. The more one examines the development of the periodic system, the more one sees continuity rather than sudden breaks in understanding. Looking at the events leading up to the introduction of Mendeleev's periodic system in 1869, the concept of periodicity can be seen as evolving in distinct stages through the work of other chemists. Thus, rather than six actual discoveries of the system it may be more correct to see it as an evolution through several systems, discovered within a period of less than 10 years."

To mark the centenary of the Periodic Table, van Spronsen[14] had identified six key researchers involved in the table's development, asserting that they had not "made equal contributions to the discovery and development of the periodic system, but rather that each of them played his own special part". As an example, he notes, "It could hardly be expected that a geologist like De Chancourtois, who arrived at the periodic system several years before the other discoverers could influence its development as much as its last discoverer Mendeleev, who, moreover, taught chemistry and published a chemical textbook." In addition to the 'six' (which includes Mendeleev and Meyer), van Spronsen[14] identifies a group of precursor researchers, and a group of post-1871 researchers, the latter of which are here subdivided into two groups: those "who contributed very positively to either the form or the theoretical derivation of the periodic system". He also notes that there were studies which "…looked upon the periodic system mainly as a catalogue of elements, about which they provided only few interesting data. Many such systems have been published in the *Journal of Chemical Education*. They offer no new possibilities or are obvious variations of the existing system."

Scientists in these four groups are shown in Table 1. These are augmented in the third group by some addi-

Table 1. Precursors, discoverers and subsequent contributors to the development of the periodic table

Precursors		**Discoverers**		**Subsequent contributors**			
				Associated theory		**Form of table**	
Name[a]	**Year**	**Name [b]**	**Year**	**Name**	**Year**	**Name [c]**	**Year**
Dobereiner		De Chancourtois	1863	Cleve [d, g]	1879	Bayley [i]	1882
Gmelin	1827, 1843, 1850	Newlands	1865, 1866	Wurtz [d, h]	1881	Crookes [j]	1887
Pettenkofer	1850	Olding	1864, 1868	Wilde[c]	1878	Bassett [i]	1892
Dumas	1851	Hinrichs	1864, 1866, 1867, 1869	Rang [c]	1893	Thomsen [i]	1895
Kremers	1852, 1856			Berthelot [d, h]	1895	Stoney [j]	1902
Gladstone	1853	Meyer	1864, 1868 1870, 1872	De Bois-baudran[c]	1895	Werner [i]	1905
Cooke	1854-1855			Ramsay [d, g]	1900	Soddy [j]	1911
Lenssen	1857	Mendeleev	1869, 1870	Abegg [e, g]	1904	Harkins and Hall [j]	1916
Dumas	1857			Van der Broek [e, g]	1907	Emerson [j]	1911, 1944
Odling	1857			Nicholson [e, g]	1911	Nodder [j]	1920
Dumas	1858			Bury [e, g]	1911	Kohlweiler [j]	1920
Mercer	1858			Bohr [d, e, g]	1922	Loring [j]	1920
Carey Lea	1860			Main Smith [e, g]	1924-1925	Clark [j]	1921, 1950
				Stoner [e, g]	1924	Piutti	1925
				Janet [e, g]	1929	Von Antropoff [i]	1926
				Müller [c]	1844	Janet [j]	1928
						Janet [i]	1929
						Romanoff [i]	1834
						Romanoff [j]	1934
						Friend [j]	1834
						Zmaczynski [i]	1937
						Finke [j]	1943
						Achimov [i]	1946
						Stedman [j]	1947
						Scheele [i]	1949
						Dufour [f, j]	1999

[a] van Spronsen (1969, p. xii); dates are of significant research achievements by scientist concerned

[b] As listed in van Spronsen (1969, chapter 5), and agreed by Scerri (2007); dates are of significant research achievements by scientists concerned

[c] As in van Spronsen (1969, chapter 6); dates are of significant research achievements by scientist concerned

[d] In Scerri (2007); dates are of significant research achievements by scientist concerned

[e] In Scerri (2016); dates are of significant research achievements by scientist concerned

[f] Scerri (2007, p. 286) considers this particular three-dimensional conical representation embodies "principles of beauty and elegance"

[g] Overall positively disposed to periodic system

[h] Overall negatively disposed to periodic system

[i] Two-dimensional representations of the periodic table

[j] Selected three-dimensional representations of the periodic table; apart from Dufour's model, only those actually illustrated in van Spronsen (1960, chapter 6) are listed here

tional 'contributors' to whom Scerri[13] refers as the 'little people', who he also uses in his subsequent book[15] to illustrate his preference for an evolutionary – rather than revolutionary – view of the development of science. The aggregated numbers of publications for the precursors, discoverers and subsequent contributors to the development of the Periodic Table are shown in Fig. 1.

There is a peak in the number of publications in the late 1860s, and publications by those 'discoverers' – most of which were generally favourable to the concept – have continued into the twentieth century. As indicated in Table 1, the publications by subsequent contributors related to the periodic table tend to focus on the implications of new interpretations of atomic structure, or representations of the Periodic Table itself. With interest in the Periodic Table having been sustained for over a century, it is difficult to see the Table's development as revolutionary.

While publications are the obvious way to track the development of ideas – as Scerri does,[13] scientists then – as now – had other ways of becoming aware of others' ideas: through personal contacts, informal networks and meetings of professional societies. An early example of the former is the Lunar Society in England,[16] which has its modern analogue in the amateur and professional science societies that have proliferated globally. However, travel may not always have been so easy, as Fortey notes,[17] "Foreign travel was difficult and expensive, so that scientists in the eighteenth and nineteenth century could not just pop over from Germany to consult the Sloane collection [of plant specimens] without the help of some serious patronage." Perhaps the best example of the latter is probably the Royal Society of London, which "throughout its history has been the most admirably neutral and cosmopolitan of entities".[18]

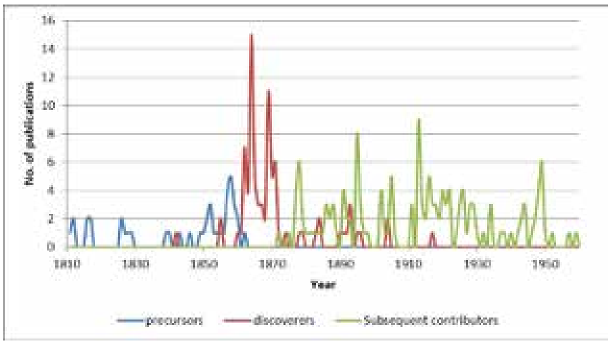


Fig. 1. Publications of precursors, discoverers and subsequent contributors to the development of the Periodic Table, compiled from van Spronsen (1969, chapters 4-6).

Thus, even if a work or idea is not explicitly cited in a paper, it may still exert influence on those who become aware of it. These were probably particularly important mechanisms for bringing the work of researchers such as Scerri's 'little people' to the attention of people such as Niels Bohr, as shown for John Nicholson and Edmund Stoner in Fig. 2.

Development of the Periodic Table as a 'quest'

Booker's observation[19] that

> "…to a far greater degree than we are consciously aware we look at the world in terms of stories all the time. They are the most natural way in which we structure our description of the world around us. We naturally see our own life as a story, as we do of others, each made up of an infinite number of episodes, large and small."

suggests that stories of science may be more readily cast as evolutionary sequences than revolutionary events, in agreement with Scerri.[15] Moreover, it may be reasonable

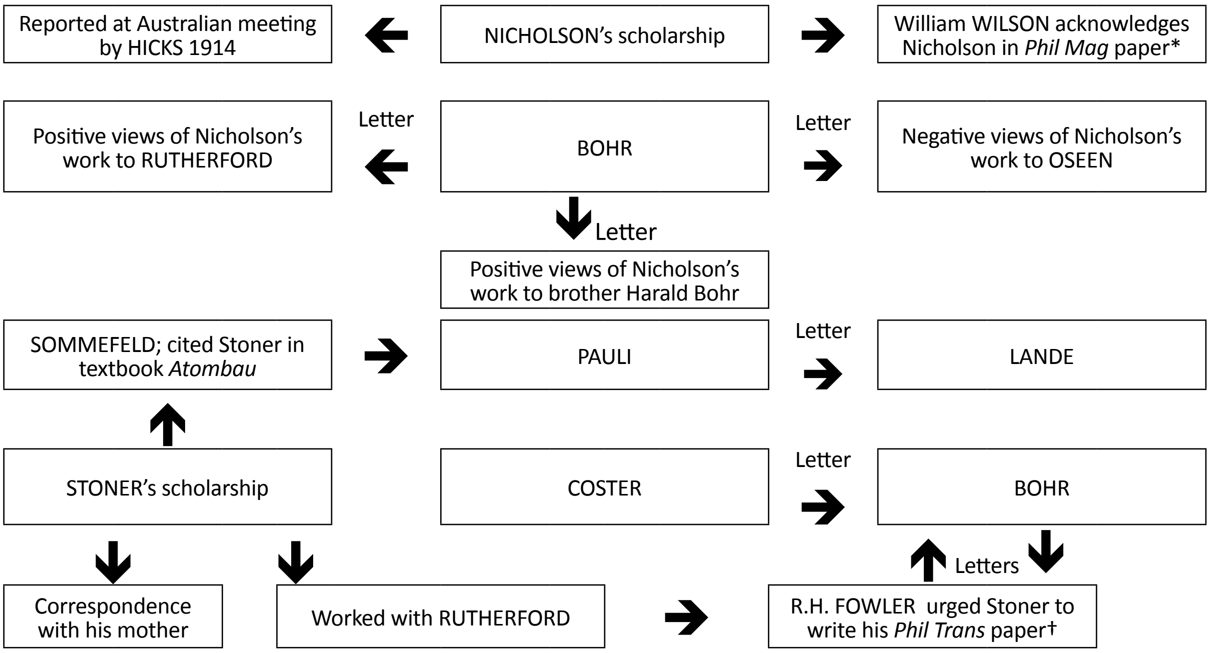


Fig. 2. Informal networks for (upper) John Nicholson, and (lower) Edmund Stoner (compiled from Scerri 2013, pp. 13-40, 117-148), respectively.

* Wilson, W. The quantum theory of radiation and line spectra. *Philosophical Magazine* **1915**, series 6, *29* (174), 795-802.

† Stoner, E.C. The distribution of electrons among atomic levels. *Philosophical Magazine* **1924**, *48*, 719-736.

to seek analogies with 'basic plots' used in fictional storytelling with actual events. One reviewer of Booker's *The Seven Basic Plots*[20] observes that Booker sees his narrative archetypes as underlying politics, both 'hard' (e.g., communism, fascism) and 'soft' (e.g., feminism, environmentalism). If that is so, then why not apply the concept to science as well?

Of the seven types, that of the 'quest' – perhaps the most common plot of all – seems the most appropriate for describing the development of the Periodic Table. The defining features of the quest are 'the call'; 'the hero's companions'; 'the journey'; 'arrival and frustration', during which the hero and companions have 'helpers'; 'the final ordeals'; and achieving 'the goal', each of which are discussed below.

'The call'

Fictional quests "begin with the reason why the hero and his companions set out on the journey in the first place";[19] typically a fearful threat means that there is an urgent need not to remain quietly at home, as in the case of Bilbo Baggins in *Lord of the Rings*[21] or Fiver in *Watership Down*.[22] The threat to chemistry may not have been of the same order as these fictional crises, but "it was apparent by the middle of the nineteenth century that something needed to be done to resolve the widespread confusion over equivalent and atomic weights",[13] and it was to that end that a conference at Karlsruhe was convened on 3-5 September 1860, perhaps the first international chemistry conference.[23] The conference was one of the factors that "hastened the sudden explosion of periodic systems published in the 1860s",[13] and can be considered to represent 'the call'.

The 'companions' and 'helpers'

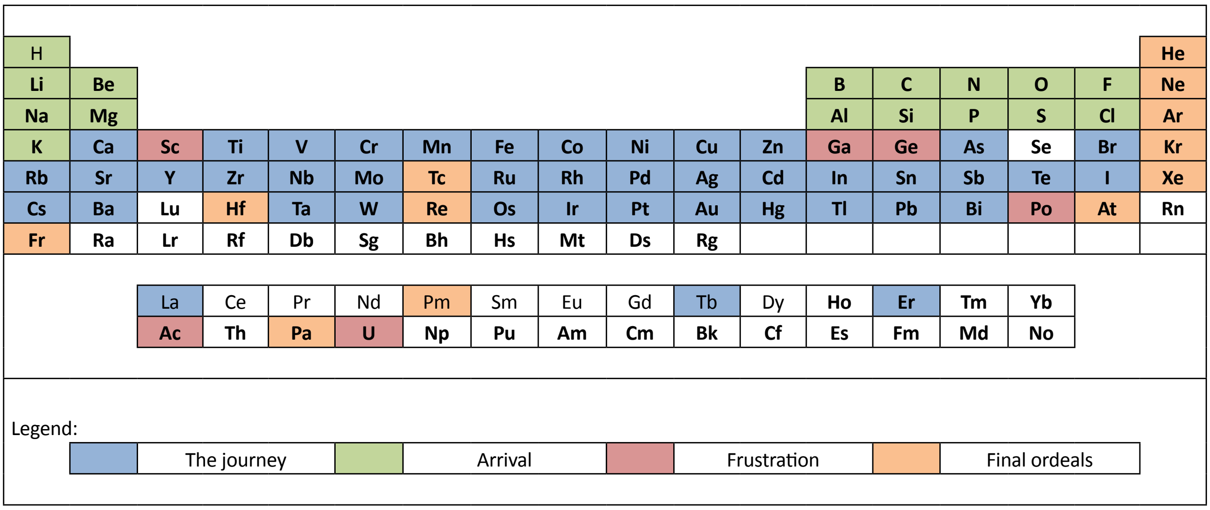
One particular feature of a quest noted by Booker is:[19]

> "…the extent to which, more than in any other kind of story, the hero is not alone in his adventures. The story does ultimately centre round the single figure of the hero. But more consistently than in any other story, we are also made aware of the presence and importance of the friends who accompany him."

As previously noted, six co-discoverers of the Periodic Table are now recognised for the Periodic Table (see Table 2), most of whom were invitees to the Karlsruhe conference. Attendance at this conference was by invitation only; Wurtz[24] records that the 127 participants came from: Belgium, 3; Germany, 57; England, 17; France, 21; Italy, 2; Mexico, 1; Austria, 7; Portugal, 1; Russia, 7; Sweden, 4; Switzerland, 6; Spain, 1. Despite Fortey's comment,[17] many populist histories of science observe that from the Enlightenment to the Romantic period, there was frequent contact between scientists of differing nationalities, with comparatively little impediment to travel or communication between countries. A particularly

Table 2. Co-discoverers of the Periodic Table

Co-discoverer	**Alexandre Emile Beguyer De Chancourtois**	**John Newlands**	**William Odling**	**Gustavus Hinrichs**	**Julius Lothar Meyer**	**Dimitri Ivanovich Mendeleev**
Nationality	France	England	England	Denmark	Germany	Russia
Profession	Geologist	Industrial chemist	Academic chemist	Academic chemist and linguist	Academic chemist	Academic chemist
Place of practice	Paris, France	London, England	London, England	Iowa, United States	Breslau, Germany	St Petersburg, Russia
Attendance at 1860 Karlsruhe conference	No	No	Yes	No	Yes	Yes



🟩 H																	🟧 He
🟩 Li	🟩 Be											🟩 B	🟩 C	🟩 N	🟩 O	🟩 F	🟧 Ne
🟩 Na	🟩 Mg											🟩 Al	🟩 Si	🟩 P	🟩 S	🟩 Cl	🟧 Ar
🟩 K	🟦 Ca	🟥 Sc	🟦 Ti	🟦 V	🟦 Cr	🟦 Mn	🟦 Fe	🟦 Co	🟦 Ni	🟦 Cu	🟦 Zn	🟥 Ga	🟥 Ge	🟦 As	Se	🟦 Br	🟧 Kr
🟦 Rb	🟦 Sr	🟦 Y	🟦 Zr	🟦 Nb	🟦 Mo	🟧 Tc	🟦 Ru	🟦 Rh	🟦 Pd	🟦 Ag	🟦 Cd	🟦 In	🟦 Sn	🟦 Sb	🟦 Te	🟦 I	🟧 Xe
🟦 Cs	🟦 Ba	Lu	🟧 Hf	🟦 Ta	🟦 W	🟧 Re	🟦 Os	🟦 Ir	🟦 Pt	🟦 Au	🟦 Hg	🟦 Tl	🟦 Pb	🟦 Bi	🟥 Po	🟧 At	Rn
🟧 Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
		🟦 La	Ce	Pr	Nd	🟧 Pm	Sm	Eu	Gd	🟦 Tb	Dy	Ho	🟦 Er	Tm	Yb		
		🟥 Ac	Th	🟧 Pa	🟥 U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Legend:
🟦 The journey 🟩 Arrival 🟥 Frustration 🟧 Final ordeals

Fig. 3. Allocation of elements of the periodic table to stages of the quest. The form of the table is that considered by Scerri to be in the middle of a continuum of versions.

compelling example is the records of scholars from diverse places visiting Tycho Brahe's Uraniborg observatory which are compiled in Christianson.[25]

The relationship between the attendees at the Karlsrhue conference is probably better described as international 'professional colleagues' who may read about each other's work and discuss it at conferences (such as the Karlsrhue conference of 1860). This stance is justified by an examination of the most significant articles by the co-discoverers cited in Scerri,[13] which shows no evidence of co-discoverers citing the work of other co-discoverers, other than one citation by Meyer[26] of Mendeleev. If a single 'hero' needs to be nominated, the choice would be between Meyer and Mendeleev. Regardless of the competing priority claims of these two candidates, history has tended to favour Mendeleev as the "undisputed champion of the periodic system".[13]

Quests generally have 'helpers' who give the heroes "positive assistance, ranging from periods of respite to crucial guidance… their role is not so much to intervene in the action as to act as guides and advisors".[19] All of the scholars who worked on the properties of elements, and the determination of the atomic weights or their proxies (e.g., specific heats and spectral evidence) which would end up being of great significance in the compilation of the table (i.e., during 'the journey') can be considered 'helpers."

'The journey'

In their descriptions of the 'journey' to the quest both Scerri and van Spronsen before him describe comprehensively the work done by the co-discoverers in understanding the behaviour of chemical elements and atomic structure, which enabled Meyer and particularly Mendeleev to see the 'bigger picture', and the details will not be traversed again here. The journey could be said to conclude with the publication of Mendeleev's 'system'.

Quests differ from other plots, where the end of the journey comes close to the end of the story: in the quest, the subsequent stages of 'frustration' and 'final ordeals' are sufficiently long that, in essence, the journey is in the middle of the story.[19] This is certainly the case with the Periodic Table. Mendeleev's role went beyond the development of the 'system'; as Scerri[13] notes:

"Not only was Mendeleev's system more complete than the others, but he worked much harder and longer for its acceptance. He also went much further than the other codiscoverers in publicly demonstrating the validity of his system by using it to predict the existence of a number of hitherto unknown elements."

The journey phase of quests in fiction usually include interactions with 'monsters', 'temptations', 'deadly opposites' or a 'journey to the underworld'.[19] Although there may well have been temptation to ignore findings that did not 'fit', credible analogies to others of these aspects are rather more difficult to find in the Periodic Table story. In particular, there was not an 'opposite' approach to the Periodic Table with which the co-discoverers had to contend.

'Arrival and frustration'

Scerri[13] provides evidence that only about half of Mendeleev's predictions were successful (Table 3), observing that this "seems to belie the notion that what counted most in the acceptance of the periodic system were Mendeleev's successful predictions". Possibly so, but the fact that some ultimately correct predictions were a long time being realised may have helped to cement his role in the story.

'Arrival' in this case can be fairly considered as the award of the Royal Society of London's Davy Medal jointly to Meyer and Mendeleev in 1882, announced by Spottiswode.[27]

In any event, success and failures of predictions certainly confirms that the period from 1870 until into the 20th century – including some of the early contributions made

Table 3. Mendeleev's prediction skills*

Mendeleev's successful predictions†			Mendeleev's unsuccessful predictions		
Mendeleev's element	***Predicted atomic weight***	***Fate***	***Mendeleev's element***	***Predicted atomic weight***	***Fate***
Beryllium	14.6	Beryllium	Newtonium	0.17	Not found
Eka-boron	44	Scandium	Coronium	0.4	Not found
Eka-aluminium	68	Gallium	Un-named	2	Not found
Eka-silicon	72	Germanium	Un-named	8	Not found
Un-named	75	Astatine	Un-named	20	Not found
Eka-manganese	100	Technetium	Un-named	36	Not found
Tri-manganese	190	Rhenium	Eka-cerium	54	Not found
Dvi-tellurium	212	Polonium	Eka-molybdenum	140	Not found
Dvi-caesium	220	Francium	Eka- niobium	146	Not found
Un-named		Actinium	Eka-cadmium	155	Not found
Eka-tantalum	235	Protactinium	Eka- iodine	170	Not found
Uranium	240	Uranium	Eka-xenon	137-180	Not found
			Eka-caesium	175	Not found

* Compiled from Scerri, 2007, table 5.5 and its associated text in Chapter 5

† Mendeleev was unable to resolve the relative positions of Iodine and tellurium

to the story by Scerri's[15] 'little people' can be recognised as a time of ordeal or frustration in the quest.

'The final ordeals' and 'The life renewing goal'

The award of the Davy medal was by no means the end of the Periodic Table story. Its predictions continued to be reconsidered in response to greater understanding of the nature of the atom (e.g., through the work of Niels Bohr) and as the 20th century progressed. In addition, the table had to be extended to accommodate the discovery of the inert gases[13] and other new elements, including protactinium, hafnium, rhenium, technetium, francium, astatine and promethium.[28] As before, these scholars can be considered 'helpers' in the quest.

The final stage of the quest is that the "life-transforming treasure [is] finally won: with an assurance of renewed life stretching into the future".[19] What better description can there be of the continued use made of the Periodic Table in teaching and research, and the endless iterations of its representation (see Table 1).

Conclusion

This paper shows that the development of the Periodic Table accords in large measure with the criteria that defines a 'quest', the most common type of story. The assignment of elements to their place in the Table occurs across all stages of the story, as is apparent in Fig. 3. In this diagram the elements identified on Mendeleev's periodic system[29] are considered relevant to 'the journey' (unless they can also be ascribed to the categories that follow as well, in which case they take precedence). Elements that featured in the citation for the Davy medal are associated with 'arrival', whereas those that are mentioned as the subject of predictions and reconsiderations are associated with 'frustrations' (Table 3). Finally, efforts that are more linked with subsequent discoveries of elements are considered associated with the 'final ordeals' stage.[28] The overall process has taken at least a century: this is no revolution, but a continual revelation.

Acknowledgement

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Book review: *Mendeleev to Oganesson. A multidisciplinary Perspective on the Periodic Table*

Scerri, E.; Restrepo, G. (eds.). *Mendeleev to Oganesson. A Multidisciplinary Perspective on the Periodic Table*. Oxford University Press: Oxford, 2018, 314 pp.

A series of essays related to the periodic table would be expected to feature 'Dimitri Ivanovich Mendeleev', and the index in Eric Scerri's and Guillermo Rostrepo's edited collection of essays includes 40 entries. Curiously, however, the name 'Oganesson' – so prominent in the title of this book – is not mentioned in the index. Perhaps it's just too modern: oganesson is element 118, named after Yuri Oganesson, notable for his part in the discovery of 'superheavy' elements,[1] and the discovery not officially announced until 2016,[2] well after the 2012 Third International Conference on the Periodic Table,[3] papers presented at which formed the inspiration for this book.

The book is without doubt multidisciplinary: the book's fifteen essays certainly "show aspects of the periodic system from different perspectives and disciplines, and include new translations of some documents by Mendeleev", each of which the Introduction describes in a few sentences (pp. 4-6[4]). At this point the reader may wonder whether there is something to come in the book that will link all the essays in this disparate collection of "interdisciplinary as well as multidisciplinary studies on the central icon of chemistry". However, by the end of p. 6, it becomes obvious that the editors have no intention of doing this, since they observe:

"There is still widespread disagreement as to whether it [the periodic table] should be regarded as a representation, a model, a law, and so on. Perhaps one should avoid even trying to categorize it according to the usual criteria that are imposed by philosophers of science; perhaps one should embrace the uniqueness of the periodic system or simply regard it as the paradigm or framework of modern chemistry."

The disciplines represented by these essays are shown in Table 1, from which it is apparent that the emphasis on mathematics and physics in the early essays decreases as the book progresses. Overall, there is a good balance between quantitative and qualitative approaches and between science-based analysis and social-sciences discourse.

The title of the first essay indicates an emphasis on the 'superheavy' and this is where the element oganessen and its discoverers might be expected to have been mentioned. However, the date of the latest reference in this paper is 2013, predating the IUPAC announcement.[2] Given that this element features in the title and that the essay already includes an epilogue (p. 41), this omission could have been rectified even at proof stage. The mathematical arguments of the second essay lead to a succinctly expressed conclusion that by "investigating the structural development of the nucleus … the periodicity of the electronic structure is the natural outcome of the nuclear lattice geometry", which is claimed to offer a "credible explanation for the identical symmetry of the nucleus and the electronic structure, for the Pauli Exclusion Principle, and for the Aufbau principle" (p. 60), all of which receive attention in later essays.

After the first two mathematically focused essays, the third essay – on representations of the periodic table – is already a welcome change. This essay makes a convincing case for the revival of Janet's "Left Step Periodic Table" (p. 69), or perhaps one of Eric Scerri's variants thereof (p. 76), but the really interesting observation of this chapter is that innovative shapes and designs of the table tend to have been developed by 'outsiders' (e.g., graphic designer Edgar Longman's mural at the 1951 Science Exhibition at the Festival of Britain (p. 74, Fig. 3.2[5])), and have been ignored by chemists. Essay-author Stewart describes on p. 76 the variant of the Janet table developed by Valery Tsimmerman as a "tetrahedron etched into a block of glass, the Adomah Periodic Cube – a beautiful and fascinating object. Its visual impact, if seen by enough chemists, might be what is needed for them to finally accept Janet's tables and his spirals and lemniscates[6] as the best representations of the periodic system" (Fig.1).[7] This is but one example of many that could be cited in the book where images in colour would have contributed significantly to the readability and appearance of the book. Essay-author Stewart concludes by speculating that professional chemists retain the medium-long form of the periodic table because they are "conservative and cautious", whereas for amateur chemists "a new idea on the periodic system can inflame their passions", tantamount to an invitation for further debate!

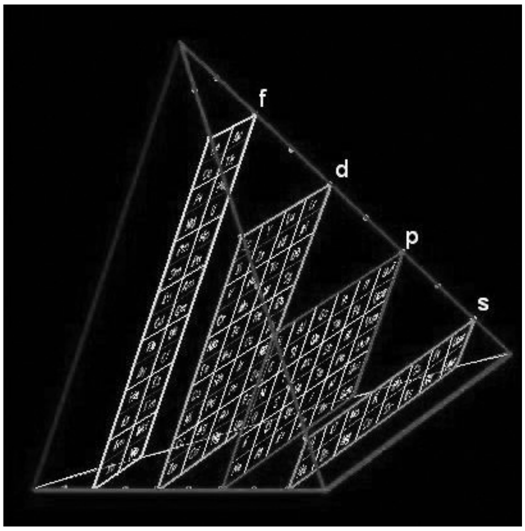


Fig. 1. Tsimmerman's periodic table in a tetrahedron, an example of the three dimensional representations made more feasible to develop with the advent of digital technology.

The fourth essay uses a 'similarity' perspective to explore whether physical or chemical properties of 'basic sub-

Table 1. Some characteristics of essays in *Mendeleev to Oganesson. A Multidisciplinary Perspective on the Periodic Table*

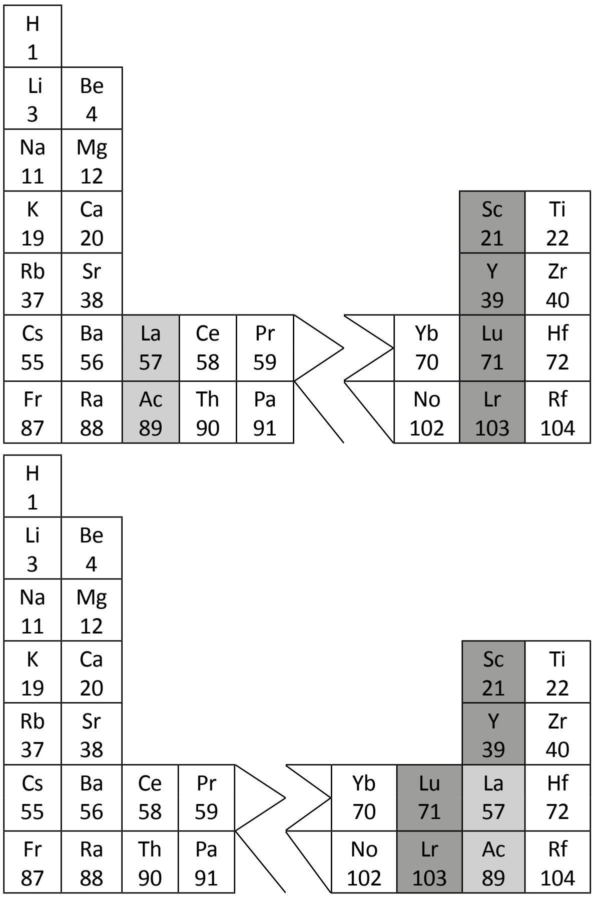
Position of essay in book, title, author, and length (as pages)				References	**Disciplines represented**						
	Title	Authors	Page range (no. of pages)	Age range Modernity*	***Science†***				***Social science‡***		
					M	Ps	C	O	S	H	Py
1	Heavy, superheavy… quo vadis?	P.J. Karol	8-42 (35)	1878-2013 1976		●	●				
2	Nuclear lattice model and the electronic configuration of the chemical elements	J. Garai	43-65 (23)	1829-2013 1969		●	○			○	
3	Amateurs and professionals in chemistry: The case of the periodic system	P.J. Stewart	66-79 (14)	1863-2008 1952			○		●	○	
4	The periodic system: A mathematical approach	G. Restrepo	80-103 (24)	1869-2013 1998			●			○	
5	The "chemical mechanics" of the Periodic Table	A. Ceulemans and P. Thyssen	104-121 (18)	1873-2017 1986		●	○			○	
6	The grand periodic function	J.C.A. Boeyens	122-139 (18)	1920-2013 1994			○				
7	What elements belong in Group 3 of the Periodic Table?	E.R. Scerri and W. Parsons	140-151 (12)	1937-2016 1996			●				
8	The Periodic Table retrieved from density functional theory based concepts	P. Geerlings	152-176 (25)	1934-2014 1994		●	○				
9	Resemioticization of periodicity: A social semiotic perspective	Y Liu	177-194 (18)	1990-2014 2003			○		●	○	
10	Organizing the transition metals	G. Rayner-Canham	195-205 (11)	1915-2014 2001			●				
11	The earth scientist's periodic table of the elements and their ions: A new Periodic Table founded on non-traditional concepts	L.B. Railsback	206-218 (13)	1922-2013 1988			●	●	●		
12	The origin of Mendeleev's discovery of the periodic system	M. Kaji	219-244 (26)	1854-2015 1938			●			●	
13	Richard Abegg and the Periodic Table	W.B. Jensen	245-265 (21)	1883-2010 1946			●		○	●	
14	The chemist as philosopher: D.I. Mendeleev's "The Unit" and "Worldview"	M.D. Gordin	266-278 (13)	1877-2012 1962			○			●	●
15	The philosophical importance of the Periodic Table	M. Weinstein	279-304 (26)	1948-2016 1985			●				●
Weighted sum of papers representing disciplines (Σw), as the sum of the number of ● and (number of ○/2)					4.5	4.0	11.5	1.0	3.5	5.5	2.0
% of discipline in book (as 100 * Σw/15)					30	27	76	7	23	37	13

* Date range of publications cited and the average year of all publications cited in essay

† Science disciplines: M, Mathematics; Ps. Physics; C. Chemistry; O, Other (including earth sciences) ●, dominant; ○, subordinate

stances' or compounds define the relationships within the periodic table, confirming Mendeleev's use of "oxides, hydroxides, hydrides, and halides, whose resemblances were employed to come up with similarities on chemical elements" (pp. 91-92). This approach yields relationships between elements that may be vertically, horizontally or diagonally adjacent, confirming the known observational complexity of inter-element relationships. This contribution to the book asserts that "the results [of the analysis] are mostly invariant to the inclusion or not of *atomic number and atomic weight*, which leads us to conclude that these properties, apart from their historical importance, *are not important for the similarity structure of the periodic system*" (p. 98; italics are those of the essay-author Restrepo). The eighth essay affirms that Mendeleev 'built' his table from "experimental data on the elements and their compounds, lacking basic physics at the atomic level" (p. 153). Essay-author Geerlings then uses electron density functions as more representative of the "'chemistry' of their elements (say their valency and the stoichiometry of their compounds, in which the atom under consideration is (strongly) perturbed by its environment, in this case its reaction partners" rather than being an "'isolated' gas phase atom" (pp. 167-168), asserting that "electron density 'determines everything'" (p. 171). Taking a contrary stance, the fifth and sixth essays revisit atomistic approaches, again with a mathematical emphasis.

The seventh and tenth essays could be considered 'classical' discussions of potential reallocations of elements. In the seventh essay, authors Scerri and Parsons debate the recognition of lutetium and lawrencium as Group 3 elements and an alternative approach involving splitting of the d-block elements: the preference being for the former. A single illustration with the particular elements highlighted and the options collected together, as shown in Fig. 2, would have saved space and reduced the amount of page-turning to compare the options suggested! The tenth essay revisits issues associated with the classification of some of the transition metals. This essay picks up the complexity referred to in the fourth essay, and provides another example where the use of shading or colour in the diagrams would have highlighted so much more clearly the options that the essay canvasses (Fig. 3). However persuasive the arguments of these essay-authors might be, the status quo on these issues might well remain if the conservativeness of chemists to which the third essay drew attention is valid.



H 1								
Li 3	Be 4							
Na 11	Mg 12							
K 19	Ca 20						Sc 21	Ti 22
Rb 37	Sr 38						Y 39	Zr 40
Cs 55	Ba 56	La 57	Ce 58	Pr 59		Yb 70	Lu 71	Hf 72
Fr 87	Ra 88	Ac 89	Th 90	Pa 91		No 102	Lr 103	Rf 104

H 1								
Li 3	Be 4							
Na 11	Mg 12							
K 19	Ca 20						Sc 21	Ti 22
Rb 37	Sr 38						Y 39	Zr 40
Cs 55	Ba 56	Ce 58	Pr 59		Yb 70	Lu 71	La 57	Hf 72
Fr 87	Ra 88	Th 90	Pa 91		No 102	Lr 103	Ac 89	Rf 104

Fig. 2. Making options clearer - I.

Upper: "Figure 7.3 Long-form periodic table with lutetium and lawrencium in group 3. The increase in atomic number shows no anomalies whatsoever" (p.147).

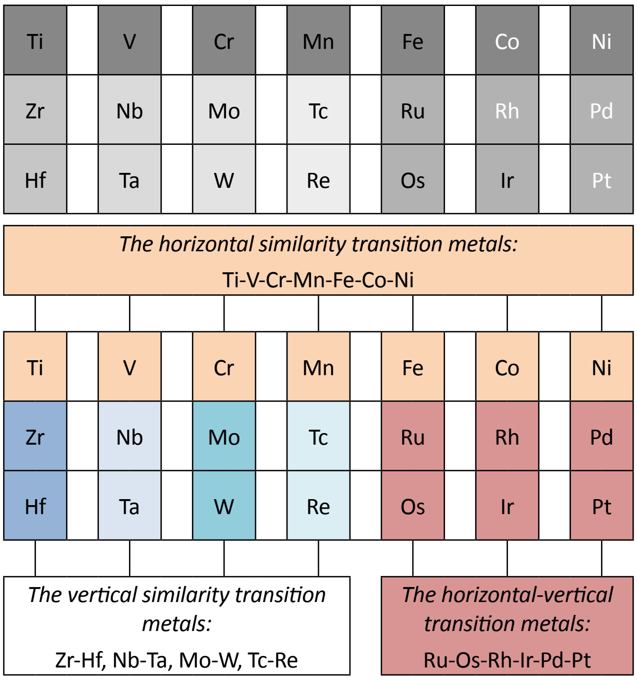
Lower: "Figure 7.4 Long form periodic table with lanthanum and actinium in group 3. Atomic number no longer increases in a regular fashion. This suggests that La and Ac are misplaced." (p. 148).

Putting the two versions side-by-side (albeit by eliminating some elements to reduce the troublesome width) and selected use of different fonts and greyscale shadings highlights immediately the differences to which the text refers (p. 146).

Similarities of properties may be yet more complicated, for example the 'knight's move', where elements such as Zn and Sn (or Ag and Tl) exhibit similar properties and behaviours, despite not being in adjacent rows or columns.[8] Such relationships may present a potential limitation on the applicability of a social semiotic approach to the visual representations of the periodic table, which is explored in the ninth essay, with particular reference to the tables developed in the 1860s by John Newlands and William Odling. Some readers may have difficulty with the notion of analysing the grammar in the headings of tabulated data as well as the data to discuss not only the form of the table but the extent to which such representations resemble the more familiar versions of the periodic table.

The twelfth and fourteenth essays usefully and interestingly extend the historical understanding of Mendeleev's work and the science of his times. Although the same might also be said of the thirteenth essay that revisits Abegg's contribution to the periodic table story, an aspect of his work that is particularly interesting in the context of the eleventh essay (to be discussed next) is his postulation:

"that electrochemical half-cell oxidation potentials could be used as a measure of an atom's attraction for electrons and that this, in turn could be qualitatively correlated with periodic trends in such properties as molecu-



Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

The horizontal similarity transition metals:
Ti-V-Cr-Mn-Fe-Co-Ni

Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

The vertical similarity transition metals:
Zr-Hf, Nb-Ta, Mo-W, Tc-Re

The horizontal-vertical transition metals:
Ru-Os-Rh-Ir-Pd-Pt

Fig. 3. Making options clearer - II. The use of colour to highlight relationships between transition elements.

Upper: Greyscale, as printed in Figure 10.3 (p. 198). Habashi has identified three categories of transition metals and named them as follows: The *vertical similarity transition metals*: [Zr-Hf]; [Nb-Ta]; [Mo-W]; and [Tc-Re]. The *horizontal similarity transition metals*: [Ti-V-Cr-Me-Fe-Co-Ni]. The *horizontal-vertical transition metals*: [Ru-Os-Rh-Ir-Pd-Pt].

Lower: A suggested use of different colours to distinguish the categories and different shades of a colour to distinguish examples within the same category.

lar polarity, *solubility*, and the *tendency to form complex ions*" (p. 246; italics added by review-author).

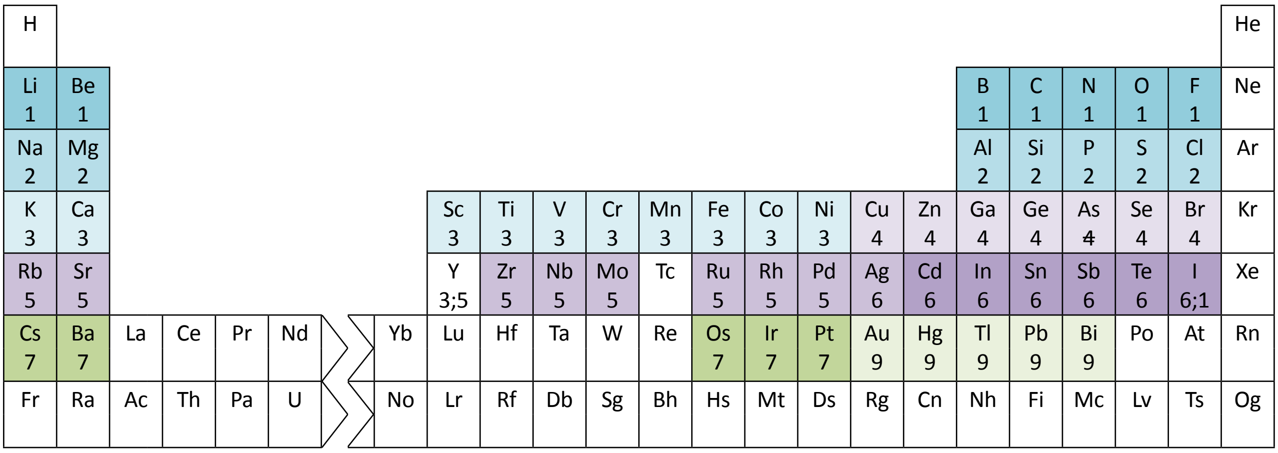
The most commonly shown of Abegg's diagrams is that in his 1904 article of an element's 'electroaffinity' as a function of its position in the 8-column, short form of the periodic table" (p. 247, Fig. 13.2).[9] Fig. 4 recasts this diagram using the modern periodic table, and its contoured form is similar to that of Fig. 5, compiled from electrode potentials (E^o).[10] The inter-element variations shown in Fig. 4 and Fig. 5 are much more extensive than shown on traditional periodic tables, and are evocative of the variation of ionic potential of the elements shown in the eleventh essay (pp. 209-210; Figs. 11.1 & 11.2). This essay describes a widely cited and well received version of the periodic table intended to cater for the needs of natural scientists.[11] While visually impressive, the table's size and complexity justifies restricting its inclusion in only skeletal form in the book (p. 208-209; Figs. 11.1 & 11.2). The intentions of the table, as written in the essay-author Railsback's initial paper,[12] are:

"The naturally occurring charged species commonly encountered by geoscientists, as well as elemental forms, [are] organized by charge. The new table [released in 2003] therefore shows many elements multiple times, unlike the conventional table. As a result, trends, patterns and interrelationships in mineralogy, soil and sediment geochemistry, igneous petrology, aqueous geochemistry, isotope geochemistry, and nutrient chemistry become apparent in this new table. The new table provides a more effective framework for understanding geochemistry than the conventional, and purely elemental, periodic table."

Chemical reactions on Earth have been highly dependent upon the variation in the abundance of oxygen throughout its history. On p. 215, the earth scientist's table is described as showing a

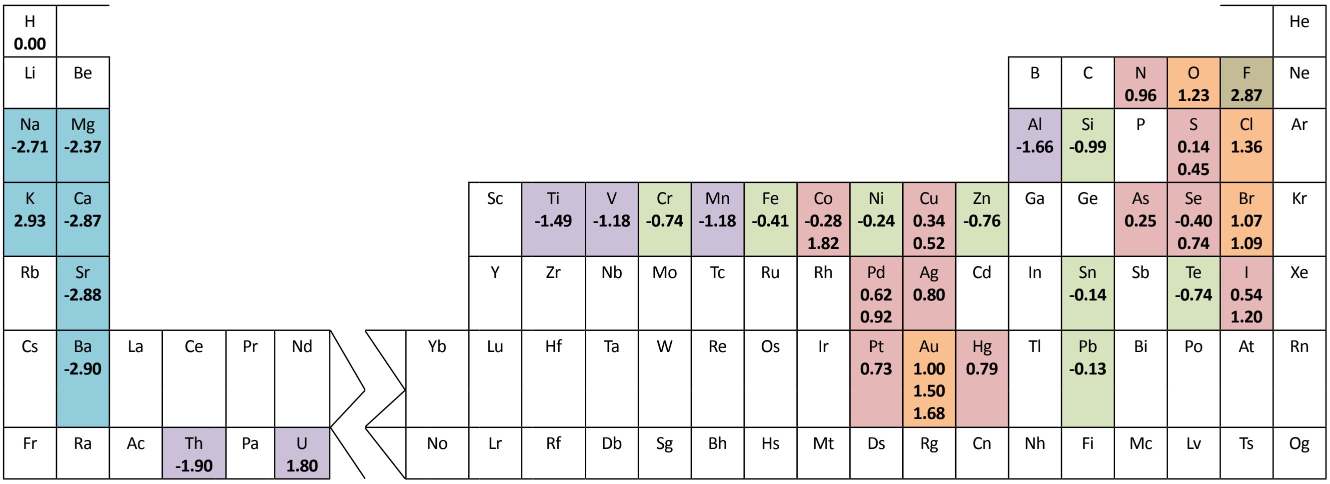
"…trend rightward across the table the 'pre-solar to Archean to early Proterozoic' direction in the table, because O_2 was absent or very scarce in the Earth's atmosphere about two billion years ago… In contrast, the trend leftward is the 'late Proterozoic to modern' direction of the Table because oxygen has been sufficiently abundant in the atmosphere over the last two billion years to oxidise many elements, among them C, S, Fe, Mo, Cr and U."

Thus, despite the complexity of the table, it still shows broad overarching trends: an enduring feature of many previous forms of the periodic table. An obvious follow-up to essay-author Railsback's initiative for earth scientists is a periodic table for biologists.[13] Railsback would doubtless describe this as another example of an 'expan-



H																						He
Li 1	Be 1																B 1	C 1	N 1	O 1	F 1	Ne
Na 2	Mg 2																Al 2	Si 2	P 2	S 2	Cl 2	Ar
K 3	Ca 3						Sc 3	Ti 3	V 3	Cr 3	Mn 3	Fe 3	Co 3	Ni 3	Cu 4	Zn 4	Ga 4	Ge 4	As 4	Se 4	Br 4	Kr
Rb 5	Sr 5						Y 3;5	Zr 5	Nb 5	Mo 5	Tc	Ru 5	Rh 5	Pd 5	Ag 6	Cd 6	In 6	Sn 6	Sb 6	Te 6	I 6;1	Xe
Cs 7	Ba 7	La	Ce	Pr	Nd	Yb	Lu	Hf	Ta	W	Re	Os 7	Ir 7	Pt 7	Au 9	Hg 9	Tl 9	Pb 9	Bi 9	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fi	Mc	Lv	Ts	Og

Fig. 4. Contoured variation of electron affinity for the chemical elements, redrawn from "Abegg's plot of an element's 'electroaffinity' as a function of its position in the 8-column short form of the periodic table".



H 0.00																						He
Li	Be																B	C	N 0.96	O 1.23	F 2.87	Ne
Na -2.71	Mg -2.37																Al -1.66	Si -0.99	P	S 0.14 0.45	Cl 1.36	Ar
K 2.93	Ca -2.87						Sc	Ti -1.49	V -1.18	Cr -0.74	Mn -1.18	Fe -0.41	Co -0.28 1.82	Ni -0.24	Cu 0.34 0.52	Zn -0.76	Ga	Ge	As 0.25	Se -0.40 0.74	Br 1.07 1.09	Kr
Rb	Sr -2.88						Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd 0.62 0.92	Ag 0.80	Cd	In	Sn -0.14	Sb	Te -0.74	I 0.54 1.20	Xe
Cs	Ba -2.90	La	Ce	Pr	Nd	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt 0.73	Au 1.00 1.50 1.68	Hg 0.79	Tl	Pb -0.13	Bi	Po	At	Rn
Fr	Ra	Ac	Th -1.90	Pa	U 1.80	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fi	Mc	Lv	Ts	Og

Fig. 5. Variation of electrode potential (E^o) for reactions such as $K \rightarrow K^+ + e^-$ (**-2.93**) and $Au \rightarrow Au^+ + e^-$ (**1.68**) in the periodic table.

sionist' approach, contrasting with the 'reductionist' approach in which physics has been emphasised (p. 216), an approach which accounts for about a quarter of the essays in this collection.

Early in the final essay of the book (p. 279) there is a somewhat deprecating view of chemistry:

"Chemistry with its long track record of unsurprising growth, with a myriad of applications taken for granted, and with a strongly supported and unifying theory may seem to be just too boring to exercise philosophers interested in resolving puzzles, developing surprising theories, and engendering novel insights."

This statement recalls the conservatism of chemists espoused in the third essay, but essay-writer Weinstein redeems himself by offering "three philosophical areas for which the periodic table is salient" – three new 'expansions', if you will.

Although the individual essays are of considerable interest and value to this field of research, this review has highlighted several areas of connection between various essays in the collection. Had the editors sought and exploited these connections, the essays could have been placed in an apparently less random order. Alternatively, they could have written an Introduction that did more than restate the table of contents, or – even better – they could have crafted a closing chapter that brought the various themes and approaches together. They could have even used such a final chapter to advocate their own preference for the future directions – whether reductionist or expansionist – of this fascinating area of multidisciplinary research.

Finally, from a technical standpoint, there are some disappointments in this book. References are not consistently formatted in the essays, and better proof-reading would have identified and addressed figure captions that describe coloured features in diagrams that are printed in greyscale, inconsistencies in the use of hyphens, and the occasional spelling mistake. While these matters are not overly disruptive to reading the book, they are surprising in a book from such a reputable publishing house.

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3. Third International Conference on the Periodic Table: http://www.chemistryviews.org/details/event/2459831/Third_International_Conference_on_the_Periodic_Table.html (accessed 3/05/2018)

4. Page numbers in parentheses are those in *Mendeleev to Oganesson. A Multidisciplinary Perspective on the Periodic Table.* Where diagrams are referred to the format used in *Mendeleev to Oganesson* is also adopted, e.g., "FIGURE 11.1".

5. A colour version of this periodic table and its exhibition setting can be viewed at The Internet Database of Periodic Tables: https://www.meta-synthesis.com/webbook/35_pt/pt_database.php?PT_id=24 (accessed 3/05/2018)

6 A lemniscate is mathematical jargon for a figure eight.

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Some Unremembered Chemists

A series of articles that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered.

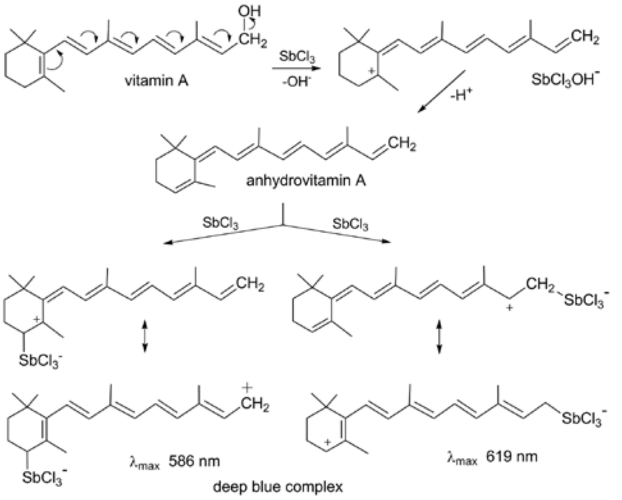
Francis Brian Shorland, OBE, PhD, DSc (L'pool), Hon. DSc (VUW), FRSNZ (1909-1999)

Dr Francis Brian Shorland (from *Brian Shorland - Doyen of New Zealand Science*, p. iii; courtesy of the New Zealand Association of Scientists)

Francis Brian Shorland (known as Brian) was born on July 14, 1909 in Island Bay, Wellington, New Zealand. His father John Olive Shorland (1864-1946) had been a long distance cycling racer in the South Island and subsequently owned and operated a cycle shop in Cuba Street in Wellington.[1] However, John's career was as diverse as it was engaging. It encompassed building, architecture, furniture and three years as a City Councillor (1917-1920). His wife, Edith Sophia Perry, was a school teacher from the South Island West Coast and they met while she was a student at Canterbury University College. They were married in 1898 and had four children of whom three survived to adulthood, Brian being the youngest.

Brian's education began in the Miss Hills' Kindergarten in Island Bay, where he stayed for two years before moving to Island Bay School at six years of age. There he had the usual rudimentary primary education prior to entering Form 3D at Wellington College in 1920. It was the lowest available as he was not a gifted student. For him college education lacked a good grounding in everything but Latin at which he excelled, and he only just managed to pass the state examinations in English and Physics (Chemistry was not taught at that time). Despite this, his school teacher-trained mother and sister had him back to the college for an extra year in Form 6B, and at the end of that 1926 year he gained a partial pass in the Matriculation exams. He stayed on gaining another partial pass the following year and full Matriculation was awarded in January 1928 with Engineering and Solicitor's general knowledge. Having missed out on a job in a Christchurch wireless shop that would have let him attend Canterbury University College, and on the advice of his sister Jessie, he was engaged in the Agriculture Department Accounts Office in 1927. After a few months a vacancy became available in the Agriculture Department Laboratory and Brian was transferred there as a cadet (trainee scientist). At that time Victoria University College (VUC) had moved to daytime lectures and the Agriculture Department and the newly established DSIR (Department of Scientific and Industrial Research) allowed their cadets to spend up to seven hours per week for tertiary study. Brian enrolled at Victoria registering for Physics 1 and Pure Mathematics 1, and subsequently moved to chemistry and zoology in his second year, graduating with a BSc in chemistry in June 1931. He was able to take six months leave of absence and, with a Jacob Joseph Scholarship, he undertook an MSc the following year. He graduated with 1st Class Honours in chemistry from work studying the reactions of glycols and dibasic acids. His thesis was entitled: *The rate of esterification of isoamyl alcohol and glycol by dibasic acids*,[2,3] and was subsequently published in the Journal of the American Chemical Society in 1935.[4] Professor Robertson (see: *This Journal*, **2015**, *79*, 51-55) was the sole organic chemist at that time and the thesis followed tradition by neither naming nor acknowledging him as supervisor.

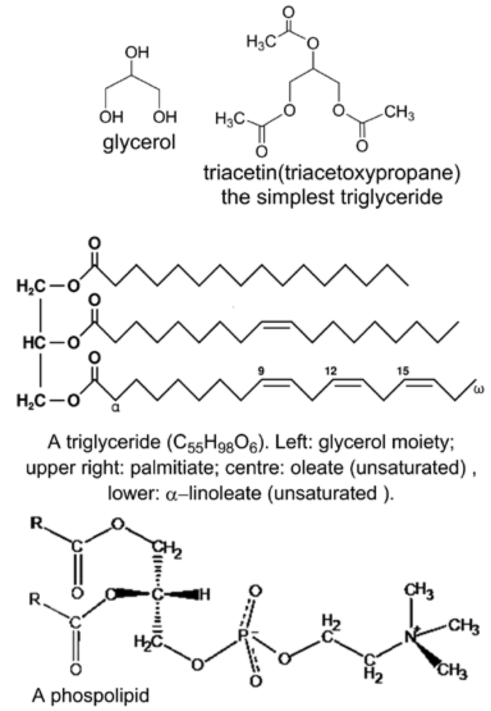
The MSc studies did not provide Shorland with his first publication. His work at the Agricultural Laboratory as a cadet was to assist staff in their projects under Bernard Aston as chief chemist. One of those there was Dr J.A. Bruce. At that time Bruce felt that New Zealand geothermal resources could be utilised, and especially steam, in energy production. Young Shorland became interested and collected samples from Wairakei for analysis and the results gave him his first two publications.[5] However, the managers of the time had little or no interest and the work lay dormant until the late 1940s when the science was advanced and a pilot plant subsequently constructed producing 20 MW power by late 1952. Following contributions to a range of projects Shorland and his cadet colleague Frank Denz were asked to test dried and processed eel from a farm on the basis that it might provide food for pigs. The tests with the oils product proved difficult and it was suggested that the project be abandoned. However, having assisted in setting up the equipment for the Carr-Price test[6] for vitamin A (something new to the department at that time), the two cadets tested the eel meal for the vitamin. It involved preparing a standard solution of 30% antimony trichloride ($SbCl_3$) and adding it to the vitamin A in chloroform to give a complex whose deep blue colour was measured colorimetrically (Scheme 1). Their success led them to examine the livers of fish caught off the Wellington coast and the results of their *unofficial* project was the beginning of Brian Shorland's lifelong adventures into fats and lipid chemistry, and the first paper he wrote.[7]



Scheme 1. The chemistry of the Carr-Price test

Following his MSc degree, Brian continued with studies at VUC taking and passing Philosophy III, Statistical Methods, and Economics, and became a classified scientist in the Agriculture Department working on his own projects. His first two years led to 12 publications on diverse topics that included geothermal heat utilisation, pampas grass as a supplement for cattle, aluminium as a causative agent in pasture bush sickness, and fish oils, one jointly with Aston. Yet the young man, now in his mid-20s wanted to progress his education to the PhD level and advance his interest in fish oils, something not then possible in New Zealand. With this intention, he applied to the Liverpool School of Fats Research to carry out PhD studies with Thomas P. Hilditch, the inaugural professor of industrial chemistry. His application was successful and he was granted leave from the Agricultural Lab with a CSIR (Council of Scientific and Industrial Research) National Research Scholarship. Although he was by this time engaged to Betty Purvis of Wellington, he left for London boarding the 12 passenger-carrying ship, the twin screw motor vessel (TSMV) Port Fairy in September 1935 arriving in London some 35 days later. His arrival in industrial North-West England and Liverpool was by train and the city was something he had never seen the likes of before. Settling was far from easy, though he had accommodation with a sensible family.

The work Brian undertook for his doctoral degree was the study of fats from farm animals and fish liver oils, which he had brought with him from New Zealand with Hilditch's approval. At that time Hilditch ran the foremost group studying fats, waxes and oils and was writing his major work *The Chemical Constitution of Natural Fats* published in five editions from 1940. The group's approach to characterising lipids was to hydrolyse them to their fatty acid components, esterify these (methanol) and separate the esters by fractional distillation. A lipid is a substance of biological origin that is soluble in nonpolar solvents. It comprises a group of naturally occurring molecules that include fats, waxes, sterols, fat-soluble vitamins, e.g. A, D, E, and K, mono-, di- and triglycerides, phospholipids, and others. The glycerides are the mono- di- or triesters formed from glycerol (1,2,3-trihydroxy-propane) and animal and fish fats are triglycerides. The phospholipids have one carboxylic ester function replaced by a hydrophilic phosphate ester (Charts 1 and 2 and below). Chromatography was still little known; the



A triglyceride ($C_{55}H_{98}O_6$). Left: glycerol moiety; upper right: palmitiate; centre: oleate (unsaturated) , lower: α–linoleate (unsaturated).

Chart 1. Glycerol, and examples of triglycerides and a phospholipid

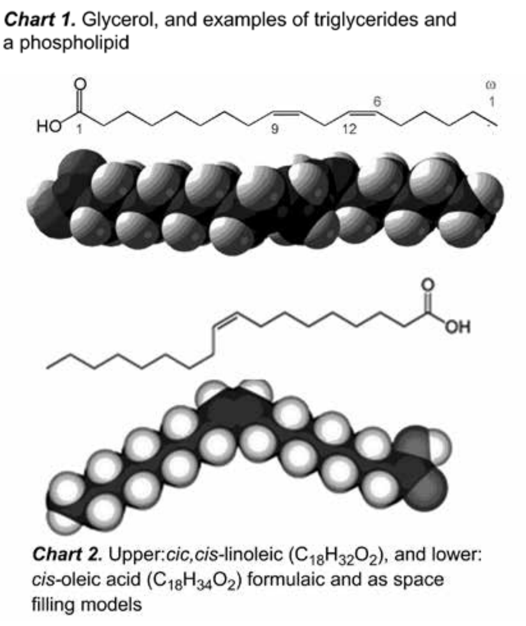
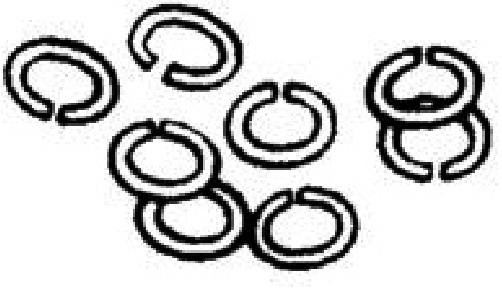


Chart 2. Upper:*cic,cis*-linoleic ($C_{18}H_{32}O_2$), and lower: *cis*-oleic acid ($C_{18}H_{34}O_2$) formulaic and as space filling models

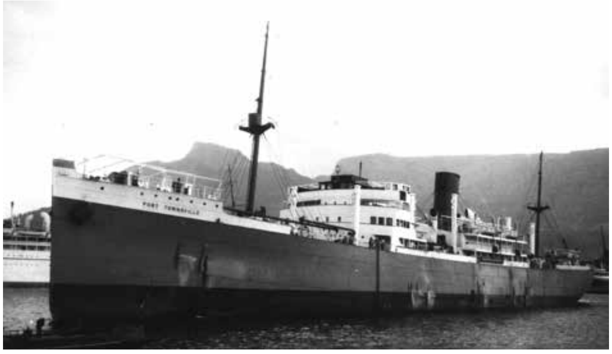
Russian-Italian botanist Mikhail Tsvet had developed paper chromatography early in the 20th century but it was not until the pioneering work of Martin[8] and Synge[9] in the early 1940s that partition chromatography became popular. In that era the constitution of fats and oils was determined using the saponification number and iodine value. The saponification number represents the number of milligrams of KOH required to hydrolyse (saponify) one gram of fat under specified conditions. It is a measure of the average molecular weight of all the fatty acids present. The long chain fatty acids (see e.g. Chart 2) present in fats have a low saponification value because they have relatively fewer carboxylic acid groups per unit mass of the fat as compared with short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat and the chain lengths are relatively small. The iodine value is the mass of iodine in grams that is consumed by 100 grams of the unsaturated compound and provides a measure of the unsaturation in fatty acids. The higher the iodine number, the greater the number of C=C double bonds present in the fat.

These tests were pivotal to Brian Shorland's doctoral studies[10] as illustrated in his 1937 and 1938 papers with Hilditch.[11,12] Moreover, Brian and an Indian doctoral candidate named Minocher Bomonji Ichaporia[13] spent Saturdays in the Hilditch lab achieving more than the local students who were at sporting events. Frenske spiral packing in columns, introduced to Liverpool by American postdoctoral fellow Herbert Longeneker, was particularly effective and the two graduate students discovered that the longer the column the more efficient the separation. Between 1934 and 1938 Brian's father, by then retired, prepared and exported as much as 144 gallons of fish-liver oil annually from Island Bay to British Drug House Ltd. in London. With the contacts that this established, Brian was able to spend his vacations in the company laboratories and use one of the first spectrophotometers to aid in determining the vitamin A content of the oils from New Zealand.[14]



Fenske spiral column packing

Brian's 1937 doctoral thesis was in essence in two parts both of which involved triglycerides. That which formed his first paper[11] with Hilditch was a determination and comparison of the composition of the component fatty acids present as glycerides and phospholipids (Chart 1; phospholipids are major components of cell membranes) in the livers of ox, cow, pig and sheep. The second was more closely related to Brian's prime interest, namely a study of aquatic (fish) fats[12] and gave a further four papers from Brian and his New Zealand collaborators.[15] At that time all such studies had involved species inhabiting the Northern Hemisphere and it was of particular interest to examine the fish oils of New Zealand species because many were (and are) peculiar to the Southern Hemisphere. The oils selected were from the livers of red cod, "English" hake, and groper as well as the head oil from this last species. The groper showed a marked seasonal variation from spring through winter in its vitamin A, iodine value and non-hydrolysable matter content. The external PhD examiner was Professor J.C. Drummond (later Sir Jack), the inaugural Professor of Biochemistry at University College London. His report was favourable and Brian returned to New Zealand with his PhD on the refrigerated cargo ship, the MV Port Townsville, which left London's Tilbury Docks on October 12 and called at a number of ports including ones in Australia before arriving in New Zealand in the spring of 1937.



The MV Port Townsville (from The AllenCollecton - Port Line, courtesy B. Watson; see http://www.benjidog.co.uk/allen/Port%20Line.html)

On return to the Agricultural Chemistry laboratory in Wellington, Brian Shorland was faced with change. Aston had retired and the deputy since 1927, R.E.R. (Dick) Grimmett who had tutored Brian in his cadetship was Director. With his doctoral degree in hand, Shorland was appointed as Chemical Advisor – Grimmett held his qualifications in zoology – and was largely able to choose his own research topics. He became recognised for expanding his horizons, not just scientifically at the bench but in terms of the space he and his projects occupied,[1] a trait that continued even into his later life and office in Victoria University's Biochemistry Department (see below). His studies continued the interest in fish and eel oils with his Director's support. The work turned to exploring the eel oil content during maturation and an examination of both types of New Zealand eel, the log-finned *Anguilla aucklandii* and the short-finned *Anguilla australis* at various stages of their life cycle. The former matures at about 20 years of age and 5 kg in weight, while the latter at 5 years old and at 1 kg; significant results followed. Study also included the body fat composition of farm animals, especially pigs and then sheep. These studies were extensively published and provided proof that fat was incorporated from diet and that this fat was deposited uniformly in the storage fat of the animal. The composition of fatty acids did not change throughout the body; diet was then accepted as the important factor in determining the structure of body fat in an animal. This work led

Brian to question the nature of diet and take him on to become a world recognised expert in the area. Between 1932 and 1949 Shorland had some 42 publication on the fats of fish and mammalia, and of grasses and other forage plants mainly of New Zealand origin.

In 1946 the Agriculture Department laboratories were moved from Wellington and amalgamated with the Ruakura Research Station near Hamilton, where Dr C. P. McMeekan, its first director, specialised in research to define the most productive management systems on dairy farms. The move was made for added focus on the facial eczema problem but it did not include Brian Shorland. He transferred to the DSIR where he was appointed Director of a newly established Fats Research Laboratory. It was established as a separate division of the DSIR to determine the fundamental nature of economically important fats, then a major source of New Zealand overseas income. At that time more than one-third of the weight of everything New Zealand exported was fat and the initial emphasis was on the vitamin A content of New Zealand butter, so as to comply with a short-lived British requirement.[3] The laboratory grew to a staff of 20 of whom half were chemists, and it soon became recognised as a leading centre for lipids research. Before the 1940s lipids research was in its infancy to the extent that lipids were proffered as having no physiological purpose other than for energy storage. Fats were considered to be comprised of even numbered straight carbon chains with no nutritional value save for the essential linoleic acid present (see Chart 1).

It was the work of the DSIR Fats laboratory and Brian Shorland that proved that fats were markedly more diverse than had been thought with odd numbers of carbon atoms and branched chains common. Phospholipids (Chart 1) and galactolipids (Chart 3) were present in addition to the common glycerol-lipids. The essential feature of a glycolipid is the presence of a monosaccharide or oligosaccharide bound to a lipid moiety whereas the galactolipid has galactose as its carbohydrate moiety (Chart 3). Shorland's work at the Fats Research laboratory (the Food Chemistry Division from 1966) demonstrated the presence of fatty acids from C4 to C26, that common fats were much more diverse than previously thought and that they included branched chain and unsaturated examples that could be either of *E* or *Z* configuration. Their studies established that the depot fats of ruminants reflected their dietary intake modified by the ruminant organisms largely saturating the unsaturated fats, whereas those of non-ruminants were directly reflective of their diet. They showed that lipid structures have a variety of important physiological roles. They went on to show that theories held relating to carcass fat composition were incorrect and that the then held evolutionary theory of animal fats was wrong and a new one was developed. As time and export markets evolved Shorland and his team explored why the odour of mutton fat was unacceptable to the Japanese. In essence, the laboratory team made significant and important discoveries to the understanding of lipids, their nutritional value of particular importance to the New Zealand industries dependent on them. And Shorland's international reputation grew.

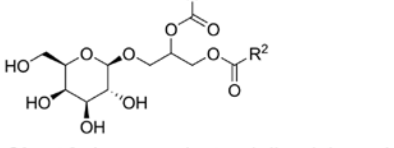
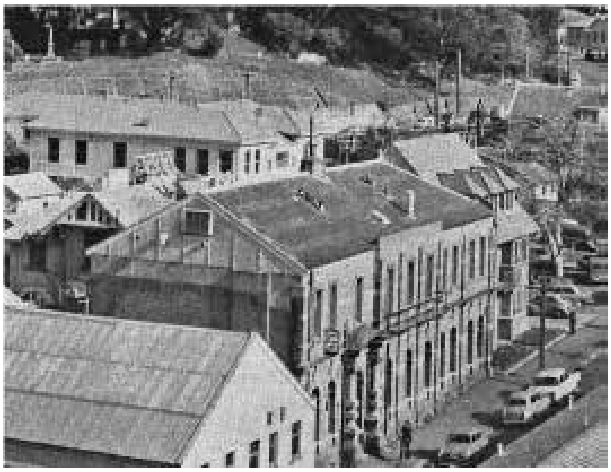


Chart 3. A monogalactosyl diacylglycerol - a galactolipid



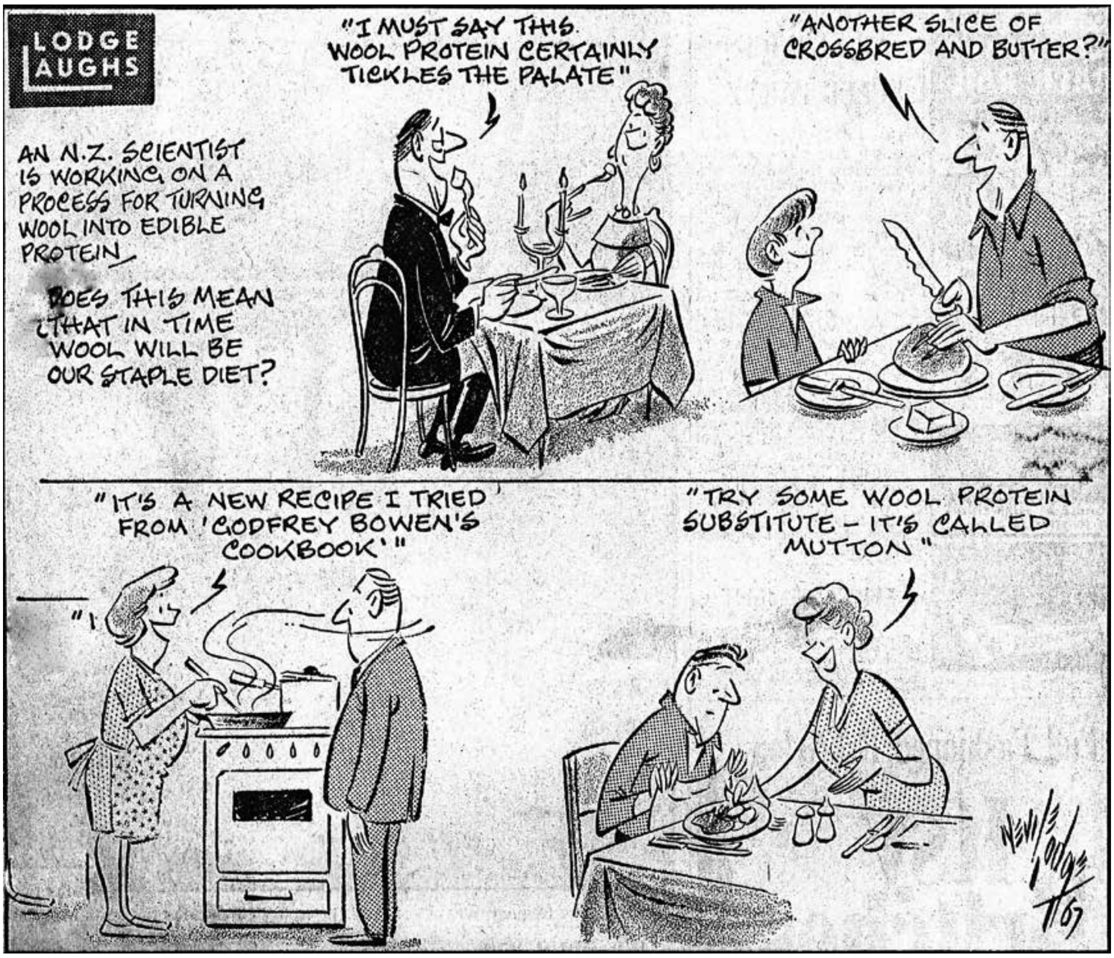
The DSIR Fats Research Laboratory, Sydney Street East, Wellington and original home of the New Zealand Dominion laboratory (from *Brian Shorland - Doyen of New Zealand Science*. p.87; courtesy of the New Zealand Association of Scientists)

When the United Nations General Assembly asked its protein Advisory Group to increase the production and use of edible protein,[16] Shorland devised high protein food from wool, at which time the country had a vast excess. He subjected wool to a chemical and a biochemical treatment and in his 1969 paper,[17] he stated: "*Edible protein derived from wool is assessed with respect to its suitability for human food. Compared to the FAO* (Food and Agriculture Organisation of the UN) *reference pattern for human requirements of amino acids, wool protein is deficient mainly in methionine, and less so in lysine and tryptophan. … It is estimated that edible wool protein can be manufactured for <25 cents/lb*". The chemical process involved use of sodium sulfide-sodium sulfite followed by precipitation with acetic acid and the biochemical process[18] employed the kiwi fruit enzyme actinidin (a member of the papain family). Irrespective of the method, the amino acids solutions were dried to a white powder that lacked the essential dietary sulfur-containing acids, and so the most important of them, methionine, was added. The successful outcome with laboratory rats led to human trials with the powder added to standard whole meal breads, ginger nuts and sponge cakes; the products were fully edible. Up to 35% of baking flour could be replaced without affecting product acceptability. Shorland and his colleagues gained widespread publicity as exemplified by the Lodge Cartoon in the Wellington evening paper. What was perhaps more remarkable was that the processing could be applied to used and dyed woollen knitted clothing including socks! His conversion of protein into food did not stop there. He published three papers on the equivalent production of food from feathers. Feathers contain 85-90% keratin that must be hydrolysed to make it digestible. In that process the disulfide and amide bonds in the keratin are broken to form more digestible smaller proteins, peptides and amino acids. Rendering the feathers was the traditional method of hydrolysis[19] but it was Draper[20] who first tried treating feathers with sodium sulfide and sodium hydroxide. Interestingly, in 2012 biotechnologists at Lund University (Sweden) refined a micro-organism to convert chicken and turkey feathers into soluble protein.[21] Their spin-out company Bioextrax now provides 900 g of protein from 1 kilogram feathers and it has a patent pending for their conversion into animal feed.[22]

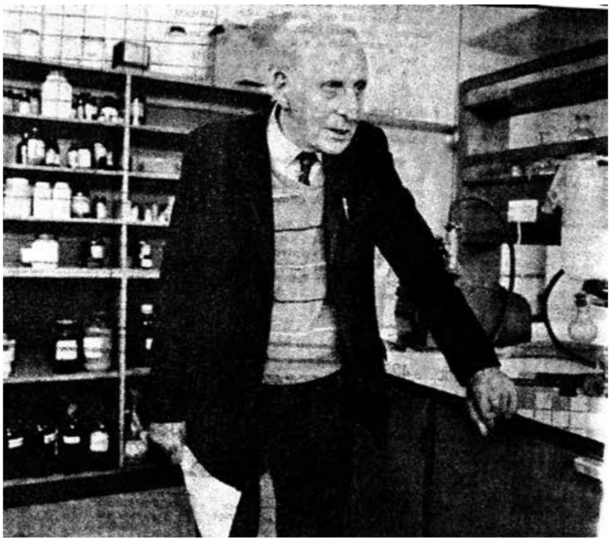
In Shorland's era, government service employees retired on pension at 60 years of age and so at the end of 1969 retirement was forced upon him. He was fortunate, however, in having professional colleagues at Victoria University and he was able to transfer and become an unpaid Honorary Lecturer in Biochemistry, a role he held until 1987 when he was redesignated an Honorary Research Fellow. He remained there filling his office with papers and files until his death in 1999. The year 1971 saw Brian appointed as convener of the government requested panel on coronary heart disease established by the Royal Society of New Zealand (RSNZ). The study took over a year with a final report clearly suggesting that cholesterol and heart disease were not causally related. Replacing butter by margarine did little but aggravate the problem while increasing the intake of ω-3 fatty acids as in fish oil and olive oil (which contains up to 1.5% of the ω-3 fatty acids linolenic acid) was beneficial. He continued with his dietary thrust, concluding in 1987 that the results of the various cholesterol-lowering regimes had been misinterpreted. More importantly, by then the biochemical understanding of the clotting mechanism was soundly based and could not support cholesterol as causative.[23]

As time passed, science in New Zealand came under government scrutiny resulting in major reorganisation in the 1990s. Brian Shorland had joined the Association of Scientific Workers in 1945 and remained involved with it through its morph into the Association of Scientists (NZAS) until his death. As a senior scientist he took it upon himself to be a critic of government and he wrote and spoke widely on the topic of reorganisation. He served on the Association Council from 1963 until the mid-1990s, was Vice-President 1965-1997, and President 1954-1955. He was Editor of the Association's Journal, *Science Review* from 1985 until the mid-1990s. He was awarded his DSc by Liverpool in 1950, elected Fellow of the Royal Society of New Zealand in 1951, gained an OBE in 1959 and given an honorary DSc by Victoria University in 1970. He was awarded the NZAS premier award, the Marsden Medal, in 1970 and was Patron of the organisation from 1955 until his death in 1999. The Association established the Shorland Medal for *lifetime contribution to scientific knowledge* in his honour later that year.

Brian Shorland was married three times. His first wife, to whom he was engaged while in Liverpool and married on January 27th, 1938 shortly after his return, was Betty Purvis. The couple had twins, John and Alison in 1948 and the New Zealand Institute of Chemistry announced the



Neville Lodge cartoon, The Evening Post, Wellington, 11 December 1967 (from *Brian Shorland - Doyen of New Zealand Science*, p. 121; courtesy of the New Zealand Association of Scientists)



Brian Shorland – the Doyen of New Zealand Science, ca. 1995 (from *Brian Shorland - Doyen of New Zealand Science*, p. 131; courtesy of the New Zealand Association of Scientists)

Brian and Betty Shorland, 27 January 1938 (from *Brian Shorland - Doyen of New Zealand Science*, p. 143; courtesy of the New Zealand Association of Scientists)

event in the March 1948 issue of its Journal as: "*We congratulate Dr and Mrs F.B. Shorland of Wellington on the discovery of two new isomeric compounds, one* trans *and one* cis". The second marriage was for eight years and the third for some five years. Brian Shorland died in his sleep at his Karaka Bay Road home on July 8 in 1999, some five days before his 90th birthday. His daughter continues to live in the old family home in Derwent Street, Island Bay, Wellington.

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Dates of Note

July

23 ***Rudolph A. Marcus***, the Canadian-born American chemist and winner of the 1992 Nobel Prize for Chemistry for his work on the theory of electron-transfer reactions in chemical systems (Marcus theory) was born this day in 1923.

25 ***Charles Macintosh***, the Scottish chemist and inventor of rubberised waterproof clothing was born in 1843. Seeking uses for coal gasworks waste products, he utilised naptha as a solvent in his 1823 method of waterproofing cloth by pressing together two rubberised layers; the name Macintosh remains associated with the raincoat made from such cloth.

26 ***Paul Walden*** was the Latvian chemist who, while teaching at Riga, discovered the inversion of malic acid by which two varieties of the malic acid could be formed. One rotated plane polarised light in a clockwise fashion, the other counter clockwise. His name is immortalised in the *Walden inversion*; he was born in 1863.

27 ***Friedrich Ernst Dorn*** was born in 1848. He was the German physicist who followed Madame Curie's discoveries by showing that radium not only emitted radiation, but released a colourless gas that was also itself radioactive. Initially called *radium emanation* or *niton*, it was renamed in 1923 as *radon* and is the heaviest of the inert gases.

In 1823, Johann Wolfgang Döbereiner investigated the effect of platinum as a catalyst. He found that hydrogen combined with air in the presence of platinum powder to form water in a reaction so vigorous that the filter paper holding the powder was charred. Only later did Berzelius (1835) coin the term catalysis.

28 ***Otto Hahn***, the German chemist who with radiochemist Fritz Strassmann is credited with the discovery of nuclear fission, died in 1968.

29 ***John Alexander Newlands*** was the British chemist credited with being the first to establish an order of elements by atomic weights and observed periodicity in their properties. Every eighth element has similar properties, hence he named the Law of Octaves on Feb 7 1863; he died in 1898.

31 ***Stephanie Kwolek***, the American chemist who invented Kevlar, died in 2014.

August

1 ***Richard Kirwan***, the Irish chemist whose *Elements of Mineralogy* (1784) was the first English systematic treatment of the subject, was born in 1733.

2 ***Leopold Gmelin***, the German chemist who discovered potassium ferrocyanide (1822), devised a test named after him for bile pigments, researched the chemistry of digestion, and published his famous *Handbook of Chemistry* to comprehensively survey the subject, was born in 1788.

3 ***Benjamin Franklin Goodrich***, the American industrialist who founded the B.F. Goodrich Rubber Co., died in 1893.

4 Aug 4, 1693 is the reputed day that ***Dom Perignon*** invented champagne.

7 ***Jons Jacob Berzelius***, the Swedish chemist and one of the founders of modern chemistry especially noted for his determination of atomic weights and the development of modern chemical symbols, died in 1848.

12 ***Karl Ziegler***, the German chemist who shared the 1963 Nobel Prize for Chemistry (with Natta) for polymer work, died in 1973.

13 ***Frederick Sanger***, the English biochemist and twice the recipient of the Nobel Prize for Chemistry (1958 and 1980), was born in 1918.

In 1913, the first true stainless steel, a steel alloy that contained 0.24% carbon and 12.8% chromium, was cast in Sheffield, England.

In 1903, the journal *Nature* reported that ***Ramsay*** and ***Soddy*** had shown that helium gas is produced by the radioactive decay of radium.

14 ***Richard R. Ernst***, the Swiss researcher awarded the 1991 Nobel Prize for Chemistry for his contributions to the development of the methodology of high resolution NMR spectroscopy, has his 85th birthday today.

Frederic Joliot-Curie, the French physical chemist and husband of Irène Joliot-Curie , jointly awarded the 1935 Nobel Prize for chemistry, died in 1958.

16 ***Frederic Stanley Kipping***, the British chemist who pioneered the chemistry of silicones, was born 1863.

John S. Pemberton, the American pharmacist who invented Coca-Cola in 1885, died this day in 1888.

Element 110 was formally named ***darmstadtium*** (Ds) in 2003.

17 ***Walter Noddack***, the German chemist who, in collaboration with his wife Ida Tacke, discovered element 75 (Jun 1925) and named it rhenium after the river Rheine, was born in 1893. Rhenium was the last stable element discovered.

21 ***Jean Servais Stas***, the Belgian chemist noted for his accurate determinations of atomic weights, was born in 1813.

22 ***Willis R. Whitney***, the American chemist who founded the General Electric Company's research laboratory and was known as the father of basic research in industry, was born in 1868.

23 ***Robert F. Curl***, Jr., the American chemist who (with Smalley and Kroto) discovered the first fullerene in 1985, has his 85th birthday today.

24 ***Rudolf Clausius***, one of the founders of thermodynamics, died in 1888.

25 ***Antoine-Henri Becquerel***, the French physicist who discovered radioactivity and shared the 1903 Nobel Prize for Physics with Pierre and Marie Curie, died in 1908.

In 1856 ***William Henry Perkin*** applied for a British patent for his invention of aniline dye "producing a new colouring matter for dyeing with a lilac or purple colour stuffs of silk, cotton, wool or other materials".

28 ***Eilhardt Mitscherlich***, the German chemist who promulgated the theory of isomorphism, died in 1863.

29 ***Christian Friedrich Schönbein***, the German-Swiss chemist who discovered and named ozone (1840) and was the first to describe guncotton (nitrocellulose), died in 1868.

31 ***Sir George Porter***, noted for his study of very fast reactions, died in 2003.

September

1 ***Carl Freiherr*** **(Baron)** ***von Welsbach,*** the Austrian chemist, physicist and engineer who invented the gas mantle that becomes incandescent white-hot in a gas flame giving greatly increased light output by gas lamps, was born in 1858.

In 1898, ***Ernest Rutherford*** coined the terms *alpha* and *beta* for two distinct types of radiation.

2 ***Friedrich Wilhelm Ostwald***, the German chemist who almost single-handedly organised physical chemistry into a nearly independent branch of chemistry, was born in 1853.

4 ***Stanford Moore***, the American biochemist who shared (with Anfinsen and Stein) the 1972 Nobel Prize for Chemistry for his understanding of the connection between chemical structure and catalytic activity of the active centre of the ribonuclease molecule, was born in 1913.

6 ***Aleksandr Butlerov***, the Russian chemist and one of the principal creators of the theory of chemical structure (1857–1861) (see *This Journal* **2018**, *82*, 46-52) was the first to incorporate double bonds into structural formulas. He was born in 1828 and has the crater Butlerov on the Moon named after him.

8 Sir ***Derek H.R. Barton***, the British chemist and joint recipient (with Hassel of Norway) of the 1969 Nobel Prize for Chemistry for work that helped establish conformational analysis, was born 100 years ago today.

Viktor Meyer, the German chemist who contributed greatly to knowledge of both organic and inorganic chemistry and invented an apparatus for determining vapour densities (and hence molecular weights) named after him, was born in 1848.

10 ***Waldo Semon***, the little remembered American chemical engineer who invented plasticised PVC, was born in 1898.

Felix Bloch, the Swiss-born American physicist who shared (with independent discoverer, Purcell) the Nobel Prize for Physics in 1952 for developing NMR spectroscopy, died in 1983.

14 ***Pierre Vernier***, the French mathematician who invented the vernier scale, died in 1638.

16 ***Guillaume François Rouelle***, the French apothecary and chemist who first proposed the modern definition of salts and was first to distinguish neutral, acid, and basic salts, was born in 1703.

17 ***Friedrich Adolf Paneth*** was the Austrian-British chemist who improved methods to isolate and measure the minute amounts of helium (as little as 10^{-10} cm^3) slowly released by traces of radioactive elements in rocks. This enabled the determination of the age of rocks on earth and of the age of meteorites. He died in 1958.

19 ***Charles-Victor Mauguin*** was a French mineralogist and crystallographer, and one of the first to make a systematic study of the silicate minerals. Using X-ray diffraction techniques, he determined the structure of a large number of micas, cinnabar, calomel and graphite, and devised the system of symbols for designating the symmetry properties of crystals adopted in 1935 as the international standard. He was born in 1878.

20 ***David Marine***, the American pathologist whose substantial study of goitre led to the iodising of table salt, was born in 1888.

This is the day in 1848 that the first meeting of the American Association for the Advancement of Science took place in the library of the Academy of Natural Science in Philadelphia, Pennsylvania.

24 ***Michael J.S. Dewar***, an early master of molecular orbital theory, was the Scottish organic chemist born in India 100 years ago.

25 ***Hieronymus Theodor Richter***, the German mineralogist who in 1863 was a co-discoverer of the element indium, died in 1898.

26 ***August Ferdinand Möbius***, of Möbius strip fame, died 150 years ago in 1868.

27 ***Adolphe Wilhelm Hermann Kolbe***, the German seminal contributor in the birth of modern organic chemistry, Professor at Marburg and Leipzig and who coined the term *synthesis* and prepared acetic acid from carbon disulfide, was born this day 200 years ago.

Bernard Courtois, the little know French chemist who discovered the element iodine, died in 1838.

29 ***Rudolf Christian Karl Diesel***, the German engineer who invented the internal-combustion engine named after him, died in 1913.

30 ***Johann Deisenhofer***, the German biochemist who (with Michel and Huber) won the Nobel Prize for Chemistry in 1988 for the determining the three-di-

mensional structure of certain proteins essential to photosynthesis, has his 75th birthday today.

October

1 ***Edwin Joseph Cohn***, the American biochemist who helped develop the methods of cold ethanol blood fractionation (the separation of plasma proteins into fractions), died in 1953.

4 ***Kenichi Fukui***, the Japanese chemist who shared the 1981 Nobel Prize for Chemistry with Hoffmann for the investigation of chemical reaction mechanisms and who introduced his *frontier orbital theory of reactions* in 1952, was born this day 100 years ago.

8 ***Otto Warburg***, the German biochemist awarded the Nobel Prize for Physiology or Medicine in 1931 for his work on cellular respiration, was born in 1883.

12 ***Vincenzo Dandol*** was an Italian pharmacist, natural scientist, writer, statesman and innovator in both science and politics. He championed the new scientific theories of Lavoisier, helped further democratic ideals in Italy, and was personally committed to the advancement of secondary education in general and to health care in particular. He was born in 1758.

15 ***Evangelista Torricelli***, the Italian physicist and mathematician who invented the barometer and whose work in geometry aided in the eventual development of integral calculus, was born in 1608.

Carl Mosander was the Swedish chemist and mineralogist whose work revealed the existence of numerous rare-earth elements with closely similar chemical properties. He discovered lanthanum (La; 1839), erbium (Er; 1842) and terbium (Tb; 1843) prior to his death in 1858.

16 ***Cyril Ponnamperuma***, the Ceylonese-American chemist and exobiologist, who was a leading authority on the chemical origins of life, was born in 1923.

18 ***Samuel Guthrie*** was the American physician and chemist who independently discovered chloroform and invented the percussion priming powder for firearms prior to the use of flints. He experimented in a laboratory near his house and had a mill about a mile away for manufacturing large quantities of his powder and other explosives, including potassium chlorate and mercury fulminate. He made chloroform in 1831 by distilling $CaCl_2$ with alcohol in a copper vessel, prior to the independent discoveries of Soubeiran (France, 1831) and Liebig (Germany, 1832), and used it during amputation surgery in his hometown of Sackets Harbor, NY. He died in 1848.

20 In 1983 the length of the metre was redefined as the distance that light travels in a vacuum in 1/299,792,458 of a second by the international body *Conférence Générale des Poids et Mesures* (GCPM) to give greater accuracy. Originally, it was based on one ten-millionth of the distance from the North Pole to the equator.

21 ***Alfred Nobel*** gined his first patent, a Swedish one, for the preparation of nitroglycerin; he was born in 1833.

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