Chemistry in New Zealand

Volume 81, No.2, April 2017

## Articles and features



## Other columns

# Comment from the President

The new year is no longer new anymore - 2017 is well underway, and hopefully going well for all our members.

I have had a busy summer, attending three conferences, all in New Zealand. In early December I attended ASBIC, the 8th Asian Biological Inorganic Chemistry Conference held in Auckland, organised by Christian Hartinger. In February, I spent three days in Dunedin at SANZ-O-MAG2, with a focus on bringing together researchers who have an interest in molecular magnetism, for a tutorial style meeting ranging from the basics to current applications. This was immediately followed by a week in Queenstown at AMN8, the 8th biannual meeting hosted by the MacDiarmid Institute for Advanced Nanomaterials. SANZ-O-MAG2 and AMN8 were organised by Sally Brooker and Paul Kruger, respectively. All three meetings had an excellent attendance from NZ, Australian and international delegates, a very lively presence from and contributions by students and emerging researchers, and a great vibe and social atmosphere brought about by the interactions between all attendees. I am highlighting these conferences because they illustrate several things – NZ chemistry is playing a vigorous role on the world stage, attracting world leaders in their respective fields to come here and discuss their work. Our emerging scientists at the student and postdoc level are producing high quality work, presenting it confidently to their international peers, and maximising the opportunities to interact and socialise with an international cohort of scientists.

2017 is shaping up to be a busy year for NZIC. We are progressing our plans to develop a new website and online membership management system. The Royal Society of New Zealand is also embarking on a project to assist with providing these services to its constituent member organisations, of which we are one. This is a great move by the RSNZ, as they have around 50 constituent member organisations, many of which struggle with the administrative burden of maintaining membership systems. We are talking with them to see if what they offer suits NZIC.

In another development, we are in the midst of preparing a bid to host the IUPAC 2023 World Congress and General Assembly in Auckland. NZIC is well-represented at IUPAC – Richard Hartshorn is the IUPAC Secretary General, Margaret Brimble (Auckland) is President of the Organic and Biomolecular Division, Gregory Russell (Canterbury) is President of the Polymer Division and Suzanne Boniface (Wellington) serves on the Committee on Chemistry Education. We won't know the outcome of our bid until the decision is made at the 2017 congress in Sao Paulo, Brazil, in July. If we are successful this will be a fantastic opportunity for NZ to showcase its chemistry to the world. We already know we are very successful at hosting specialist meetings on the world stage (as I illustrated above). Bringing it all together to host a very large congress involving all chemistry disciplines will be a challenge for all of us, will involve the entire Institute and chemistry profession within NZ. Let's hope we get the opportunity.

2016 NZIC President Paul Plieger hands the Presidential Chain to the 2017 President Penny Brothers.

**Penny Brothers**
University of Auckland
NZIC President 2017

# New Zealand Institute of Chemistry

***supporting chemical sciences***

## April News

### FNZIC

Congratulations to *Joseph* ***Lane*** (University of Waikato), *Guy* ***Jameson*** (University of Otago) and *Sylvia* ***Sander*** (University of Otago) who have been elected Fellows of NZIC.

### AUCKLAND

#### The University of Auckland

Professor *Kevin* ***Smith*** has resigned and returned to Boston after three years as the Head of School. A farewell party for Kevin took place on 24 February so stay tuned for pictures in the next issue. In February, Associate Professor *Gordon* ***Miskelly*** began his three-year term as the new Head of School of Chemical Sciences. Congratulations to Gordon for taking on this leadership role.

Dr Muhammad Ali Awan joined the School in January as a Professional Teaching Fellow for a one year appointment. Hannah Matthew, joined the School in November as a Technician to provide support for SCI-QUEST, Floors 8 and 9 of building 302 and Chemistry Stores.

#### *Building 302*

Our new Science Centre is now fully occupied and is buzzing with exciting research. The School of Chemical Sciences occupies floors 7 to 10 with reception on level 6.

#### *AsBIC conference*

Professor *Christian* ***Hartinger*** and his team organised a very successful conference in Auckland (Dec 4-9, 2016). The 8th Asian Biological Inorganic Chemistry Conference had over 330 participants from over 25 different countries. There were four parallel sessions of oral presentations including 7 plenary, 25 keynote and 110 invited lectures along with 54 contributed oral presentations. In addition, there were three award lectures, including the AsBIC Outstanding Achievement award lecture by Professor Shunichi Fukuzumi and Graeme Hanson, and Early Career Researcher award lectures by Professor Ho Yu Au-Yeung and Dr Anna Renfrew. There were also two poster sessions featuring 107 poster presentations. The conference also included an early career bioinorganic chemistry forum with panel discussions on topics such as *Teaching bioinorganic chemistry*.

Congratulations to poster prize winners: Shenghua Han, Norifumi Muraki, Pria Ramkissoon (Metal Ions in Life Sciences); Suguru Endo, Runming Wang (Royal Society of Chemistry);

Joshua Kyle Stanfield, Naoya Tsuruoaka (RSC Metallomics), and oral presentation prize winners: Angelo Frei, Edward O'Neill, Michael Gotsbacher (Flash Presentations); Lucas Prieto, Matthew Sullivan, Yuchuan Wang (Early Researchers Forum presentations).

### *11th Polymer Electronics Research Centre (PERC) and 2nd Biocide Toolbox Symposium*

This joint event held at the University of Auckland in November 2016 featured over 30 talks spread over two days, as well as networking opportunities for the students of both research groups. Sessions included diverse topics and areas of expertise including: *sensors, biosensors and antioxidants*; *Biomedical and functional materials*; *drug delivery/medical applications*; *biocidal materials, synthesis and activity* and *surface biocides/scanning methods*.

Congratulations to Thomas Kerr-Phillips (1st), Alissa Hackett (2nd) and Chloe Cho (3rd) for winning the three best student presentations. Thomas and Alissa are supervised by Professor *Jadranka* ***Travas-Sejdic*** and Chloe is supervised by Dr *Jianyong* ***Jin***.

### *Radio NZ*

Green Chemistry and the Biocide Toolbox were featured on the *Our Changing World* radio show on 14 December 2016. In the following link PhD student Charlotte Vandermeer is interviewed on her project applying winery waste to active packaging in conjunction with her supervisor Professor *Paul* ***Kilmartin***. See: http://www.radionz.co.nz/national/programmes/ourchangingworld/audio/201827370/from-wine-waste-to-safer-food-packaging

### *SapVax*

A very exciting development from Distinguished Professor *Margaret* ***Brimble***'s research is the formation of a spin-off related to research into novel cancer vaccines. The new start-up, SapVax, was formed by Margaret, Geoff Williams and Rod Dunbar (School of Biological Sciences) and is now partnered with an accelerator company BioMotiv from Cleveland, Ohio. SapVax will develop a suite of first-in-class cancer vaccines based on a novel peptide platform technology. The deal was signed just before Christmas, and a press release with more details can be found here: http://www.scoop.co.nz/stories/SC1701/S00026/new-startup-to-research-novel-cancer-vaccines.htm

### *Teaching and learning showcase*

The first teaching and learning showcase for the School of Chemical Sciences took place on 28 February.

### *Congratulations*

Congratulations to the following people:

*Margaret* ***Brimble*** for winning the very prestigious Marsden Medal! This is a lifetime achievement award. More information can be found at the following links: https://www.auckland.ac.nz/en/about/news-events-and-notices/news/news-2016/09/top-university-of-auckland-scientist-awarded-marsden-medal.html, http://www.mauricewilkinscentre.org/news/distinguished-professor-margaret-brimble-receives-marsden-medal.aspx and http://m.nzherald.co.nz/nz/news/article.cfm?c_id=1&objectid=11706151

*Brent* ***Copp*** on being awarded one of the three Dean's Awards for Teaching, for his personal commitment to student success, especially in large classes.

*Duncan* ***McGillivray*** for being awarded a University Teaching Award.

*Laurie* ***Melton***, who has been appointed by Elsevier as Editor-in-Chief of a new Encyclopedia of Food Chemistry.

*Christian* ***Hartinger***, who received the New Zealand Institute of Chemistry and Maurice Wilkins Centre Prize for Excellence in Chemical Research.

The PhD candidates who successfully presented and defended their PhD theses:

- Melissa Cadelis (Associate Professor *Brent* ***Copp***)
- Morgan Jay-Smith (Distinguished Professor *Margaret* ***Brimble***)
- Mona Damavandi (Professor *David* ***Barker*)**
- Tack Ngen (Distinguished Professor *Margaret* ***Brimble***)
- Hugo Fong (Associate Professor *Brent* ***Copp***)
- Scott Kang (Associate Professor *Tilo* ***Soehnel*)**

*Benjamin* ***Frogley*** and *James* ***Wright*** who have had their paper entitled, *A metallaanthracene and derived metallaanthraquinone* published in Angewandte Chemie (http://dx.doi.org/10.1002/anie.201608500). The Editor commented that "*According to the evaluation of referees the results reported in your Communica-*

Participants of the 8th Asian Biological Inorganic Chemistry Conference.

*tion are "highly important" or even "very important". Less than 10% of our manuscripts receive such a positive review*." Furthermore, the paper has been highlighted on the front cover of the Journal by a cartoon produced by New Zealand's science and chemistry cartoonist Dr *Nick* ***Kim*** (http://dx.doi.org/10.1002/anie.201610955).

Natalija Vyborna on being accepted into the University of Auckland Doctoral Leadership Initiative programme for 2017. This is a competitive entry seminar series for PhD students that prepares students for an academic career, with topics including leadership in academia, teaching, research, and professionalism.

### *Promotions*

Promoted to Professor: Associate Professor *Cather* ***Simpson***.

Promoted to Associate Professor: Dr *Duncan* ***McGillivray***, Dr *Jonathan* ***Sperry***, Dr *Geoffrey* ***Waterhouse*** Promoted to Senior Lecturer (above the bar): Dr *Bruno* ***Fedrizzi*** Dr *Johannes* ***Reynisson*, **Dr *Geoff* ***Willmott.***

Promoted to Senior Lecturer: Dr *Ivanhoe* ***Leung.***

Promoted to Senior Research Fellow (above the bar): Dr *Daniel* ***Furkert***.

## CANTERBURY

### University of Canterbury

### *Congratulations*

Congratulations to PhD student *David* ***Young*** who successfully defended his thesis entitled, *The modulation of structural components in metallosupramolecular assemblies and metal-organic frameworks* supervised by *Paul* ***Kruger***.

Professor *Ian* ***Shaw*** did a segment on TVNZ's Fair Go (28 November) on the environmental and human health effects of plastics (https://www.tvnz.co.nz/ondemand/fair-go/28-11-2016). This was followed by a blog which attracted 70,000 hits…wow! (https://www.facebook.com/FairGoNZ/).

Dr *Sarah* ***Kessans***' astronaut journey moves forward another small step! Sarah recently received a phone call from the NASA Astronaut Selection Office congratulating her for being selected as one of the ~60 Finalist Interviewees for the 2017 NASA Astronaut Candidate Class of 2017. Sarah will head back to the Johnson Space Center in April of 2017 for a final round of interviews. In June 2017, NASA will then choose 8-14 of these finalists to become the Astronaut Candidate Class of 2017, reporting for duty starting in August 2017 (http://astronauts.nasa.gov/content/timeline.htm). Sarah is a postdoctoral fellow with Professor *Emily* ***Parker's*** research group in the Department of Chemistry.

### *UC research influences Government's micro-bead ban*

University of Canterbury research has influenced a Government proposal to ban personal care products containing plastic microbeads, announced on January 16. A University of Canterbury-led project highlighted the problem with microbeads, tiny plastic balls in cosmetic products. One tube of microbead facewash could contain more than 300,000 beads. Most end up washed through water treatment systems and into the sea, where they can be ingested by marine animals. UC environmental chemistry senior lecturer Assoc. Prof. *Sally* ***Gaw*** says it is difficult to remove plastics once they had been released into the oceans. She is pleased that the research has influenced the Government's proposal and praises the ban as a valuable first stage. "Banning microbeads in personal care products is a great step forward that will remove one source of microplastics from entering the oceans." University of Canterbury (UC) researchers, including Dr *Sally* ***Gaw*** and Water Resource Management PhD student Phil *Clunies*-***Ross***, in collaboration with the University of Otago, found concentrations of microplastics on Canterbury beaches were comparable to concentrations found overseas in more heavily populated areas. Dr Gaw says "We need to re-evaluate our love affair with plastic, and get smarter about how and when we use plastic if we are to protect our oceans."

### *Chemsoc*

2016 was fantastic for UC Chemsoc, starting with our largest membership yet, the ever-successful TriSci Ball (with the Physics and Biology societies) and finishing it off with our end-of-year barbecue, with many other amazing events in between. It has been excellent to be a part of such an inclusive, lively department and we hope to host more incredible events this year.

We had a great turnout at our AGM and a lot of interest in joining the executive. This year we see the return of some old hands and welcome some new faces. The committee is larger than ever, thanks to the success and growth of the club over the past few years.

Chemsoc has many goals for the year ahead, which started with Clubs Day in February. Our events list for the year consists of some of our old favourites but also sees the addition of some new events. Returning are, among others, the popular quiz night, TriSci ball and end-of-year barbecue. We also intend to try a new event, the Chemistry Cocktails evening which, of course, will feature chemistry-themed drinks! The chemsoc committee would like to thank the Canterbury Branch of the NZIC for their continued collaboration and support as we look forward to a successful year ahead.

### Ara Institute of Canterbury

Ara Institute of Canterbury, formerly CPIT, offers a well-established Graduate Diploma in Laboratory Technology that has been running since the early 1990s. This qualification prepares BSc graduates for laboratory technician employment. Perhaps the most-often quoted reason for students joining the programme is a 240 hour work placement, arranged by staff from Ara. Students entering this programme will choose either a chemistry or a microbiology emphasis; in chemistry, we emphasise analytical and environmental chemistry, and in microbiology we focus on food safety and environmental monitoring. Key content areas that are almost invariably missing from most students' backgrounds are legislative compliance, laboratory quality, and statistical validation of analytical results. The Graduate Diploma in Laboratory Technology covers all of these areas, along with boosting hands-on practical skills with a strong leaning toward project-based learning.

Staff research is a mixture of applied academic research and research seeking direct commercial outcomes. In the applied academic research category, *Dr David* ***Hawke*** works mostly on the biogeochemistry of high nutrient environments. His most recent work looks at the uptake of selenium brought ashore by seabirds. Dr *Barbara* ***Dolamore*** has just concluded a project on algal toxins in native eels inhabiting a highly eutrophic local lake, an important food source for local Maori.

In November, the Department of Science and Primary Industries ran its annual chemistry competition for year 10 students from across south Canterbury. Traditionally, this has incorporated a practical activity and a quiz. However, in 2016 a problem-based scenario was used that highlighted the interaction between science and society. This year the competition thrived with more teams entering than ever before and fun was had by all.

## MANAWATU

The Manawatu Branch NZIC AGM was held on 5 December last year; a warm welcome to the new and continuing members of the committee. Special thanks to *David* ***Nixon*** for being our branch editor last year - he has stepped down to focus on his studies. Best of luck, David.

In February, *Michael* ***Brown*** and *Jenna* ***Buchanan*** presented their research at the Southampton-Australia-New Zealand Workshop on Molecular Magnetism 2 at the University of Otago.

The Institute of Fundamental Sciences warmly welcomes Associate Professors Wei Chen (National Engineering Research Center of Industry Crystallization Technology, Tianjin University) and Cui (Tracy) Zhang (Institute of New Catalytic Materials Science, Nankai University), who are visiting this year to collaborate with Professor *Shane* ***Telfer***'s research group.

3rd year chemistry student *Holly* ***Flay*** was awarded the Massey University 2016 NZIC prize for chemistry.

Massey University welcomed several speakers. *Geoffrey* ***Waterhouse*** (Associate Professor of Chemistry, University of Auckland) gave a MacDiarmid Seminar on 1 December entitled, *Development of efficient semiconductor photocatalysts for solar energy capture*.

James H. Clark (Green Chemistry Centre of Excellence, University of York) presented a seminar on 6 December entitled, *Green chemistry and the circular economy*.

Professor Rudi Marquez (Head of the Department of Chemistry at Xi'an Jiaotong–Liverpool University, China) gave a seminar on 14 December entitled, *Development of novel delivery vehicles for anti-parasitic drug delivery and transfection*.

Daniel Harki (Associate Professor of Medicinal Chemistry, University of Minnesota) delivered a seminar on 15 February entitled, *Taming the mutator: discovery of chemical probes of APOBEC3 DNA cytosine deaminases*.

## OTAGO

### University of Otago, Department of Chemistry

Huge congratulations to *Nigel* ***Perry***, who has recently been promoted to Professor. From the University of Otago press release: Nigel Perry has been working on natural products chemistry all of his career, starting with commercial flavour research in England after his first degree at the University of Bristol. He came to New Zealand in 1980 to do a PhD at the University of Otago, working on the unique chemistry of New Zealand's trees, including the strange structure of laurenene. A model of the molecule laurenene is being erected on the side of our new teaching building. Postdoctoral research at the University of Canterbury led to the discovery of several new classes of antitumour and antiviral compounds from sea sponges, and to SCUBA diving under the Antarctic sea ice. Nigel Perry returned to Otago in 1991 to set up the continuing collaboration with Plant & Food Research, including recent discoveries on honey chemistry.

The Plant Extracts Research Unit people have worked with two summer students this year. *Ani* ***Morison*** has been researching the perfume potential of the flowers of tī kouka, the New Zealand cabbage tree, on a Plant & Food Research Māori-Pasifika studentship, linked to Ngāi Tahu. *Sarah* ***French*** has been synthesising intermediates in the biosynthesis of hops bitter acids, also advised by *Bill* ***Hawkins***.

Otago hosted two very successful conferences in January/February. The 10th Australasian Organometallics Meeting (OZOM10) was held at the University of Otago, 10-13 January 2017, organised primarily by *Nigel* ***Lucas*** as well as *James* ***Crowley***, *John* ***McAdam*** and *Bill* ***Hawkins***. This was only the second time the conference has been in held in New Zealand and attracted 94 delegates, including 54 from around Australia. The programme offered a broad mix of talks covering many aspects of organometallic and coordination chemistry, with the majority of presentations given by postgraduate students and postdoctorals. The oral programme was complemented by two evening poster sessions at Arana College, which was also the venue for the conference dinner. Judges of the student talks and posters noted the high quality of the presentations and following extensive deliberations arrived at four prizes: Benjamin Frogley (Auckland) and James McPherson (UNSW) received the oral presentation prizes while Chenxi Kathy Ma (ANU) and Kenny Ortega (Otago) received the poster prizes. Based on feedback received by the organising committee, OZOM10 was thoroughly enjoyed by all delegates. *Nigel* ***Lucas*** (chair), on behalf the committee, particularly thanked the University of Otago (Department of Chemistry & Division of Sciences), NZIC (Otago Branch), RSC (NZ section) and CSIRO Publishing for their generous financial support of OZOM10. OZOM11 will be held in January 2018 at the University of Western Australia.

*Sally* ***Brooker*** chaired the SANZ-O-MAG2 magnetism workshop at the University of Otago 8-10 February. The 75 delegates were treated to a series of excellent tutorials on a wide range of magnetism topics, as well as to outstanding research talks by the six students selected from the abstracts by the advisory panel to compete for the Murray Prize. The runner up for the Murray Prize (prize sponsered by the MacDiarmid Institute) was *Santiago* ***Rodríguez Jiménez*** and the winner (prize sponsored by the University of Otago) was Katrina Zenere of the University of Sydney.

Professor Roberta Sessoli (Florence) is a William Evans Fellow and Professor Annie Powell (KIT), a visiting Professor, were both at the University of Otago during February/March with *Sally* ***Brooker***, starting their visit by presenting tutorials at SANZ-O-MAG2. Professor Eugenio Coronado (Valencia) also visited Otago University in February, presenting the final tutorial at SANZ-O-MAG2. After the workshop, Eugenio and Santi cooked up a paella for us.

Otago hosted NanoCamp 2017, the annual, week-long nanotechnology camp for high school students, run by the MacDiarmid Institute. 12 students listened to lectures and participated in practical exercises on Raman spectroscopy, computational chemistry, AFM, magnetic molecules, nanoparticles, Mössbauer spectroscopy and liquid crystals, as well as visiting the electron microscopy centre. Feedback from the students was extremely positive and special thanks go to *Guy* ***Jameson*** for doing a fantastic job in organising the camp. In the words of one student: *"…we would like to thank Guy Jameson for being there throughout the whole thing, and bringing us together into this little but awesome family".*

NanoCamp was run in concurrence with 2017 Hands On at Otago. The Department of Chemistry hosted week-long student projects in natural products and nanochemistry with a lot of fun had by both the students and the lecturers/demonstrators!

Snapshot of delegates at SANZ-O-MAG2, including in the front row (left to right): Dr Tony Keene (chair of SANZMAG1), Prof Keith Murray (after whom the Murray Prize is named) and Prof Sally Brooker (chair SANZ-O-MAG2).

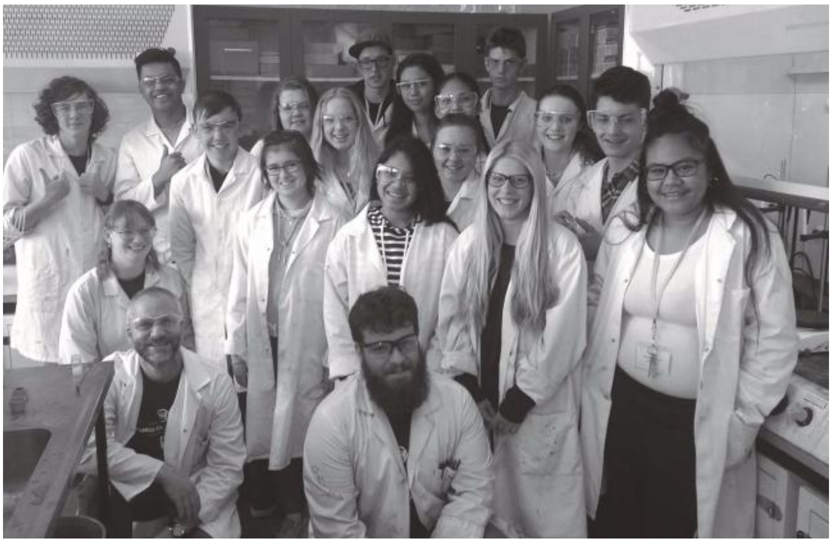
Student competitors for the Murray Prize (left to right): Santi Rodríguez-Jiménez, Ross Hogue, Edward O'Neill, Professor Keith Murray, Simone Calvello, Chanel Leong, Katrina Zenere.

The GeSIM Bioscaffolder 3.1 that *Jaydee* ***Cabral*** successfully raised funds for through the Lotteries Commission, the University of Otago's large equipment round and a variety of other places has arrived. Jaydee also presented a talk entitled, *In vitro adipogenic and osteogenic differentiation of bone-marrow derived mesenchymal stem cells using a chitosan/dextran-based hydrogel* at BioEngineering 2017: BioMEMS, 3D-BioPrinting & Synthetic Biology in Boston, USA in March.

The Department of Chemistry had a number of attendees at the Advanced Materials and Nanotechnology conference (AMN8) held in Queenstown in February. *Carla* ***Meledandri*** delivered a keynote lecture and contributed talks were given by *Keith* ***Gordon****, Nigel* ***Lucas****, Anna* ***Garden****, Ross* ***Hogue****, Santiago* ***Rodriguez Jimenez*** and *Humphrey* ***Feltham***. Posters were presented by PhD students *Joshua* ***Sutton****, Tom* ***Hall****, Fabrice* ***Karabulut****, Stuart* ***Malthus*** and *Hannah* ***Davidson***.

*Carla* ***Meledandri*** participated in an outreach event related to women in science in association with the AMN8 conference: *Science for survival – AMN8's nano trio* (www.catalystnz.org/events/event/science-for-survival-amn8s-nano-trio/). Carla was also awarded the NZIC Shimadzu Prize for excellence in Industrial and Applied Chemistry & the 2016 Division of Science Industry Links Award. Congratulations to three students from the Meledandri research group who have been busy finishing theses lately; *Dagmara* ***Jaskólska*** successfully defended her PhD thesis entitled, *Synthesis of shape-controlled magnetic nanoparticles and a novel route for their surface modification in suspension for biomedical applications*. *Gemma* ***Cotton*** submitted her PhD thesis entitled, *Silver nanoparticle antibacterial materials for applications within the oral cavity*, which is currently under examination. *Joe* ***Hughes*** successfully completed his MSc thesis entitled, *AgCl nanocomposites for dental applications*.

2017 MacDiarmid Institute NanoCampers with organiser Guy Jameson.



2017 Hands On at Otago chemistry project group with helpers Marina Roxburgh, Dave McMorran and Aidan MacKay.


Jaydee Cabral and the new GeSIM Bioscaffolder.

A recent addition to the labs of *Keith* ***Gordon*** is a Wasatch-based 1064 nm Raman experiment. This system allows rapid analysis of the vibrational fingerprint region, pertinent for current studies investigating meat and materials chemistry. In addition to the AMN8 conference, Keith also attended the Dodd-Walls 2017 Symposium in Dunedin and the 28$^{th}$ New Zealand Conference on Microscopy (MNZ) 2017 in Auckland; he spoke at both meetings and gave a workshop on Raman spectroscopy with Matthias Kresse (WITEC) at the MNZ meeting. He also attended the Infrared and Raman Discussion Group meeting in London (December 2016).

Keith's students have been busy lately; *William* ***Pelet*** did a summer scholarship with the Gordon group and according to him, he "thoroughly enjoyed completing his ten week summer internship with KCG. It was an invaluable experience learning and being guided by the members of the group! I learned many spectroscopic (mainly Raman) techniques while investigating the electronic properties of a series of ferrocene compounds. It was great to finally to get a taste of chemistry research and put to use some of the skills learned from my undergraduate degree."

Congratulations to *Georgina* ***Shillito*** who published her first paper as first author, looking at the photophysics of materials synthesised in the group of Nigel Lucas (*Inorg. Chem.*, **55**, 11170 -11184). *Greg* ***Huff*** also published a paper (*Inorg. Chem.,* **55** 12283 -12253) which looks at the excited state spectroscopy of donor-acceptor ligands and the effect of these with metal chelation. This work was collaborative with the group of *James* **Crowley.** *Jono* **Barnsley** published with an international group of researchers (based at Wollongong and Pennsylvania) who are looking at *Design and engineering of water-soluble light-harvesting protein maquettes* (*Chem. Sci.*, **8**, 316-324).

We welcomed *Joshua* ***Sutton*** who started as a PhD student in February working on photovoltaic polymers and *Joseph* ***Mapley*** who started as a honours student and will be working on the spectroscopy and computational chemistry of porphyrins modified with acceptor groups.

*Geoffrey* ***Weal*** has joined the group of *Anna* ***Garden*** working on optimisation techniques for metal nanoclusters and *Charlie* ***Ruffman*** and *Mingrui (Ray)* ***Yang*** have joined the group as honours students working on structure and catalytic properties of $MoS_2$ nanoribbons and atomistic potentials for CuPd nanoclusters respectively. Anna recently attended the eResearch NZ conference and spoke about using high-performance computing in rational catalyst design as well as speaking at the second annual Research Bazaar (ResBaz) workshop on using digital techniques in research. Professor Egill Skúlason (University of Iceland) visited Anna's group in February.

## WAIKATO

### University of Waikato

*Michèle* ***Prinsep*** attended the *AustraLarwood VII Symposium*, an annual meeting for bryozoologists in Wellington and gave a talk entitled, *Chemical ecology of New Zealand marine bryozoans current knowledge and future directions*.

### Scion

Scion hosted the *Plant Cell Wall Symposium* (jointly sponsored by Scion and the International Academy of Wood Science) on 21 February. This international meeting had around 40 delegates with speakers from New Zealand, Australia, USA, Germany, Korea and Sweden. The symposium concerned all aspects of plant cell wall science covering biology, chemistry, physics and analytical techniques. *Stefan* ***Hill*** gave a talk co-authored with Philip Harris of the University of Auckland entitled, *How many chains in a cellulose microfibril and why can't everyone agree?*

## WELLINGTON

The final Branch meeting of 2016 was the Royal Society of Chemistry Australasian Lecture, given by Cameron Jones (Monash) on 2 December. Professor Jones exemplified the catalytic and other characteristic transition metal properties of low oxidation state main group elements.

Wellington hosted the *Tertiary Teaching Symposium* on 2 February, organised by *Suzanne* ***Boniface***. This provided an excellent opportunity to learn about the educational advances our colleagues are developing and using. Flexible and technologically modern teaching labs (*Sarah* ***Masters***, *Jan* ***Wikaira***, *Dave* ***McMorren***, *Dave* ***Warren***), outreach innovations (*Mark* ***Waterland***), a computational chemistry concept inventory (*Matthias* ***Lein***) and large-class learning and tools (*Jo* ***Lane***, *Sheila* ***Woodgate***, *Suzanne* ***Boniface***) were subjects covered. The guest speaker was Daniel Southam (Curtin) who spoke on the changes in chemistry course accreditation to an outcome-driven model and improving teaching techniques for first year chemistry.

Christoph Hasenoehrl, previously our student representative on the Branch Committee, is now at WorkSafe NZ, employed as an advisor on hazardous substances.

## VUW

*Neil* ***Curtis*** attained the impressive milestone of 60 years of active service at Victoria University on 1 February, with a celebration on 10 February that included dedication of the X-Ray facility in honour of his contributions to structural and chemical science. For more information see page X of this issue.

*Emily* ***Parker*** has joined VUW in a joint appointment between the Ferrier Institute and the School of Chemical and Physical Sciences.

The Chemistry Teachers' Day, held on 30 November 2016, was the 17th of these annual occasions. To link with the NCEA achievement standard about "aqueous solutions", *Keith* ***Woolley*** from Wellington Water and *Andrew* ***Watson*** from Beka Engineering talked about how Wellington water is treated, which generated lots of lively discussion because of both the chemistry involved and the relationship of the topic to the everyday lives of the listeners. The quality of Wellington's water also emerged as a theme in the talk *Brewing - better beer through chemistry* given by *Kelly* ***Ryan***, a well-respected Wellington brewer from the Fork and Brewer – apparently the softness and quality of the water in Wellington provide good reasons to make beer here. *Monica* ***Handler*** from Victoria University's School of Geography, Environment and Earth Sciences spoke about applying elemental and isotopic analyses to Earth systems. It was interesting to hear the elements Mn and Fe featuring in her discussion about charting the changing chemistry of the Earth's crust through time and then later to note their potential to spoil the quality of our domestic water supplies. Other subjects covered were the Markovnikov rule, electronegativity and entropy. *What can you do with a chemistry degree?* was the theme of a panel discussion with graduates *Teresa* ***Vaughan*** (EPA), *Stephen* ***Tat*** (MBIE) and *David* ***Koedyk*** (Baldwins) who discussed and answered questions about their current jobs, their chemistry background and the usefulness of their chemistry study to their current role. As part of the day, teachers had the opportunity to share resources for their internal standards, and the annual forum, which focussed on the follow-on effect of schools not offering all three of the NCEA external standards.

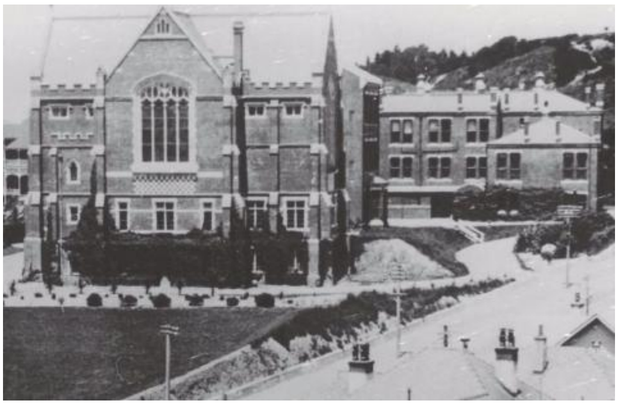
At the graduation ceremony on 14 December, eight chemistry PhD degrees were awarded! They were to *Thomas* ***Bevan*** (Supervisor *Joanne* ***Harvey***), *Joe* ***Gallaher*** (Supervisor *Justin* ***Hodgkiss***), *Matthias* ***Herzog*** (Supervisor *Jim* ***Johnston***), *Andrew* ***McGrath*** (supervisor *Richard* ***Tilley*** and *Robin* ***Fulton***), *Anne-Hélène* ***Puichaud*** (Supervisor *Ruth* ***Knibbe***), *Joanne* ***Rogers*** (Supervisor *Ken* ***MacKenzie***), *Eldon* ***Tate*** (Supervisor Jim Johnston) and *Jingjing* ***Wang*** (Supervisor Joanne Harvey).

International visiting speakers in late 2016 and early 2017 have given informative and thought-provoking seminars: James Clark (York) on sustainable and green chemistry, Thomas Bennet (Cambridge) on non-crystalline and gel-based MOFs, Henry Snaith (Oxford) on metal-halide perovskites for photovoltaic applications, Thomas Schimmel (Karlsruhe) on fabrication of surfaces that reduce drag, corrosion and fouling, and Egill Skúlason (Iceland) on electrochemical reduction of $CO_2$ and $N_2$.

Feature

# Neil Curtis celebrates 60 years at Victoria University

Wednesday February 1 saw Emeritus Professor Neil Curtis of the School of Chemical and Physical Sciences (SCPS) at Victoria University celebrate 60 years of continuous service. It marked a significant day in the history of Victoria University of Wellington.



Chemistry Departments of Victoria University courtesy of Image Services VUW. Upper: The West Wing Chemistry Building (1910-1957) (courtesy VUW Press); Lower L: The Easterfield Building (1958-1999) (VUW2-140); Lower R: With Gerry and Eileen Gordon, and the inaugural 1997 Curtis-Gordon scholars (VUW2-140).

Professor Neil F. Curtis. L: 1960 (VUW S-19); R: in his Easterfield lab in 1998 (Notlab).


Neil Curtis at the February 10 Celebration (VUW 32122-REC004 and REC020, courtesy Image Services VUW).

Neil joined the Department of Chemistry in the old Chemistry Building of what was Victoria University College. In those days the Chemistry Department was located in the West Wing alongside and attached to the Hunter Building. Neil has seen the subject of chemistry evolve through its ups and downs, from its then large staff of six to its present sixteen, through the final era of the old historic building, then the Easterfield Building (1958-1999) and subsequently the combined SCPS of today. One of his early students, Gerry Gordon, became a highly successful industrialist in the US and his recognition of Neil and this institution led to his $1 M donation and institution of the Curtis-Gordon Scholarships in 1997 that are still offered.

Apart from the routines of teaching and administration (including as a former Head of Chemistry), Neil rose through the ranks from appointment as a temporary lecturer (that transposed into a permanent position within a few months of joining) to become senior lecturer, reader, and then he was elevated to a personal chair in 1971. That transitioned to Professor of Inorganic Chemistry in 1987 after Professor James Duncan retired. However, it is Neil's dedication to research and scholarship that sets him apart from his peers and numerous colleagues. From his laboratory benches in the various buildings to that on Level 1 of the Laby Building, vacated just before Christmas, Neil's fame for vials, pots and beakers that provided a hue of magical colours grew. But woe betide anyone who changed their order for Neil knew what each contained and exactly where it was on the packed bench!

Neil's researches have been within the inorganic chemistry sphere where co-ordination compounds are now legion in the discipline and the arena of organometallics well known. Neil pioneered the area of macrocyclic metal-organics worldwide, an area which received recognition from the 1985 Nobel Prize in Chemistry. However, it was the benches of Victoria University that saw the first macrocyclic metal-organics come from the hands and skill of Neil Curtis. While science in this country was essentially unrecognised in the mid-1900s, it was at the retirement symposium run in his honour that appropriate recognition for his work was made.

To mark Neil's 60 years at Victoria the new X-ray diffraction facility in the SCPS was named after him at a ceremony on February 10. This saw two of his former PhD students and Lower Hutt residents, Peter Whimp (1967) and Keith Morgan (1979) present, together with colleagues from the former DSIR and Victoria University. We wish Neil many more years of enjoyment.

**Brian Halton**

# Fire! The chemistry that made man: an exceedingly brief history of a protracted courtship

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**Keywords:** *fire, pyrotechnology, pyrolysis, charcoal, coal*

## Abbreviations

B.C.E.: before the current era

B.P.: before present

C.E.: current era

Bya: billions of years ago

Kya: thousands of years ago

Mya: millions of years ago

## Introduction

*"He has discovered the art of making fire, by which hard and stringy roots can be rendered digestible, and poisonous roots or herbs innocuous. This last discovery, probably the greatest, excepting language, ever made by man, dates from before the dawn of history"* Charles Darwin.[1]

*"Having described everything that exists as a result of man's talent for making art copy Nature, I marvel to think that scarcely anything is brought to a finished state without the involvement of fire. It takes sand and melts it, as occasion offers, into glass, silver, cinnabar, lead, pigments and drugs. Ore-minerals are melted to produce copper. Fire produces iron and tempers it, purifies gold, and burns limestone to make mortar that binds blocks together in buildings. Other substances benefit from being subjected to fire more than once, the same substance taking on different forms after the first, second or third firings. Charcoal starts to acquire special powers when burnt and quenched; when it is apparently dead it's potency increases. Fire is a vast, violent element of Nature, and it is a moot point as to whether it's essence is more destructive or creative"* Pliny the Elder.[2]

Arguably one of the greatest scientists who ever lived and the most accomplished encyclopaedist of antiquity radically understated the importance of our ancestors first and most fundamental chemical manipulation, the control of fire. The oxidation of combustible material to release heat and light allowed the cooking of food, which acted not only to prolong its "shelf-life" but to increase the nutrients that might be extracted from it, with profound consequences for human evolution. Our ancestors were able to colonise colder climates and stay up past bedtime thanks to this self-sustaining chemical reaction. To Pliny's list of chemical feats requiring fire might also be added the production of pottery, the hardening of wood for spears and other implements and the burning of plant material to release minerals for fertilization, opening new areas to agricultural exploitation.

Very little of our chemical manipulations or indeed ourselves as humans has not been influenced by this fundamental "element", as the ancients frequently designated it.

## Fires dawn

Fire requires three components to exist: oxygen (or another oxidiser), fuel and heat (sufficient to reach the ignition temperature of the fuel). Fire may be extinguished by removal of any one of these components. An autolytic chemical chain reaction that can produce sufficient heat to sustain rapid oxidation or combustion is also required for fire to propagate. The burning of wood (the form of combustion most pertinent to the human experience) involves the heating of the wood using a match, friction, focused light, etc. resulting in the breakdown of the cellulosic material to form volatile gases at ~150°C (comprised of hydrogen, oxygen and carbon compounds). When the gases are hot enough (~260°C), the molecules break apart and the atoms recombine with oxygen to form water, carbon dioxide and other products releasing a great deal of heat. The visible light produced by a wood fire or candle originates from the heating of solid particles of soot produced by incomplete combustion.

Cellulose, one of the primary polymers in the cell walls of plants and the most abundant organic polymer on earth, is comprised of chains of D-glucose. The release of energy from glucose, whether via combustion or via cellular respiration, is considerable. The general equation for combustion of glucose is:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2 + 2870kJ$$

Until relatively recently, in geological terms, there was no such thing as fire, due to a lack of oxygen and fuel in the form of plant matter. The atmosphere currently contains a little less that 21% oxygen, but more than 4 billion years ago (Bya), oxygen was present only in trace amounts (roughly 1 ppm) with the bulk of the atmosphere being made up of nitrogen, carbon dioxide and water vapour.

There is evidence to suggest that the earliest single-celled life was formed around hot sulfurous vents called "black smokers", extracting energy from a range of inorganic elements and compounds including hydrogen sulfide, sulfate and sulfite compounds as well as nitrates and nitrites. These bacteria were anaerobic; not only did they live in the absence of oxygen, it was toxic to them. Modern anaerobes are killed by oxygen levels above 0.1% of present atmospheric levels. The anaerobes were, in great measure, superseded by photosynthetic cyanobacteria that produced oxygen as a waste product. The oxygen thus produced reacted with minerals dissolved in the oceans or eroded from rocks. The process of sequestering oxygen in the form of mineral oxides probably proceeded for hundreds of millions of years before the atmosphere and oceans started accumulating excess oxygen.[3]

While details remain uncertain, it appears oxygenation of the earth's atmosphere occurred in two steps. The first rise in atmospheric oxygen is thought to have occurred between ~2.45 and 2.2 Bya leading to an increase in atmospheric and ocean surface oxygen concentrations. Most of this oxygen was absorbed by the oceans and seabed rock before starting to outgas from the oceans around 1.85 Bya. The second increase appears to have taken place during the late Neoproterozoic era around 800-542 million years ago (Mya) leading to the oxygenation of the deep ocean ~580 Mya. The appearance of complex life around the start of the Cambrian period (~540 Mya) is probably due to the presence of high levels of oxygen, aerobic metabolism being more efficient than anaerobic, opening new possibilities for oxygen-consuming life.[4] Since the start of the Cambrian period, atmospheric oxygen levels have fluctuated between approximately 13 and 35%.

The fossil record of fire, in the form of the proxy measure charcoal, first appears in the late Silurian period (~420 Mya), and continues uninterrupted to the present. Charcoal appears with the establishment of land-based flora which occurred at approximately the same time.[5] Fire also requires a spark, sufficient energy to partially volatilise photosynthesised organic matter and set off a chain reaction, releasing enough surplus energy through oxidation to continue. The early earth offered a number of sources of initiating energy, with lightening predominating, but also including volcanic activity, falling rocks and meteor impacts.[6]

## Fire makes man

Fast forward to 3-5 Mya and fire, like rain and wind, would have been a regular feature of the lives of our hominid ancestors, although their use of it would remain passive and opportunistic until more recently. A bush fire might provide a smorgasbord of asphyxiated, charred and semi-cooked animals and insects, fire improved the taste of the meat and, more importantly, its preservation (roasted meat can remain edible for days). The warmth radiated at night following such a fire is also known to be enjoyed by many mammals and the remaining ashes provided salt. The benefits of actively collecting and preserving fire and actually making it would have been considerable.

Of all earth's species, only the hominids have made the step to controlling fire and employing it wilfully. When precisely this control over fire started is still a matter of debate. The consensus amongst most archaeologists, however, is that sufficient evidence exists to conclude that *homo erectus* was using fire in parts of Europe and Asia at least 400,000 years ago - long before the appearance of *homo sapiens*. A few much older sites in Kenya and South Africa point to the hominid use of fire as early as 1.4-1.5 Mya.[7]

Using, however, is not the same as kindling or manufacturing. The oldest stone tools date from ~2.6 Mya. The actual manufacture of fire (as opposed to its use) appears relatively recently ~250 thousand years ago (Kya). Our hominid ancestors would have required a number of attributes in order to achieve this transition including an erect posture with resultant freedom of movement of forelimbs, as well as at least the equivalent of ape intelligence in order to experiment and accumulate experiences.

Fire could be transported from hearth to hearth in the form of embers or torches reignited with grass, all without rekindling the source. Evidence for hearths include the presence of bones and stones changed by heat along with a hearth structure recognisable by the concentration of charcoal and ash, sometimes bordered by rocks. Thanks to the use or manufacture of fire, caves could be put to practical use as accommodation and migration into colder climates became possible. Fire provided heat and light as well as offering protection from predators; the smoke repelled snakes, rodents and insects.

The influence of fire on the evolution of our ancestors themselves was profound and took a number of forms. The extending of "daylight" in the form of a campfire would have influenced key hormonal cycles and socialisation.

Photoperiodicity, the response of organisms to cycles of day and night, is a function of the earth's rotation and the sun. Life forms have used the periodicity of these cycles to create patterns of activity, growth and reproduction.

Changing day and night cycles had major implications for the social structure of pre-humans, who, like other primates, were social animals. Language acquisition may have been enhanced by the extended day afforded by fire. We know that both fire light and industrial light suppress levels of the hormone melatonin. Melatonin is the only known hormone secreted by the pineal gland in animals and regulates sleep and wakefulness. Melatonin influences the pituitary gland, which in turn controls all other endocrine glands vital to the function of growth, reproduction, pigmentation and water balances.

Mammals sense the progression of the seasons from the night-time rise in melatonin. Critical day length is the minimum day length that will induce a physiological response. In most mammals, critical day length is the trigger initiating the breeding season. Seasonal breeders depend on the pineal gland to determine the timing of reproduction, since the pineal gland secretes melatonin according to the amount of daylight, which in turn depends on the time of the year.

The interruption of normal daylight would have consequences for all systems affected by melatonin. Melatonin directly affects female levels of estrogen and male daily testosterone surges, and is ultimately responsible for the onset of puberty. Mesopic light (between photopic daylight vision that employs cones to process light and scotopic vision that employs rod cells under low light conditions) at dawn and twilight are equivalent in brightness to the campfire and sufficient to suppress melatonin production. The ability to extend daylight liberated our ancestors from the natural light-dark cycles and seasonality, increasing their ability to reproduce and populate other niches. Consequent changes in the hormonal system and patterns of brain activity over time may have been a critical factor explaining the divergence of our species from kindred apes.[8]

If the light provided by fire influenced the levels of the crucial hormone melatonin in early hominids, offered protection from predators and access to previously inaccessible caves and cooler locales, the heat produced and its application to food had an equally profound effect on the physiology our ancestors.

Monkeys and apes dig in the ground to find corms, bulbs and tubers. These fleshy storage organs of plants provide good nutrition. Some, however, are so hard or so large they cannot be eaten, while others may contain toxic compounds. Placing them in the embers of a fire changes that so they soften, the pulp becomes accessible and the toxins are inactivated. The achievement of roasting tubers is most likely associated with *homo erectus*. Cooking food does not necessarily yield more energy in relation to raw food, the calorie density remains the same whether raw or roasted. This observation conflicts with the evidence that humans and animals get more energy from cooked foods. Cooking gelatinises starch, denatures protein and softens everything. As a consequence of these and other processes cooking substantially increases the amount of energy we obtain from food.

The world's major plant staples are all starchy foods (wheat, rice, maize, potatoes, cassava, etc.) and make up more than half the diets of tropical hunter-gatherers today. These foods may well have been eaten in similar quantity by our human and pre-human ancestors in the African savanna.

Our digestive system consists of two distinct processes. The first is digestion by our own bodies starting in the mouth and continuing into the small intestine. The second is digestion (more accurately fermentation) by 400 or more species of bacteria and protozoa in our large intestine, also known as the colon or large bowel. Raw starch is poorly digested, often only half as well as cooked starch. Starch granules eaten raw frequently pass through the digestive system whole, entering the colon unchanged. Studies have shown we use cooked starch very efficiently. The percentage of cooked starch that has been digested by the time it reaches the ileum (which immediately precedes the large intestine) is at least 95% for oats, wheat, potatoes, plantains, bananas, cornflakes and white bread.[9]

The principle way cooking achieves this increased digestibility is by gelatinisation. Starch inside plant cells comes in small dense packages of stored glucose called granules <0.1 mm in length. They are so stable that in dry environments they can persist for tens of thousands of years. However, as starch granules are warmed in the presence of water they start to swell. At around 58°C in the case of wheat starch, the bonds in the glucose polymers weaken, causing the tight crystalline structure to loosen. By 90°C, the granules are disrupted into fragments. At this point, the glucose chains are unprotected and gelatinised. The more gelatinised the starch, the more easily digestive enzymes can break it down.

The effect of cooking starchy foodstuffs is readily detected in blood glucose levels. Consume glucose or cooked cornstarch and blood glucose levels rise rapidly, but consume raw cornstarch and blood sugar levels remain low, peaking at less than a third of the level achieved by consuming cooked cornstarch.

Animal protein has been almost as important as starch in diets throughout our history. Until recently, whether the cooking of protein improved its digestibility was a matter of contention, but studies using egg protein have demonstrated that cooked protein is much more completely digested than raw protein. Cooking eggs in a fire was almost as easy as throwing in a starchy tuber to roast. For example, Australian aborigines would throw emu eggs into the air to scramble them while still intact then place them in hot sand or ashes, turning regularly to cook them evenly.

The effect of heating on food is not confined to improved digestibility, it also makes food softer and more tender. Heat softens tubers and has a tremendous effect on the material in meat most responsible for its toughness: connective tissue. The main protein in connective tissue is collagen which turns to jelly on heating. At 60-70°C, the helical structure of collagen starts to unwind, converting it into gelatine.

Tenderness matters! Softer foods are digested faster and thus demand less metabolic effort, leading to energy saving during digestion. Humans get more energy from cooked food than raw, not only because of processes such as gelatinisation and denaturing, but also because cooking softened food reduces the energy cost of digestion.

This energy saving may well have had a profound effect on the development of increased intelligence in hominids. Intelligence offers numerous evolutionary advantages. Clever species can forage in creative ways, such as extracting insects from holes with twigs and grasses, or lifting stones to crack nuts. Big-brained species can also manage complex social relationships, using coalitions more effectively. It was proposed in the mid-1990s that the reason some animals evolved big brains is that they had small guts, made possible by a high quality diet. Brains are exceptionally greedy for glucose. Despite being about 2.5% of our bodyweight, the human brain utilises around 20% of the calories consumed by an inactive person (primates on average use 13% and most other mammals less again, 8-10%). The rate of metabolism does not differ significantly between humans and the other primates, so the extra energy allocated to the human brain must come at the expense of something else.

Across the primate species, the size of the intestinal system varies considerably, with gut size being linked to the quality of the diet. Many vegetarian species, such as the apes, eat all day and their intestines work overtime consuming calories. The smaller the primate gut, the larger its brain. Cooking meant our ancestors did not have to allocate as much energy to simply digesting food and consequently could afford to power more brain tissue. Cooking, in all probability, is also the reason *homo erectus* (and humans) had such small teeth compared with other primates. Cooking results in less need to chew, affecting tooth size and the musculature of the jaw. Primates of our size spend approximately 48% of their time chewing whereas humans spend on average less than 10%.[10]

## Man makes fire

The heat generated by an open wood fire can achieve more than merely making food more digestible and providing warmth and illumination. Fire enabled the clearing of large swaths of land and the resulting ash fertilised soil.

When fire heats wood to 100°C its water boils and escapes as steam. As the wood dries it releases combustible gases at ~300°C, which ignite when they are exposed to a flame, gradually raising the temperature of the wood to ~600°C (depending on fuel and its moisture content an open fire might range in temperature from 500 to 900°C). Eventually the wood releases all its gases leaving charcoal and ash. Charcoal, which is essentially carbon, can burn at temperatures exceeding 1100°C, the amount of oxygen reaching the charcoal being the limiting factor.[11]

Wood ash provides important nutrients for plant growth, an observation that did not escape the attention of our ancestors as they made the transition from hunter-gatherers to settled agriculture in the Neolithic period. Slash and burn agriculture or fire-fallow cultivation employs fire to clear land making it suitable for preferred plants and animals as well as fertilising the soil. During the combustion of wood, organic compounds are mineralised and the basic cations transformed into their oxides which slowly hydrate and subsequently carbonate under atmospheric conditions. Below 500°C carbonates and bicarbonates predominate, oxides become prevalent above 1000ºC (a process that ultimately gave us concrete and produced the strong caustic compounds employed in early soap making). While values vary considerably, median values for macronutrients in wood ash are approximately 0.06% N, 0.42% P, 18% Ca, 0.97% Mg and 2.27% K. Major micronutrients include, in descending order of abundance; Fe, Al, Si, Mg, Mn, S, Na, Zn, Cu, Pb, Mo, Cr, Ni and Cd.[12]

Fire could be employed to clear land and cook food, but the latter ability, though crucial in regards to human evolution, was still primitive. Prior to the invention of cooking pots, cooking was clearly possible but rudimentary. Tubers might be tossed into a fire and left to bake or meat placed upon a primitive spit. Hot stones near the flames might be used to heat pastes made from cereals or nuts mixed with water, but, until Neolithic cooks learned to make pottery vessels, cooking in the modern sense could not begin and many potential food sources remained unexploited. The use of ceramic cooking pots meant that grains and vegetables could be made into pottages, tubers and meat could be simmered in water to create soups and stews (a more energy efficient process than heating on a rock beside the fire). Babies could be fed easily digested porridges or mash and weaned earlier, freeing their mothers for other tasks.[13]

Clay is composed of fine-grained natural rock or soil material that is plastic when wet but becomes hard, brittle and non-plastic on drying. Heating clay at temperatures achieved in open wood fires results first in loss of water of hydration and the partial (depending on the temperature reached and its duration) vitrifaction and aggregation of the rock grains to produce a durable, fire-resistant material (essentially turning the clay back into the rock from which it came), starting at temperatures of around 450°C.

Our ancestors may have noted the effects of heating on clay simply by witnessing the hardening and colour change of clay beneath a hearth after a fire died. Although the manufacture of useful objects using stone, bone and other natural materials had reach a high level of sophistication by the end of the Palaeolithic period, the first thoroughly artificially-fired clay objects can be credited to the Gravettian figurine makers at Dolni Vestonice (located in Moravia in the Czech Republic), dated to around 30,000 B.P. These figurines took the form of rather fleshy clay goddesses or fertility figures.[14] Clay figures of men, women, animals and birds were often baked in household fires after this time, but it was not until around 10,000 B.C.E. that the oldest pottery vessels appeared, made by the Jomon people of Japan. The Jomons (the name means "cord markings" in Japanese) lived along the seacoasts of Japan. Jomon ware was used for cooking, food preparation and storage and was impressed with rope, shell or matts. It appears pot-making sprung up independently in multiple areas throughout the world during the Neolithic period, generally developing when a culture embraced agriculture and became sedentary. Handsome cooking pots and other utensils were being made in Mesopotamia two thousand years after the Jomons began making their wares. Soon after, the pre-dynastic peoples along the Nile in Egypt were making pottery as well.[14]

Pottery making represented one of the most straightforward pyrotechnological processes. In order to move forward, however, to achieve the higher temperatures that would allow the extraction of important metals from their ores, improvements in fuel, insulation (in the form of refractory materials used to construct furnaces) and air supply would be required.

While an open fire might be sufficient to partially vitrify clay objects (maximum temperature of open fires is around 900°C at best) and melt metals such as tin (m.p. ~232°C) and lead (m.p. ~328°C), metals such as silver (m.p ~960°C), gold (m.p. ~1063°C), copper (m.p. ~1083°C) and iron (m.p. ~1540°C) required higher temperatures than could be produced by an open fire.[15]

It was at this point in time, after hundreds of thousands of years of experience, humans began to truly manipulate fire by making changes to the fuel and oxygen supply, to produce ever increasing temperatures and the duration of heating, as well as improving the means of ignition.

Charcoal was probably the fuel source that enabled the first commando raid into the smelting of metals such as copper and its alloys. Its origins are bound up with the beginnings of metallurgy ~5000 years ago. Attempts to smelt metals with wood fires would have been less than successful, as when wood is burned there is a large quantity of water and other volatiles driven off which limits the temperature the fire can achieve. Burning charcoal, on the other hand, produces a much higher fire temperature with little smoke, ideal conditions for metal smelting. The earliest method of producing charcoal probably involved the 'pit kiln' process in which wood was slowly burned in a shallow pit covered with soil. The intensity of this fire could be controlled by opening and closing air inlets, which ensured the wood smouldered, rather than burst into flames. All iron production until about 1700 C.E. was based on the use of charcoal, until deforestation made alternate fuel sources, such as coal, attractive and necessary.[16]

Coal is a fossil fuel formed when dead plant matter is converted into peat, which in turn is converted into lignite, then sub-bituminous coal, after that bituminous coal, and lastly anthracite. This involves biological and geological processes that take place over time.

Coal was used by the early Bronze Age inhabitants of Wales to cremate their dead. Known in Roman Britain, it could be readily carved and polished to produce jewellery as well as being flammable. Roman soldiers burned coal in their forts and priests of Minerva, the goddess of wisdom, burned coal at her shrine in Bath. Its use as a fuel was not, however, widespread and warranted little mention by Roman authors. By the time of St Bede (700s C.E.) the practice of burning coal had virtually died out. It was not until the 1100s that coal's use as a fuel was revived. Coal, however, is not suitable for the smelting of iron, being high in impurities, especially sulfur. It was not until around 1709 when an English iron worker, Abraham Darby found a way of making cast iron using coke produced from coal that the use of charcoal declined in the West and the industrial revolution, powered by Britain's substantial coal deposits, took off.[17]

The driest, cleanest burning, most efficient fuel is pyrotechnically pointless without enough oxygen to burn it. Indeed, getting enough oxygen to a fuel to achieve the temperatures necessary for the smelting of copper and iron ores was probably more of a problem than the fuel itself. A particularly hot fire, fanned by wind may suffice to smelt lead from one of its ores, galena, but these conditions would, at the very best, produce only a few blobs of copper from malachite ore. The efficient smelting of copper (m.p. ~1083°C) would require higher temperatures and a reducing atmosphere. Charcoal provided part of the answer but improvements in the means of delivering air were also crucial.[18]

The supply of air to a fuel bed constitutes the primary means of control over the rate of heat generation and the performance of a furnace. The weight of air necessary for combustion is considerably greater than the weight of the fuel to be burned. One kg of charcoal requires approximately 5 kg of air for its combustion. Therefore there is a considerable weight of air that needs to be drawn or pushed through a fuel bed to achieve full combustion. In early antiquity, combustion air supply for charcoal fuel came from three sources: ambient air drawn in by natural draft or wind, human breath or a bellows.

Human breath through blow pipes has limited efficacy when it comes to increasing the temperature of fire. Human breath, a waste product from an oxidation reaction in the human body, contains only about two-thirds as much oxygen as ambient air. Human breath also contains higher levels of $CO_2$ and water vapour that conspire to absorb heat in combustion reactions. The amount of air that might be delivered using breath was also limited by human physiology; the sustainable rate of air output of an adult human male is between 70 and 80 litres per minutes. However, using sufficient blow pipes, temperatures sufficient to melt and smelt copper and bronze could be achieved.

Natural draft was also employed to provide oxygen, this was produced when relatively less dense, buoyant hot air above the fuel bed generated a negative pressure by rising and pulling in cooler surrounding air. Prevailing wind might be used with tuyeres (a nozzle through which air is forced into a smelter, furnace or forge) arranged to face the wind, resulting in an appreciable increase in air flow through the fuel bed. This additional pressure does not become significant until wind velocities exceed about 20 km/hr. Although wind furnaces can be employed to produce iron blooms, such furnaces are entirely dependent on a steady wind velocity and locations where such steady wind conditions might be found are rare.

Bellows eliminated the issues of limited capacity using breath and the vagaries of weather with wind furnaces, offering the best of both worlds. The basic bellows concept involves drawing air into a cavity, trapping it with one or more valves, then expelling it by a force that decreases the volume of the cavity. While numerous means of doing this have been developed, worldwide three methods prevail. The first consists of simple leather bags, the second ceramic or wooden pots with loose, flexible leather covers, with valves operated by finger or toe and the third employed wooden leaves hinged at one end, with sides and opposite end closed by flexible leather by automatic valves. Using a bellows resulted in much less physical effort being required to maintain a fuel bed at a desired temperature and considerably higher temperatures were possible.[19]

We do not know precisely when the bellows was invented (possibly the 5$^{th}$ century B.C.E.) but by the 4$^{th}$ century B.C.E. the double-acting piston bellows was in widespread use in China. This device allowed a continuous stream of air (or liquid) to be expelled. The ability of the piston bellows to provide continuous blasts of air was crucial in the superiority that Chinese metallurgy and ceramic production enjoyed for centuries after its introduction. Essentially, the device involves a piston being pushed in and pulled out of a solid cylinder or box. Feathers or pieces of paper are wedged around the piston to make it airtight and to lubricate its passage. There is an inlet valve at each end of the box allowing air to be sucked in whether the piston is being pushed or pulled and expelled by either motion into a side chamber connected to a nozzle or tuyere.[20]

The means of igniting a fire underwent technical improvements as well. While not the equivalent of a friction match one might readily purchase today (it was English chemist John Walker in 1826 who first invented matches that would ignite when struck against a rough surface), early matches consisted of wood soaked in sulfur. Having a low ignition temperature, these would burst into flame at fire's slightest touch. Such matches were first mentioned by the 1st century C.E. Roman poet, Martial (Epigrams I 41, XII 57),[21] although the Chinese too lay claim to the invention. Purportedly, in 577 C.E. court ladies short of tinder due to a military siege in the Chinese Kingdom of Northern Ch'i created matches using pinewood and sulfur.[20] Our ancestors knew the immense power, potential and danger of fire, which explains why Prometheus was at once loathed by the gods and lauded by humanity. Mankind's relationship with fire does not end with matches, though this essay must needs end somewhere. The preceding paragraphs constitute, at best, a mad-dash through time, with only the very briefest stops to smell the historical roses. Originally envisaged as a first chapter in a book about chemistry in antiquity, I hope the paragraphs above engender just a little appreciation of the importance of this most fundamental of man's chemical manipulations and our continuing fraught Mickey Mouse/Fantasia-like relationship with **FIRE**.

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Article

# Materials within New Zealand geothermal environments

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**Keywords:** *metal, atmospheric corrosion, geothermal, hydrogen sulfide*

## Summary

New Zealand has numerous geothermal systems, particularly in the central part of the North Island. Geothermal emissions with sulfur-containing gas species, such as hydrogen sulfide and sulfur dioxide, can be aggressive towards most construction materials. These may include metals, timbers, paints and composites. This paper reports the preliminary results derived from BRANZ field exposure testing in Rotorua, a population centre with known influences of geothermal activity on the performance and durability of materials, buildings and infrastructure assets. It has been found that material deterioration in geothermal environments can be very different from that in other environments, such as marine, industrial and rural. The first-year corrosion rates of some metals were also found to correlate well with hydrogen sulfide concentration. This research will continue to produce more results to better understand the mechanisms behind unusual material deterioration, and to develop guidance for material and protection specification in geothermally influenced environments.

## Introduction

New Zealand has numerous distinctive geothermal systems in the North and South Islands. They are mainly as geysers, springs, mud pools, steaming grounds, hydrothermal eruption craters and fumaroles and can discharge various gaseous species, including predominantly steam (water vapour), $CO_2$, $SO_2$, $H_2S$, $NH_3$, $CH_4$, HCl, HF, $N_2$, Ar and $H_2$.[1-5] Within these, the sulfur-containing species, e.g. sulfur dioxide ($SO_2$) and hydrogen sulfide ($H_2S$), can cause many durability and performance problems with susceptible materials. For example, airborne $H_2S$ at high concentrations is highly corrosive to aluminium (Al), copper (Cu), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn).[6] It can also cause blackening of some paints with metal-based pigments or drying agents, especially basic lead carbonate pigment, $2PbCO_3{\cdot}Pb(OH)_2$.[7] Exposure to geothermal environments can result in discolouration and severe decay issues to timbers.

A unique aspect of New Zealand's geothermal systems is that most of them have conurbations nearby. For example, more than sixty-five thousand people usually live in Rotorua, one of the major cities located within the Taupo Volcanic Zone (TVZ), according to 2013 census from Statistics New Zealand. Material deterioration problems have been frequently observed with buildings and infrastructure assets within these geothermal regions, resulting in huge costs for repair and maintenance, and also high risks to emergency management. The New Zealand Standard, NZS 3604: Timber-framed buildings, then requires Specific Engineering Design for building and construction within environments influenced by geothermal hot spots.[8]

However, a survey of the literature showed that limited research had been done to investigate the interactions between geothermal discharges and building and construction materials. In the 1980s, BRANZ measured the atmospheric corrosion rates of mild steel and hot dip galvanised zinc coating at 168 sites across New Zealand.[9] Some exposure sites were within geothermally

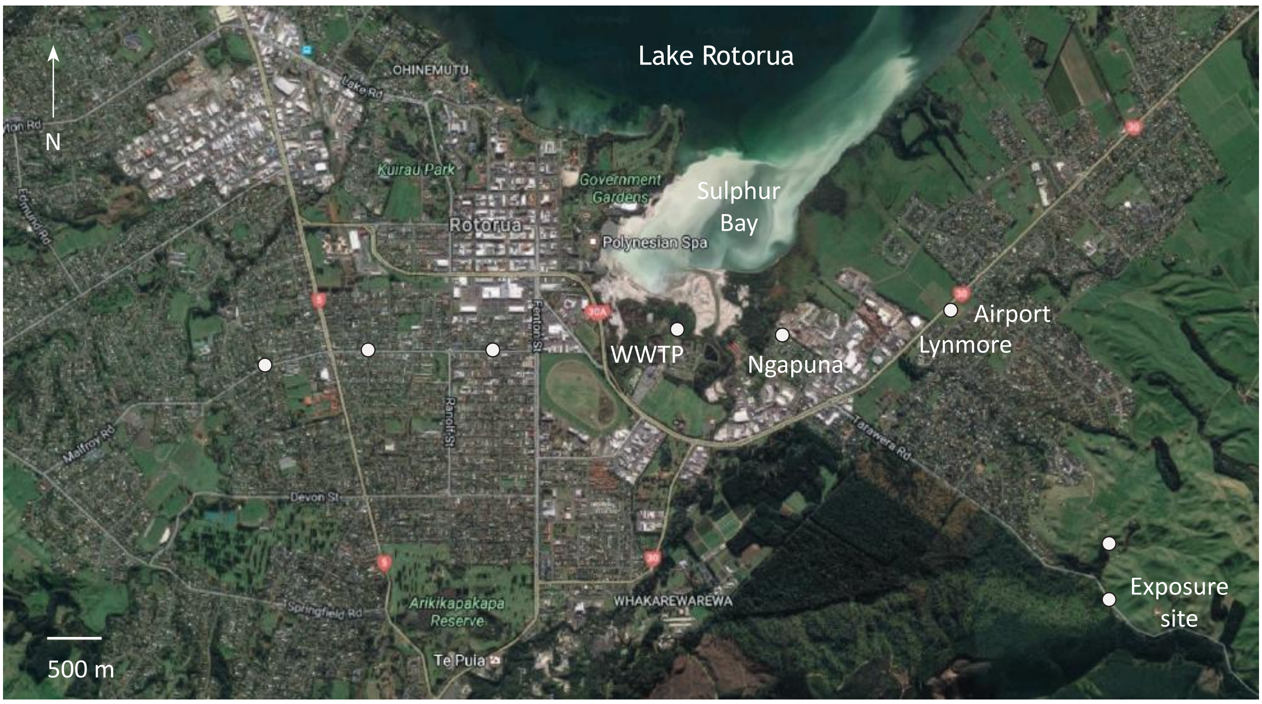



*Fig. 1.* Exposure sites in Rotorua.

influenced regions, particularly the Taupo Volcanic Zone (TVZ). Extremely high mass losses, 4800 g/m$^2$ and 141.6 g/m$^2$, were observed with mild steel and zinc coating in the first year of exposure at the Lake Rotoatamaheke site. However, corrosion rates measured at other sites were comparable to those in other typical New Zealand atmospheric environments. In the 1990s, the then Industrial Research Ltd (IRL) also evaluated the performance of 27 types of metallic materials (carbon steels, low alloy steels, stainless steels, and nickel-based alloys) when exposed to geothermal volcanic environments at White Island, New Zealand.[10] These studies gave very little guidance to design, specification and maintenance of buildings in geothermal regions, except a general warning to be wary. International study on this topic is also limited since most geothermal sites in other countries are sparsely populated, thus there is low demand for this knowledge.[11]

This research aims to carry out systematic studies to address this information shortage. Its outputs will support the development of material specification schemes for design, construction, and maintenance of new and existing buildings and infrastructure assets in New Zealand's geothermal regions.

## Experimental

### Field exposure testing sites

Rotorua is a large population centre in the TVZ and has many unique geothermal systems. Surface geothermal activities are mainly confined to three areas: Whakarewarewa/Arikikapakapa, Kuirau Park/Ohinemutu, and Government Gardens/Ngapuna/Sulfur Bay.[12,13]

Six field exposure sites were selected and established, roughly along a straight line crossing the Rotorua city from the west to the east (Fig. 1). Three of them are on the south side of Malfroy Road (west city area). The remaining three are in a Waste Water Treatment Plant (WWTP, close to Sulfur Bay), Ngapuna and Lynmore (east city area), respectively. This site arrangement is to investigate the concentration and distribution of sulfur-containing species in the city region and their influences on local atmospheric corrosivity and material degradation.

### Environmental monitoring

The environmental information, e.g. ambient temperature, humidity, rainfall and wind speed, for Rotorua was downloaded from the National Climate Database, CliFlo, NIWA. The meteorological station is located within the Rotorua Airport, ~6 km northeast from the city centre. The concentration of airborne hydrogen sulfide ($H_2S$) at each site was measured with diffusion tube sensors (DIF 200 RTU). With this technique, hydrogen sulfide is chemically adsorbed and transformed into a stable compound in the black acrylic tube. It is then quantitatively determined by UV/Visible spectrophotometry with reference to a calibration curve derived from the analysis of standard sulfide solutions. The typical monitoring period was around 3 weeks. Within this research, the $H_2S$ tube sensors were installed ~2 meters above the ground.

### Materials

Mild steel and zinc coupons with typical dimensions of 150 × 100 mm were used for this atmospheric corrosion testing. The surface of the mild steel coupons were grit blasted to SA2.5 grade while the surface of the zinc was finished with 800 grit SiC paper. A roughened surface was chosen to provide optimum conditions for absorption reactions and promotion of corrosion within reasonable time frames. Their nominal chemical compositions are given in Table 1.

The dimensions of each sample were measured accurately to calculate the exposed surface area. Prior to exposure, they were cleaned with acetone, dried with hot air and weighed to 0.001 g. The numbered samples were then sealed in separate plastic bags, shipped to the exposure sites and mounted onto exposure racks using nylon fasteners.

### Sample testing

Samples were retrieved for laboratory analysis after one-year exposure. To monitor the atmospheric corrosion process, the mild steel samples exposed at the Waste Water Treatment Plant site were removed after 1, 3, 6 and 12 months. Their surface morphology was examined visually and microscopically. The corrosion products were then cleaned thoroughly following the procedures recommended by ASTM G1.[14]

- Mild steel: 0.5 L/L hydrochloric acid (HCl, specific gravity = 1.19) + 3.5 g/L hexamethylenetetramine ($C_6H_{12}N_4$) at 20-25$^o$C; and
- Zinc: 100 g/L ammonium chloride ($NH_4Cl$) at 70$^o$C and/or ammonium persulphate 20 g/L $(NH_4)_2S_2O_8$ at 20-25$^o$C.

The chemically cleaned samples were then washed with flowing water, dried with hot air and re-weighed. Several clean, unexposed mild steel and zinc samples were also

***Table 1.*** Chemical composition of metals

| Metal | Element (wt.%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Mild Steel | C | N | Al | Si | P | S | Ti | V |
| | 0.18 | 0.003 | 0.007 | 0.04 | 0.027 | 0.014 | 0.005 | 0.002 |
| | Cr | Mn | Ni | Cu | Mo | Sn | Nb | Fe |
| | 0.03 | 0.69 | 0.02 | 0.03 | <0.001 | <0.001 | <0.001 | Bal. |
| Zinc | Al | | Cu | | Ti | | | Zn |
| | ≤0.015 | | 0.8-1.0 | | 0.07-0.12 | | | Bal. |

immersed into the chemical solutions for the same period as the cleaning process. Their mass losses were recorded for corrosion rate correction.

## Results and discussion

### Airborne hydrogen sulfide concentration

The average concentrations of hydrogen sulfide at the six sites during a three-week exposure (started late December 2014 and late June 2015) are given in Fig. 2. In general, the $H_2S$ concentration on the west or the east side was much lower than that in the central part of the city. For example, the highest concentration, 27.7 ppb, was observed at the Waste Water Treatment Plant site close to Sulfur Bay (for monitoring started late December 2014). This concentration could be ~150 times higher than that measured at the far west location. Further, it appeared that the $H_2S$ concentration on the east side was slightly higher than that on the west side.

This location dependent $H_2S$ concentration is similar to that observed by other researchers using either passive samplers[15] or Chemcassette® tape.[16] However, these monitoring processes showed somewhat different $H_2S$ concentrations. This is mainly a result of differences in exact monitoring location, instrument and measurement period. Overall, these results still consistently indicate that the area running north-south through central Rotorua city is very likely to experience high $H_2S$ concentrations. Meanwhile, the west and east have lower concentrations.

This measurement also showed that the averaged three-week $H_2S$ concentration in the air was dependent on monitoring period or season. For example, the $H_2S$ concentration at the Waste Water Treatment Plant site was measured to be 5.2 ppb during June – July 2015, i.e. 5 times lower than that measured during December 2014 – January 2015. This decreasing trend was also observed at the west city sites. This might be partly related to the climatic difference between these two measurement periods. From Fig. 3, it can be seen that the June - July 2015 period has a higher rainfall than the December 2014 – January 2015 period. This is expected to dissolve more $H_2S$ into rainwater, i.e. lowering its concentration in air. However this could not explain higher $H_2S$ concentrations observed at some east city sites during the rainy season.

### First-year corrosion rate and surface morphology

The atmospheric corrosion rates of mild steel and zinc after one-year of exposure (from December 2014 to December 2015) at the six sites in Rotorua city are presented in Fig. 4. The corrosion rates of both mild steel and zinc show a large dependence on exposure site location. Corrosion rates lower than 200 g/m$^2$/year were measured with mild steel at three sites in the west and east areas of the Rotorua city, i.e. 216 & 116 Malfroy Road and Lynmore. Corrosion was severe at the other three sites in or close to the central part of the city. The corrosion rates, particularly those of mild steel, are very high when compared with those obtained from exposures in New Zealand's industrial and/or marine environments.[17,18] The highest was observed at the Waste Water

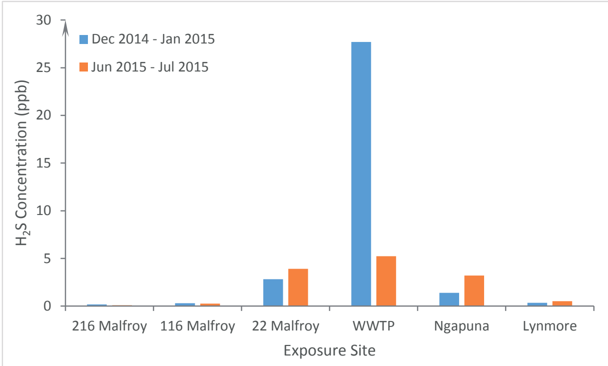



***Fig. 2.*** Average $H_2S$ concentration during three-week monitoring.

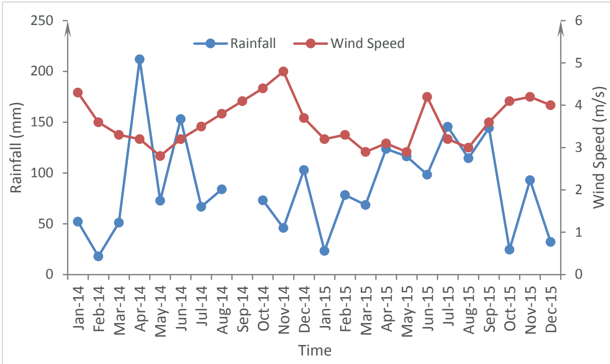



***Fig. 3.*** Rainfall and wind speed data from January 2014 to December 2015.

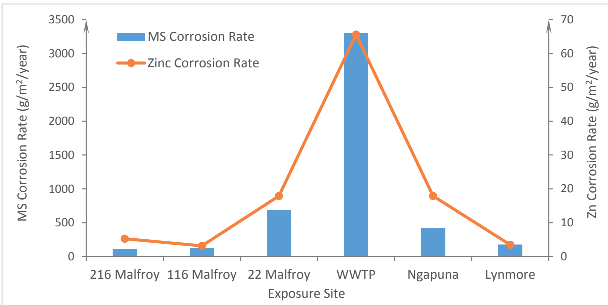



***Fig. 4.*** Atmospheric corrosion rate of mild steel and zinc after one-year exposure in Rotorua.

Treatment Plant site, 3302 g/m$^2$/year and 65.6 g/m$^2$/year for mild steel and zinc, respectively. The atmospheric corrosivity of this site can then be classified as CX (Extreme), the highest category defined by the ISO 9223:2012.[19]

This large difference in corrosion rates measured at different exposure sites was also strongly supported by the difference in surface morphology of the corroded samples. At the Waste Water Treatment Plant site, an extremely thick corrosion product layer was formed on the mild steel samples. A relatively thick top sub-layer was easily detached from the sample surface during characterisation (Fig. 5a). Cracking and fracture features could also be observed on the exposed underlying surface (Fig. 5b). In comparison, the corrosion product layer formed on the mild steel sample exposed in the west city area was relatively compact with less physical defects (Fig. 5c).

Similarly, the corroded surface of the zinc sample exposed at the Waste Water Treatment Plant site was rough. It had lots of clusters growing from underlying pit-like features. They were connected to each other and developed into a network-like structure that was sitting on the top of a relatively dense layer composed of fine particles (Fig. 6a). The corrosion products on zinc exposed in the west city area, e.g. 216 Malfroy Road, were roughly growing along the original fine grinding lines to form a relatively uniform, compact and thin layer (Fig. 6b).

As reported in Section 3.1, airborne $H_2S$ concentrations on the west and east sides of Rotorua city are much lower than those in or close to the central city. The location dependences of corrosion rate and $H_2S$ concentration are then very similar, i.e. a high $H_2S$ concentration corresponds to a high corrosion rate. This observation, similar to other studies,[20] implies that $H_2S$ plays an important role in corrosion of metallic materials exposed at these six sites.

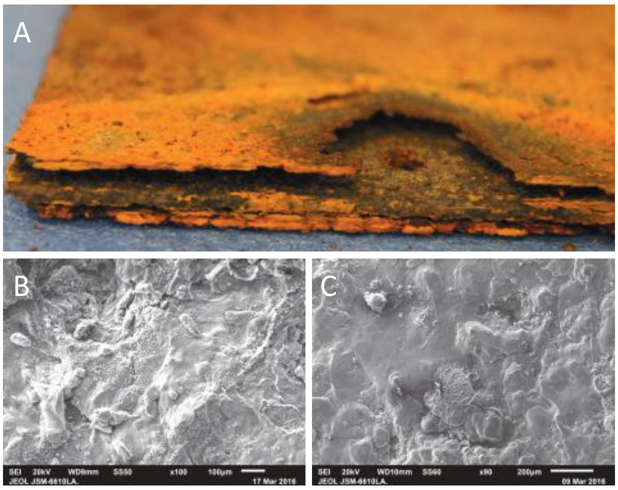



***Fig. 5.*** Surface morphology of mild steel sample exposed in Rotorua at **(a & b)** the Waste Water Treatment Plant and **(c)** 216 Malfroy Road in the west city area.

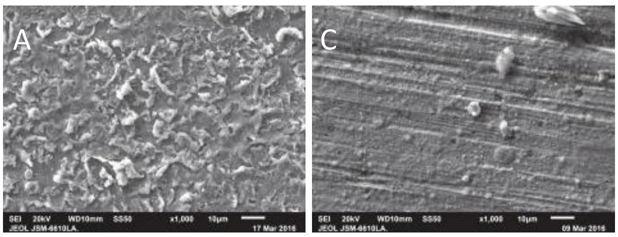



***Fig. 6.*** Surface morphology of zinc exposed in Rotorua at **(a)** the Waste Water Treatment Plant and **(b)** in the west city area.

## Time dependent corrosion rate

The time dependent corrosion rate of mild steel samples exposed at the Waste Water Treatment Plant (Rotorua) and Judgeford (Wellington) is given in Fig. 7. Previous field tests in a variety of environments showed that atmospheric corrosion of mild steel will normally decrease with time.[21-24] The reason is that corrosion products formed could act as a barrier for inward or outward mass transfer, therefore providing a certain level of protection to the underlying steel substrate. The present result shows that this behaviour might not be applicable to the short-term corrosion processes occurring in environments with relatively high concentrations of sulfur-containing species, e.g. $H_2S$. In the first three months, the corrosion rate of mild steel increased significantly from 2677 to 3719 g/m$^2$/year. After 6 months, the corrosion rate showed a decreasing trend, from 4019 to 3302 g/m$^2$/year. However, the corrosion rate measured after 12 month of exposure was still higher than that measured after 1 month of exposure.

This observation indicates that the corrosion products formed in the initial stage on the sample surface could not provide any protection to the underlying substrate. Instead, their formation was, to some extent, promoting corrosion. This behaviour has not been commonly observed in other atmospheric environments. The mechanisms behind this unusual behaviour are not clearly understood however, it is supposed that the following might be contributing.

- Morphological observations during the initial exposure stage showed that the surface of the mild steel samples was very rough and covered with corrosion products composing porous clusters, open-mouth bubbles and cracks (Fig. 8). These morphological features could significantly increase the effective surface area of the exposed sample. This could promote surface absorption of corrosive contaminants from the air, therefore increasing the local concentration of corrosive species.
- As previously shown, $H_2S$, a highly corrosive species to steel, has a very high concentration at this site. Climatic monitoring showed that the 2-3 months after December 2014 had relatively low rainfall and wind speed (Fig. 3). This climatic condition favours the long-term presence of $H_2S$ in the air at high concentrations.

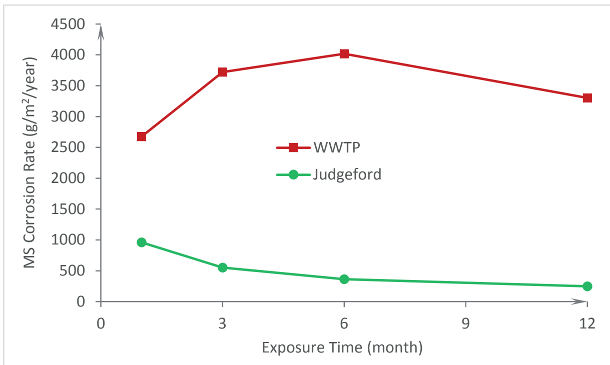



***Fig. 7.*** Time dependent corrosion rate of mild steel samples exposed at the Waste Water Treatment Plant (Rotorua) and Judgeford (Wellington).

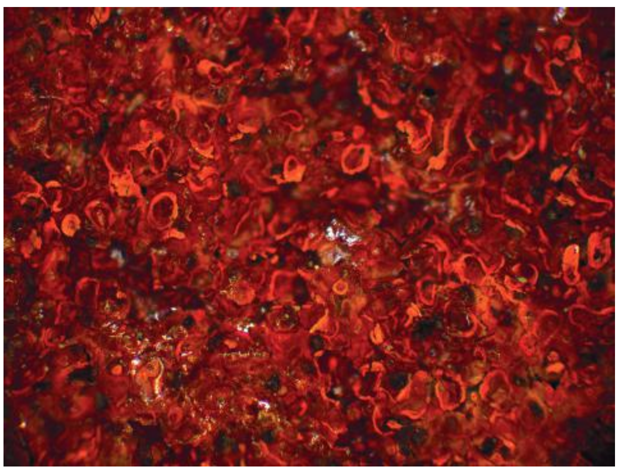


***Fig. 8.*** Surface morphology (x32) of mild steel after one month of exposure at the Waste Water Treatment Plant site in Rotorua.

### Correlation between $H_2S$ concentration and metal corrosion rate

Atmospheric corrosion of metals is mainly governed by the interactions between climate, pollutant and material. In relatively clean and benign environments, moisture and/or rainwater will significantly contribute to corrosion as they create an environment promoting electrochemical corrosion processes. In contaminated atmospheres, such as marine and industrial, corrosion of metals will be accelerated by chloride-containing particles and/or sulfur-containing species. This is mainly because these contaminants could interact with climatic factors to create more aggressive micro-scale environments on the metal surface, e.g. higher time of wetness and lower pH, and to produce corrosion products of lower protection capability.

Since sulfur-containing species, particularly $H_2S$, are present at some exposure sites at high concentrations, it is expected that they will exert some influence on the corrosion of the metals exposed in geothermal areas. As reported in Sections 3.1 and 3.2, the location dependences of $H_2S$ concentration and mild steel corrosion rate are very similar, indicating a potential correlation between them.

In this study, the $H_2S$ concentration was plotted against the first-year corrosion rate of mild steel (Fig. 9). Two types of trendlines were tested. The first used linear fitting with two slightly different groups of data points (Fig. 9 top). One only used the five sites with relatively low $H_2S$ concentrations, i.e. excluding the Waste Water Treatment Plant site. This is because a turning point existed where the $H_2S$ concentration increased sharply from 2.82 ppb to 27.7 ppb. A correlation of $H_2S$ concentration ($x$, in ppb) and mild steel corrosion rate ($y$, in g/m$^2$/year) was produced correspondingly as Equation 1 with an $R^2$ value of 0.9902.

$$y = 217.18x + 86.249 \qquad \text{(Eq. 1)}$$

The other fit used all the six sites and produced Equation 2 with an $R^2$ value of 0.9926.

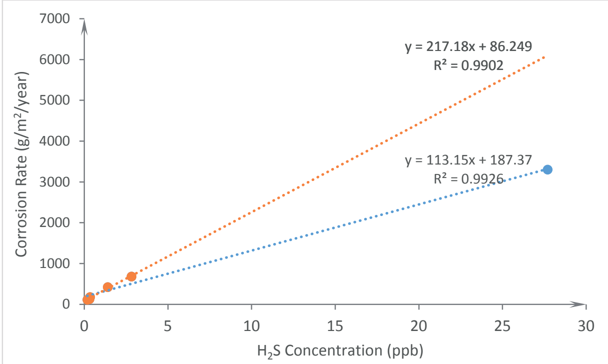
$$y = 113.15x + 187.37 \qquad \text{(Eq. 2)}$$

The second option was using power fitting with all data points (Figure 9 bottom), producing Equation 3 with an $R^2$ value of 0.9951.

$$y = 339.03x^{0.6819} \qquad \text{(Eq. 3)}$$

These results indicate that in geothermally influenced areas, the environmental $H_2S$ concentration could be correlated with mild steel atmospheric corrosion rate through some functions. Further, it seems that the power series produces a slightly better fitting result.

The concentration of $H_2S$ used in this fitting was only measured in the initial 3 weeks of field exposure. Meanwhile, the metal corrosion rate was derived after 1 year of exposure in the environment concerned. As previously discussed, $H_2S$ concentration is highly variable, on daily and/or monthly scales. In areas with relatively low $H_2S$ concentrations, mass loss due to direct $H_2S$ attack might still be limited and climatic factors may exert influences. Under these conditions, the linear fitting model would not always produce excellent results.



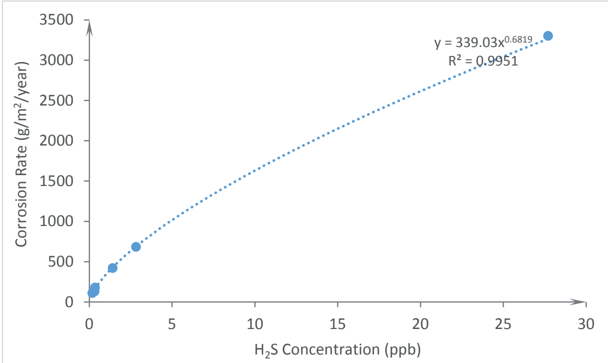




***Fig. 9.*** Correlation between $H_2S$ concentration and first-year mild steel atmospheric corrosion rate (top: linear fitting and bottom: power fitting).

## Conclusions

Preliminary results derived from the first-year exposure testing at six sites in Rotorua city showed that:

- Atmospheric corrosion of mild steel and zinc are highly location dependent. Low corrosion rates were observed for samples exposed in the west and east city areas where low concentrations of $H_2S$ were also found through two runs of three-week monitoring. High mass loss was observed at sites close to or in the central part of the city. It appears that the first-year corrosion rate of mild steel could be correlated with the short-term $H_2S$ concentration. However it is expected that the functions could be improved with the addition of more environmental parameters to the fit.
- Extremely high corrosion rates were observed at the Waste Water Treatment Plant site close to Sulfur Bay. Compact and uniform corrosion product layers were not developed on the samples, particularly mild steel exposed at this site. The time dependent corrosion rate of mild steel also showed a behaviour not commonly observed in other New Zealand environments. Unveiling the mechanisms behind would greatly support effective maintenance of buildings and infrastructure assets in regions with heavy influences of geothermal emissions.

Studies are continuing to achieve a better understanding of material degradation in geothermal environments, especially those with high concentrations of sulfur-containing gaseous species.

## Acknowledgements

This paper was originally published in the conference proceedings of Corrosion & Prevention 2016, Auckland, 13-16 November 2016. The Australasian Corrosion Association is acknowledged for permission in allowing this paper to be republished.

The work described is supported by the New Zealand Building Research Levy. We would also like to thank the Rotorua District Council, Scion, and several private home owners for allowing the installation of exposure racks on their properties.

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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.**

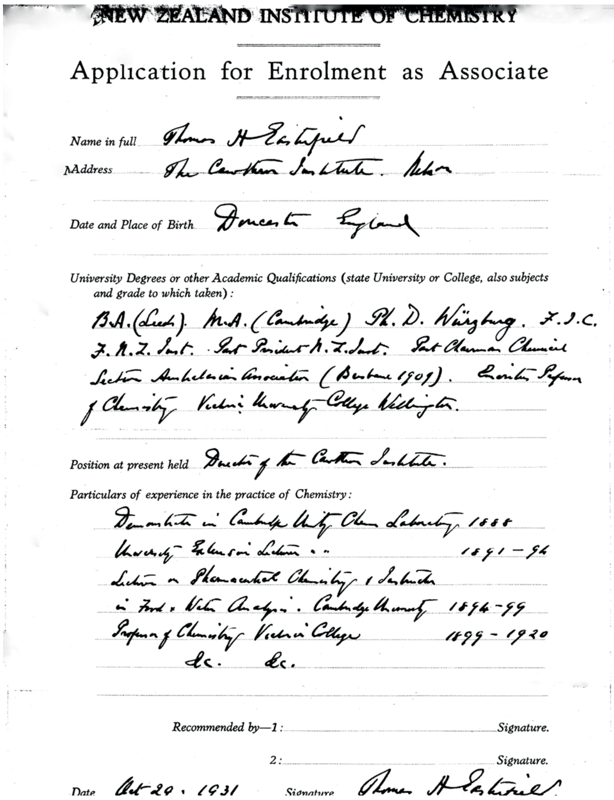
## *Sir Thomas Hill Easterfield (1866-1949)*

Brian Halton

School of Chemical & Physical Sciences, Victoria University, PO Box 600, Wellington 6140 (email: *brian.halton@vuw.ac.nz*)

T.H Easterfield (VUW 2-163) and in retirement (VUW 2-197) (both with permission).

Thomas Hill Easterfield was born on March 4, 1866 in Doncaster, Yorkshire, England, the son of Edward and Susan (neé Hill) Easterfield. His father was a banker who rose to become secretary and then manager of the local branch of the Yorkshire Savings Bank. Thomas Easterfield entered Doncaster Grammar School and won prizes in Classics, divinity, French, German and science during his time there.[1,2] His younger years had him contemplating a career in the textile industry by study in the department at Yorkshire College Leeds (the forerunner of Leeds University). In May of 1881 he won one of the Akroyd Scholarships[3] (in geology[4]) valued at £20 annually for two years to attend the college. He subsequently became a Brown Scholar and published two papers, one on photography,[5] the other on a glacial deposit[6] from his time there. Although not previously noted,[1,2,4,7-10] his time at Yorkshire College led to the award of a BA degree. This is given as his first qualification in the October 29, 1931 invited application to join the New Zealand Institute of Chemistry as a founding member (see below).[11] Initially he was an Associate, then ten years later in 1941 he became a Fellow. From Leeds, Thomas proceeded to Cambridge's second oldest college, Clare, as a senior foundation scholar studying geology, physics and chemistry, and being awarded a first-class degree with honours in chemistry and geology in the natural science tripos in 1886. As an aside, shortly after Easterfield left Leeds, the famous 'penny bazaar' started in 1884 as a stall in the Leeds Kirkgate Market, and went on to become Marks and Spencer, one of the UK's largest chain stores. Apart from his academic acumen Easterfield was a notable middle-distance runner, representing the university in the mile and three-mile events, the former at the Oxford-Cambridge meetings over 1886-1888. He became a Cambridge blue.



NEW ZEALAND INSTITUTE OF CHEMISTRY

Application for Enrolment as Associate

Name in full: Thomas H Easterfield

Address: The Cawthron Institute. Nelson

Date and Place of Birth: Doncaster England

University Degrees or other Academic Qualifications (state University or College, also subjects and grade to which taken): B.A.(Leeds). M.A.(Cambridge) Ph.D. Würzburg. F.I.C. F.N.Z. Inst. Past President N.Z. Inst. Past Chairman Chemical Section Australasian Association (Brisbane 1909). Emeritus Professor of Chemistry Victoria University College Wellington.

Position at present held: Director of the Cawthron Institute.

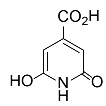
Particulars of experience in the practice of Chemistry:
Demonstrator in Cambridge Univ. Chem Laboratory 1888
University Extension Lecturer .. 1891–94
Lecturer on Pharmaceutical Chemistry & Instructor in Food & Water Analysis. Cambridge University 1894–99
Professor of Chemistry Victoria College 1899–1920
&c. &c.

Recommended by—1: Signature.
2: Signature.

Date Oct 29. 1931 Signature Thomas H Easterfield

Easterfield's application for Associateship of the NZIC.

Following his time at Cambridge, Easterfield gained postgraduate experience at the Zurich Polytechnic College and the University of Zurich in Switzerland, and then at Würzburg University on the Main river in Germany. There he worked under the noted organic chemist Emil Fischer who had him study two topics, one relating to the structure of sugars and the other to the three-dimensional structure of carbon compounds,[1] with his PhD work on the chemistry of citrazinic acid (**1**) that was also started there. His doctoral degree was awarded in 1894 based on a 35-page thesis entitled: *Zur Kenntnis der Citrazinsäure* (knowledge of citrazinic acid).




**1**, citrazinic acid

There is some confusion as to precisely when Easterfield went to Würzburg but he returned to Cambridge in 1888 *as a lecturer under the University Extension Movement, and worked in the University Organic Chemistry Laboratory* according to Marsden,[8] or as Davis[1] gives it *a demonstrator in the chemical laboratory, became university extension lecturer and was, for a while, part-time science master at Perse Grammar School in Cambridge*. In contrast, MacFarlane[2] tells us that Easterfield appears to have returned to England several times during his PhD studies and gained a variety of practical experiences, especially over the 1891-1894 period and prior to the award of his PhD degree. Irrespective of the precise detail here, Easterfield's publications on the topic of his PhD are jointly with W.J. Sell,[12] a demonstrator at Cambridge who had published from that position *On the Volumetric Determination of Chromium* in the *Transaction of the Chemical Society* in 1879. Moreover, Sell published on derivatives of citric and aconitic acids with Easterfield in 1892 and continued with the citrazinic acid study until after Easterfield left Cambridge, publishing the results with F.W. Dootson in 1897 and with H. Jackson in 1899. It is the view of this author that much if not most of the Easterfield PhD experimental work could have been performed in Cambridge with Sell as the assistant supervisor. Easterfield's ability to teach, lecture, and research grew over the 1887-1894 period as judged from his twelve publications from that period.[13] As important is the fact that during his time in Germany, Thomas met and courted Bavarian Anna Maria Kunigunda Büchel and married her in Würzburg on September 1, 1894.

From Würzburg, Easterfield returned to Cambridge in 1894 to a lectureship in pharmaceutical science and in the chemistry of sanitary science.[7] He filled these positions with success and continued his research studies publishing a further four papers on aspects of charcoal, Indian hemp resin (*Cannabis sativa*), and cannabinol. When the Victoria College Wellington Board chose to appoint its inaugural professors, four chairs were advertised, one being in chemistry and physics. Easterfield applied for this, was interviewed in England, and accepted the offer of appointment as announced in the New Zealand Herald, on January 13, 1899. His appointment came with funds to purchase and ship needed scientific equipment, £100 for the physics and £50 for chemistry were initially allocated, spent and the supplies dispatched, only to be damaged in transit. Subsequently, the situation was made passable with the gift of £25 from George W. Wilton, the founder of what became one of New Zealand's major importers of scientific equipment through the 20th century.

Easterfield, his wife, and by then two daughters, joined John Rankine Brown (Classics) and his family on the steamship *Kaikoura* in Plymouth for their travel to New Zealand on the evening of February 11th, 1899, in the foulest of weather. Hugh MacKenzie (English Language and Literature) and his family had boarded in London. The Brown and Easterfield families were taken out to the ship by tender, and were in a bedraggled and collapsed condition when they reached it in Plymouth Sound. When the *Kaikoura* put out to sea things were even worse, for she headed into a first class gale which lasted three days and destroyed a large part of the captain's bridge. However, the sea was calm and pleasant by the time they reached Tenerife, and on rounding the Cape the three professors had learned something of one another's idiosyncrasies.[14] The fourth appointee, the unmarried Richard Maclaurin, came independently via the US, arriving in Auckland and transferring to Wellington.[15]

The *Kaikoura* sailed into Wellington harbour on Saturday, April 1, 1899, one of Wellington's glorious autumnal days. *If, on that 1st of April when the Council met them* (the professors), *they had felt a little foolish they might be forgiven. Somehow, before they left England, they had been given to understand that their college was not only adequately endowed, but actually physically in existence - that their task as founders was, as it were, to walk in and begin lecturing.*[15] The reality was very different. There was no college edifice and little finance. On being met by the college councillors, Easterfield was told by one that he had gained his appointment by just one vote – and that because there was no Scotsman available! The professors were given a little time to accustom themselves to their new surroundings before a formal welcome in the offices of the Education Board on Wednesday April 12. However, the first students registered just one week after their arrival and were met by the professors. Term 1 started on April 18 with 30 students in chemistry and 11 in physics. The first two of the inaugural lectures were presented that same evening.[16,17] In his address, *Research as a Prime Factor in Scientific Education*,[18] Easterfield espoused his views on education and to a colonial audience 118 years ago he must have seemed a revolutionary. He was the inaugural appointee of the four who came German-trained with a definite purpose. He was plain in saying that early specialisation by students with research work and original investigation should come before a degree was awarded and that a good laboratory was an absolute necessity for staff and student research in science. That some of the research could benefit the country also had to be recognised. Research was in marked contrast to the reality of Wellington College. There was no building and no facilities for science. Consideration had been given to using a boarding house on Tinakori Road (now the Prime Minister's formal residence) for the college but that was discarded after Easterfield announced that the ground floor could be suitable for science but not the upstairs bedrooms. After the term started, three upper rooms in the Technical School Building on Victoria Street were made available.[17] It was there that Easterfield fashioned a laboratory himself out of boards and trestles.

View of the Wakefield Street addition to the Wellington Technical School, built 1898-1899. The Alcorn Family Collection, Alexander Turnbull Library PAColl-3271-1; photographer unknown (with permission).

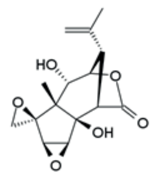
The balance that Easterfield had been given by his Cambridge colleagues, and a prize possession, was placed on a packing case in one corner. It was here that science was taught and where Thomas Easterfield began his New Zealand researches carrying out his own experiments and directing those of his students. There was no assistant and no lab attendant (a technician in the modern idiom), and the students had to bring up the water and empty the slop buckets themselves. On one occasion this was missed and the corrosive liquid ate through the bucket, permeated the ceiling, and made a significant mess in the Technical School Director's office directly below.[16,19] The adjacent room was the physics laboratory and lecture room, from which the students were required to remove their chairs and collapsible tables when they left - much to the annoyance of those in the room below. Yet, such primitive surroundings did not deter the research efforts. Early students gained notable college honours and the enthusiasm of the foundation professor was undeterred in establishing his discipline.

During that first year of 1899, Easterfield and Victoria College secured £3000 for equipping the laboratories. When the students arrived back for the 1900 teaching year the upstairs rooms of the Technical College had been transformed and a chemistry laboratory created, this to the extent that the arts students from below asked to come and draw it. One of these budding artists, Sybil Johnson, painted what was to Easterfield the most beautiful representation of his creation.[16] This painting became part of his collection, subsequently to be donated to the University College by his widow. His own researches were dominated by New Zealand natural products involving native plants, to which he had referred in his inaugural lecture. Easterfield used the laboratory fund wisely, and when the university opened its building in Kelburn in 1906 some of the facilities had been paid for from the residue of the fund and the kauri laboratory benches transferred from their city location. When tenders were called for what became the Hunter Building, Easterfield was not backward in coming forward. In his view, the instructions given to the architects were rather vague and three of the firms approached him for his opinion on the College Building. This he offered, not just to those three but to all the contenders, and the edifice that stands carries many of his ideas. During his first decade at Victoria he held the chairs of chemistry and physics and was relieved of the latter only in 1909 with the appointment of Prof. T.H. Laby.

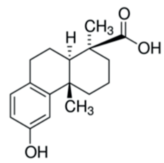
In his second year, he not only published his own research results with B.C. Aston, the government chemist in the Department of Agriculture, but also read the paper of one of his first students, P.W. Robertson, to the New Zealand Institute (Wellington), the forerunner of the Royal Society of New Zealand. Easterfield was quick to introduce himself to the few chemists in Wellington, notably William Skey, who was the Colonial Analyst in Wellington, and Aston. With Aston, he set to work on the Tutu plant (*Coriaria*) and isolated the poisonous principal which they named tutin (**2**). Their work was published on the three species of coriaria found in New Zealand, namely *C.*

Sybil Johnson: *Victoria College: First Chemistry Laboratory, 1901*. 1901 watercolour on paper. VUW Art Collection, gift of Lady Easterfield and reproduced with permission.

*ruscifolia*, C. *thymifolia,* and C. *angustissinza*, firstly in this country and then in the UK in 1900 and 1901, respectively.[20] Their collaboration continued with studies of karaka (*Corynocarpus laevigatus*) and rimu (*Dacrydium cupressinum*) resin, which is now known to contain podocarpic acid (**3**). Easterfield continued his work teaching, carrying out research, and directing his students, most of whom went on to notable careers in New Zealand science. He was also consultant to industry but the difficulties in funding research and the limited recognition his efforts drew began to weigh more heavily on him and his interests moved more towards agricultural chemistry from about 1908. Nonetheless, his research was recognised in 1913 with the award of the second of the New Zealand Institute's Hector Memorial Medal and Prize. Then, during the Great War with shortage of synthetic medicines he processed the opium seized by the police under New Zealand's anti-drug laws in his Victoria laboratory to provide morphine.[21] His consultancies are nicely illustrated by some of his last experiments as College Professor that were performed at the Miranui flax mill near Levin. These were to determine if industrial alcohol (ethanol) could be produced by fermenting the juices of the flax leaf. This factory was the largest and most well equipped mill of the era and his test runs produced 198.4 gallons of 95% ethanol daily. This was not used but allowed to flow down the Miranui drains! The output equates to 50,000 gallons per annum and would have been worth £3750 per year at 1s 6d per gallon in 1919.[16]




**2**, tutin




**3**, podocarpic acid

Following the death of Thomas Cawthron in 1915, the will that the gentleman made in London some thirteen years earlier was granted probate by the Supreme Court in Wellington on November 12, 1915. The bulk of the £250,000 estate was set for *the purchase of the erection and maintenance of an industrial and technical school institute and museum in Nelson, New Zealand, to be called the Cawthron Institute*.[22] The suggestion that most of this wealthy bachelor's estate could be put to such usage was made by Cawthron's friend Joseph H. Cock when asked how best his wealth could be divided.[22,23] As the executors had little knowledge or understanding of science they established an advisory commission to which Easterfield was appointed along with Professors Benham (Biology, Otago) and Worley (Chemistry, Auckland), the noted biologist Leonard Cockayne, and Sir James Wilson, President of the Board of Agriculture; Easterfield was appointed secretary. As with everything he did, Thomas Easterfield was thorough, conscientious and efficient. Within three months of arriving in Nelson the advisory commission's report had been sent to the trustees and gone for legal approval. As secretary, Easterfield was asked to report on the form and functions of the yet to be established institution and in 1917 he presented the aims and ideals of the trustees at a public lecture in Nelson. It became the first annual Cawthron Memorial Lecture. When it came to the appointment of the first director, the trust board had two candidates in mind – Easterfield and his former student Theodore Rigg. The older Easterfield had all the attributes that the trustees considered essential for its inaugural director and he was appointed Founding Director in October 1919. By then he had given all that he could to establishing chemistry at Victoria University College as it then was, and he accepted the offer. He then had to live up to his comments in the Cawthron Lecture – that the Institute would have a bright future! During his 21 years at Victoria, Easterfield published no less than 26 papers,[2] several of them in this country then with the Chemical Society (UK); 23 of them are recorded in SciFinder©. Easterfield's research record at Victoria (University) College was solid and particularly significant as research was not high on the agenda of the New Zealand University Colleges during his tenure. He was appointed Victoria's first emeritus professor.

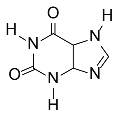
As founding director of The Cawthron Institute in Nelson, Easterfield found himself in a position akin to that on his arrival in Wellington. Although the Cawthron Trustees had purchased land and property on a 10.4 acre site in Annesbrook in 1917, and some five kilometres from the city, conversion to the facilities of a scientific Institute did not happen. Half the property was kept as an orchard almost until 1959, but as in Wellington in 1899, Thomas Easterfield had to make do with temporary accommodation. This was until Fellworth House, the John Sharp property on Milton Street, was bought later in 1920.[22] The house stood in three acres of ground and consisted of some fifteen rooms that were modified for science usage. The trustees had recognised early on that the strengths of the Cawthron would be in agriculture and horticulture, and it was in this area that Easterfield directed his attention. This contrasts with his 1917 lecture in which he was clear that research should not be restricted to applied areas but include 'pure science'.

The Cawthron Institute (Fellworth House) taken from ref. 18, opposite p. 5; with permission.

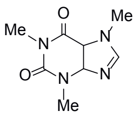
During his first year, Easterfield appointed Theodore Rigg as his assistant and agricultural chemist and then W.C. Davies (museum curator and photographer), Drs. R.J. Tillyard (entomologist) and Kathleen Curtis (mycologist who became the first woman elected to RSNZ Fellowship in 1936), H. Harrison (librarian), and two technicians A Philpott and E.J. Champtaloup. And then he gave each of the scientists the ability to appoint their own technicians. This engendered a good staff with excellent working relationships and loyalty to the Institute.[22] These appointments doubled the country's agricultural research capacity and were followed in 1921 by a fifth position in orchard chemistry part funded by the fruit growers association. They gave Nelson an intellectual force.[23]

From taking up his position, the Cawthron Institute was the sole organisation devoted to agricultural and horticultural problems not simply in New Zealand but in the entire southern hemisphere. Requests for assistance had started to arrive shortly after Cawthron's will was made public, but Easterfield elected to address those of the Nelson region first. The Cawthron's main departments of scientific research, horticulture and agriculture were established in 1920 with a sound chemical base, and these were maintained with little change until a Biochemical Department was added at the end of 1941 to handle plant and animal nutritional problems more effectively. Easterfield's profound belief in research was applied as vigorously with his colleagues at *The Cawthron* as it had been in Wellington and a voluminous quantity of research was published during its first decade leading to the international reputation that the institute gained.

From the turn of the century, second-class back blocks of land had been brought into production in the area, not least in the immediate post-war years. One of the early needs came from the pipfruit growers to improve their soils and to rid their crops of woolly aphis, bitter pit, black spot and codling moth.[22,23] Tillyard went to the UK to learn about woolly aphis and persuaded Easterfield to acquire one of the best entomological libraries in England that was then available. Kathleen Curtis attacked the black spot problem, while Rigg attended to the poor Moutere soil. Their combined studies were of immense value to the industry and were seen in improved yields and quality of the fruits. The woolly aphis problem was essentially solved by 1930 when spraying of apple trees was no longer needed following introduction of the *Aphelinus mali*, the elucidation of the life history of the black spot fungus of apples led to its eradication, and the fertiliser requirements of the Moutere Hills (and other soils) were solved or, at worst, improved in other areas. Furthermore, the Cawthron identification of the major causes of apple storage defects were of great value not only to the apple industry of Nelson but to fruit culture throughout New Zealand. The impact of the Cawthron work had the whole of the fruit growing business back in boom by 1926 when the crop output exceeded the shipping capacity. Apple exports soared from 6000 to 227,000 cases and by 1930 the acreage was so high and the demand for seasonal pickers so great that there was no accommodation left available for them. The tobacco industry also prospered with the number of growers in Waimea County rising from 150 to 700 between 1926 and 1933.



**4**, 3,7-dihydropurine-2,6-dione (xanthine)



**5**, 1,3,7-trimethylpurine-2,6-dione (caffeine)

As director of the Cawthron Institute, Thomas Easterfield played an important role in its establishment and in the development of research programmes. The early phenomenal success of the Institute was due in large measure to his enthusiasm, broad vision, and sound judgment in selecting the pioneer staff. But, as for all research establishments, funding was an on-going concern. The requirement of stamp duty on the Cawthron bequest reduced the interest returns and the continuing existence of the Institute depended on grants, donations and bequests. The lack of funding expressed itself as early as 1923 when Thomas Easterfield paid the salary of one his staff from his own pocket because there were inadequate monies available. The lack of funding was felt most strongly by Easterfield from his inability to undertake pure research in his time. Monies were subsequently boosted following the 1925 visit to Nelson of Sir Ernest Rutherford and then the 1926 visit of Sir Francis Heath that rapidly led to the establishment of the New Zealand DSIR. Easterfield's researches at the Cawthron led to ten publications, three on mineral oils of New Zealand and two on the occurrence of xanthin (**4**) [a close relative of caffeine (**5**)] in sheep, all of a technical nature. What Easterfield did with aplomb was to gain the trust of the industries and to provide them with relevant pamphlets and other appropriate educational aids, and become a friend of the local farmers, growers and industrialists, as well as a noted figure in the Nelson community. To his staff he was a man to be emulated. Elsa Kidson, a staff member at the Cawthron and first female demonstrator in a New Zealand University, recounted in an unpublished address given to the P.W. Robertson Society (an organization for Victoria's chemistry students and graduates established in 1970) on April 9, 1974: *I found him able to instil confidence and make me feel more capable, I am sure, than my abilities justified ….. but I can say that I never heard a word of criticism against him. He was always courteous and I never saw him get angry*.[2, 24] He was easily approachable, had a great sense of humour, and was a great reader in his spare time.

Top: Sir Ernest Rutherford and T.H. Easterfield, Nelson, 1925 (from VUW-S19). Bottom: Sir Francis Heath and Professor Thomas Hill Easterfield, Nelson, February 24, 1926 (File print collection, Box 2. Ref: PAColl-5584-50, Alexander Turnbull Library, Wellington, New Zealand with permission; see: http://natlib.govt.nz/records/22805451).

L-R: Woolly Apple Aphid, R. Bessin & J. Hartman College of Agriculture, University of Kentucky (provided by Dr Bessin); Summerred bitter pit (*Malus domestica*) (Rasbak, Wikipedia); Black Spot (*Venturia inaequalis*) apple image (© Plant and Food Research); Codling Moth, Olaf Leillinger (Wikimedia).

In the first Cawthron Lecture, Easterfield had said:

*I foretell a brilliant future for the Institute. The problems solved in it will lead to results of the greatest value to this city, the Dominion and to the human race. And the Institute itself is destined to become a centre of light, learning and culture honoured throughout the civilised world and a lasting tribute to Thomas Cawthron.*

The results of his labours as Director of the Institute show that not only was Easterfield a dedicated founding chemist in this country, but that his ability to tell the future also was accurate.

In 1933 on the eve of his retirement, he delivered the annual Cawthron lecture that was entitled *The Thomas Cawthron Centenary Lecture* in which he summarised the successes of the Institute from its inception to that date.[25] Because of the role the Cawthron Institute played in solving the district fruit and dairy problems, the Nelson area was not impacted upon to the same extent as the rest of this country during the Great Depression of the 1930s. Moreover, the establishment of the McKees Fruitgrowers Chemical Company from 1931 in an abandoned coolstore in Mapua next to the wharf made the needed chemicals easily available in that era when chemical aids were regarded more favourably than now.[23] The successes of the Cawthron Institute over the early years are also appropriately described by Miller in his 1963 book *Thomas Cawthron and the Cawthron Institute*[26] and the reader may wish to refer to it.

Thomas and Anna Easterfield had five children, two daughters before they arrived from England and then two more daughters (Muriel Helen; February 26, 1900 and Theodora Clemens; June 12, 1902) and a son (Thomas Edward; 1912) all of whom distinguished themselves. The two New Zealand born daughters became medics whilst Edward gained an MSc from Canterbury University College in 1934 (following private school education in Wellington and Nelson) and subsequently an overseas PhD and a career becoming a Principal Scientific Officer in the DSIR in London. Thomas Hill Easterfield died in Nelson on March 1, 1949, survived by his wife and children. He made an outstanding contribution to science in New Zealand. Remembered for his high spirits and cheerfulness, he set high standards in the training of students and in the conduct of chemical research. He established two notable institutions in Victoria's chemistry department and the Cawthron Institute. It was his vision, judgement and enthusiasm for research that set chemistry in Wellington on track and brought the Cawthron to the international position it was to hold at his retirement and maintains today.

Thomas Easterfield was appointed to the New Zealand Order of Merit in 1925, was awarded a King George V Silver Jubilee Medal in 1935, and knighted (KBE) in 1938. He was a Fellow of the New Zealand Institute that became The Royal Society of New Zealand and its 1921-1922 President, a Fellow of the NZIC, and a member of many other chemical societies.

## Acknowledgement

I am grateful to Richard Rendle for suggesting the topic and providing Easterfield's NZIC application form, and to Andrea Mead of the Cawthron Institute for assistance and the provision of much useful information especially through reference 22.

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Article

# Smoking underwater: chemistry at the margins

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**Keywords:** *undersea volcanoes, origin of life, hydrothermal fluids, trace metals*

Early in 2017, underwater photographs of active volcanoes at the Kermadec Trench were screened as part of a television news bulletin. Media would have found it hard not to respond to the news release from GNS Science on 24 January that declared:

"Twenty-metre high chimneys belching out hot acidic mineral-rich fluids, forests of long-neck barnacles clinging to craggy rock formations, and beds of mussels lining vertical rock walls…. This is one of the most active stretches of seafloor volcanism in the world. Many of the volcanoes have multiple hydrothermal vents where hot, mineral-rich fluids billow continuously into the ocean…. The aim of the expedition was to investigate seafloor vents and their dense, metal-rich fluids and find out how they influence the chemistry of the seawater and the diverse marine life along the Arc. Scientists also wanted to see the extent of marine species migration between volcanoes."[1]

Cornel de Ronde, one of the investigators, is reported as saying, "The chemistry of the vent fluids at the different volcanoes was widely divergent, with some fluids having a pH of 1.1 – similar to battery acid", and "chimneys at Brothers Volcano pumping out fluids at 312 degrees Celsius – a new temperature record for vent fields in the Kermadec Arc". A comparison between the composition of hydrothermal fluid associated with back-arc volcanism (similar to Kermadecs) and that associated with mid-ocean ridges is plotted in Fig. 1.[2] A subsequent news release was more concerned with the technology – *Sentry*, an 'autonomous underwater vehicle', which "provides the appropriate level of detail on the geology of the seafloor, the hydrothermal systems, deep-sea habitats, and the occurrence of mineral deposits".[3] GNS scientists – and their precursors at the New Zealand Geological Survey – have been investigating the active and dormant volcanoes of the Kermadec Trench for decades,[4] but the recent videos that are evocative of alien landscapes are much more appealing to the public than the tables of chemical compositions of the fluids involved, inventories of strange creatures never or rarely seen before that inhabit this hot underwater world, or even tape-recordings of 'live' volcanoes.[5]

The deep-sea vents at are often referred to as either 'black smokers' or 'white smokers', depending on the nature of the particulate matter formed: the particles in black smokers are usually sulfides (often including galena – lead sulfide), deposited at high temperatures and a highly reducing environment; while the particles in white smokers are typically pale-coloured barium- or calcium-bearing minerals, which are deposited at rather lower temperatures (Fig. 2). These vents are found at the compressional margins of the Earth's tectonic plates: plate boundaries where one plate is subducted beneath another, as at the Kermadec trench (giving rise to undersea volcanoes compositionally similar to Ngauruhoe - andesites); but also at the extensional margins of the plates: plate boundaries where tectonic plates are separating, as at the mid-Atlantic Ridge.

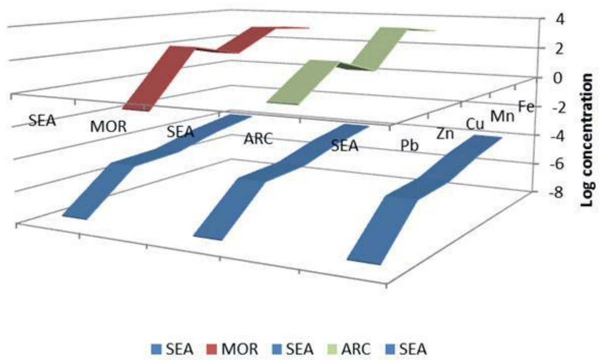


***Fig. 1***. Variation in average concentrations (in mmol kg$^{-1}$) of selected trace elements from hydrothermal waters associated with a mid-ocean ridge (MOR) and a back-arc undersea volcano (ARC), compared with seawater (SEA). It is clear that the concentrations of these metallic elements are much higher in the hydrothermal waters than in seawater, suggesting that they are derived from the magma [Compiled from data in *Oceanography* **2007**, *20* (1), 55, table 1; with concentrations in seawater calculated from Krauskopf, K.B.; Bird, D.K., *Introduction to Geochemistry*, McGraw-Hill: New York, 3rd edition, 1995, 589-591, Appendix IV.]

Similar vents also associated with volcanoes far from plate boundaries ("intra-plate volcanoes", of which the Hawaiian Islands are the archetype), the 'plumbing' for which was the subject of a cartoon in the mid-1970s (Fig. 3).[6] Where volumetrically large and long-lived, these are probably associated with plumes of molten material rising from deep in the mantle – "hot spots", but other intraplate volcanoes, such as those on land in eastern Australia – and those in Auckland – are often considered to originate at shallower depths in the mantle and are described as "wet spots".[7] In fact, debate about the origin of intraplate volcanoes has been simmering for decades.[8]

Closer to home, forty years ago investigations of marine sediments in the Bay of Plenty showed clear evidence of a spike in the concentrations of trace elements near White Island along a transect extending northeast from Whakatane (Fig. 4).[9] This was attributed to mineralised waters draining from the White Island crater into the sea, although the authors made a grudging reference to another "possibility for metal enrichment [which] is provided by the presence of submarine thermal activity as indicated by the occurrence of bubble zones around White Island".[10] Whether the ultimate source of the metals was the marine sediments, the volcanic rocks, or the fluids

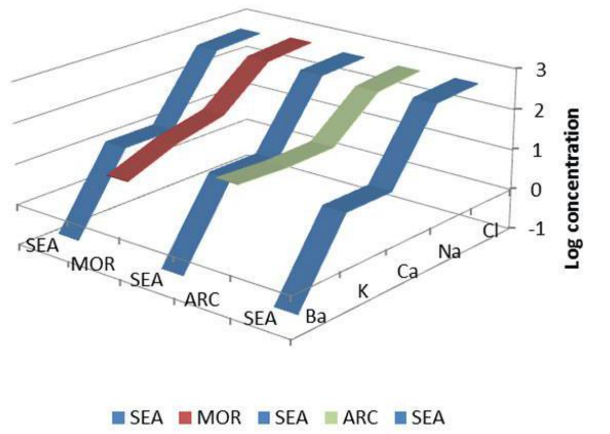


***Fig. 2.*** Variation in average concentrations (in mmol $kg^{-1}$) of selected elements in hydrothermal waters from a mid-ocean ridge (MOR), a back-arc undersea volcano (ARC), being a 'black smoker' and a 'white smoker', respectively; and seawater (SEA). Of particular note is the relatively higher concentration of Ca and Ba in waters associated with the back-arc volcano than with the mid-ocean ridge volcano, leading to the precipitation of Ca- and Ba-bearing minerals (which are generally white in colour). The concentrations of Na and Cl in the hydrothermal waters are not that different from seawater. [Compiled from data in *Oceanography* **2007**, *20* (1), 55 (table 1).]

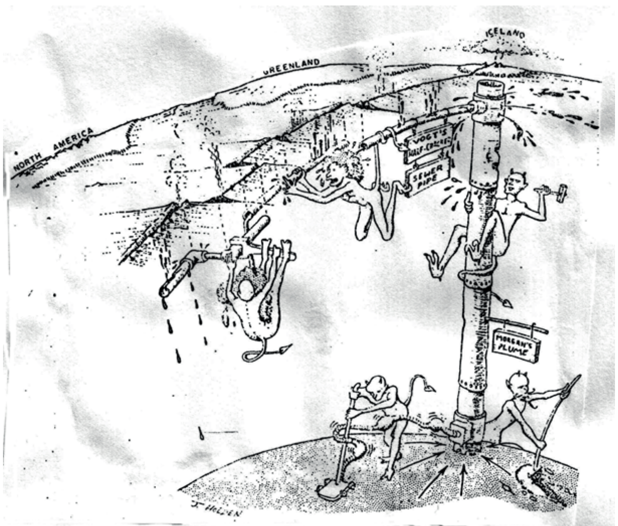


***Fig. 3.*** Volcanism derived from a plume rising from the Earth's mantle at the mid-ocean ridge. Clearly there are issues with the plumbing, so interactions between seawater and the fluids associated with the magma are to be expected. [Reproduced from *EOS Transactions of the American Geophysical Society* **1977**, *58*, 576, fig. 6.]

associated with the volcano itself is a debate which goes back centuries. The source of metals in ore deposits…

"was first addressed in the sixteenth century by Agricola, who considered that heated rainwater leaches metals from rocks and then transports the metals to the sites of ore deposits. A century later, Descartes proposed that vapours released during cooling and crystallization of the Earth's interior are responsible for filling fractures with ore." [11]

In this instance, the source of the metals was considered to be from an acidic stream from the crater. Scavenging of the trace elements in the water by metal hydroxides already precipitated, were mentioned as the likely mechanisms for relative enrichment or depletion of specific elements.

In deeper marine waters, such as at the Kermadec Trench, the environment in which chemical reactions occur is rather different:

"The complexity of the chemistry of waters found beneath the earth's surface becomes apparent if we consider the variations we would encounter along a surface 5 km below sea level. In deep ocean areas this surface would pass through seawater at 1 to 2 °C and 500 atm. The $CO_2$ content of this water would be somewhat higher than its surface counterpart and its $O_2$ content 2 to 4 times lower."[12]

At the deep-sea volcanoes, the temperature of the water is much higher than that at 'a surface 5 km below sea level'. This affects the nature of many of the possible reactions, whether involving chemical species in the seawater ($MgSO_4$, $Mg^{2+}$), chemical species derived from the volcanic fluids (e.g., the sulfur species $HS^-$ and $S^{2-}$) or both. At temperatures above 200 °C, almost all complexing reactions favour enhanced association with rising temperatures. The dissociation of water and bisulfide ion are among the few reactions that are more complete at 300 °C than at 25 °C.[13]

There have been extensive laboratory investigations undertaken in order to understand the nature of water-metal interactions at high temperatures and pressures, particularly demonstrating the role of complex ions in transporting trace metals in hot chloride- and/or sulfur-rich fluids in order to produce economic ore deposits when the fluid cools and/or depressurises.[14] However, these experiments primarily sought to explain the behaviour of mineralised fluids in geothermal areas associated with terrestrial volcanism.

The identification of thermophilic (warmth-loving) bacteria in the same types of geothermal waters that were of interest among geochemists may have in part prompted the establishment of the Thermophile Research Unit at the University of Waikato, which for more than thirty years has collaborated with a number of kindred research groups around the world, has attracted international funding, and generated several commercial entities.[15] A consequence of the Unit's early research on hot springs was identification of the warm reducing environment of geothermal systems as potentially conducive to the development of life on Earth,[16] although the deep-sea hydrothermal environment was ultimately favoured over this terrestrial analogue.[17]

Dispelling the notion of life originating in a "little lightning-struck dish of lukewarm primordial soup",[18] one author of a populist book preferred a marine origin for life,[19] attributing the idea to Erasmus Darwin (grandfather of Charles),[20] on the basis of a poem *The Temple of Nature* (Fig. 5), citing it as the source of a line: "Organic life beneath the shoreless waves was born…."[21] Apparently less noticed, but more interesting from a physical chemistry point of view, are some of the poem's earlier lines:

"First HEAT from chemic dissolution springs
And gives to matter its eccentric wings:
With strong REPULSION parts the exploding mass,
Melts into lymph or kindles into gas.
ATTRACTION next, as earth or air subsides,
The ponderous atoms from the light divides,
Approaching parts with quick embrace combines.
Swells into spheres and lengthens into lines.
Last, as fine goads the gluten-threads excite,
Cords grapple cords, and webs with webs unite;
And quick CONTRACTION with ethereal flame
Lights into life the fibre-woven frame.
Hence without parent by spontaneous birth
Rise the first specks of animated earth…."[22]

The poem's references to 'gas' and 'swelling into spheres' has an almost uncanny similarity to a model proposed in 1997, the resulting publication about which was entitled '*The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front*'.[23] In the abstract of that paper the authors proposed that:

"life emerged on Earth from a redox and pH front at *c.* 4.2 Ga. This front occurred where hot *(c.* 150°C), extremely reduced, alkaline, bisulphide-bearing, submarine seepage waters interfaced with the acid, warm *(c.* 90°C), iron-bearing Hadean ocean. The low pH of the ocean was imparted by the ten bars of $CO_2$ considered to dominate the Hadean atmosphere/hydrosphere. Disequilibrium between the two solutions was maintained by the spontaneous precipitation of a colloidal FeS membrane. Iron monosulphide bubbles comprising this membrane were inflated by the hydrothermal solution upon sulphide mounds at the seepage sites."

The authors went on to hypothesise:

"that the FeS membrane, laced with nickel, acted as a semipermeable catalytic boundary between the two fluids, encouraging synthesis of organic anions by hydrogenation and carboxylation of hydrothermal organic primers. The ocean provided carbonate, phosphate, iron, nickel and protons; the hydrothermal solution was the source of ammonia, acetate, $HS^-$, $H_2$ and tungsten, as well as minor concentrations of organic sulphides and perhaps cyanide and acetaldehyde. The mean redox potential (ΔEh) across the membrane, with the energy to drive synthesis, would have approximated to 300 millivolts. The generation of organic anions would have led to an increase in osmotic pressure within the FeS bubbles. Thus osmotic pressure could take over from hydraulic pressure as the driving force for distension, budding and reproduction of the bubbles.

"Condensation of the organic molecules to polymers, particularly organic sulphides, was driven by pyrophosphate hydrolysis. Regeneration of pyrophosphate from the monophosphate in the membrane was facilitated by protons contributed from the Hadean ocean. This was the first use by a metabolizing system of protonmotive force which also would have amounted to *c.* 300 millivolts. Protonmotive force is the universal energy transduction mechanism of life. Taken together with the redox potential across the membrane, the total electrochemical and chemical energy available for protometabolism amounted to a continuous supply at more than half a volt.

"The role of the iron sulphide membrane in keeping the two solutions separated was appropriated by the newly synthesized organic sulphide polymers. This organic takeover of the membrane material led to the miniaturization of the metabolizing system. Information systems to govern replication could have developed penecontemporaneously in this same milieu. But iron, sulphur and phosphate, inorganic components of earliest life, continued to be involved in metabolism."

Although the overall process is summarised in Fig. 6, the extensive quotation of the abstract is justified, not only because of its link to Erasmus Darwin's idea, but also because of the continual attractiveness of the idea of a 'protonmotive force' mentioned therein. This notion has re-

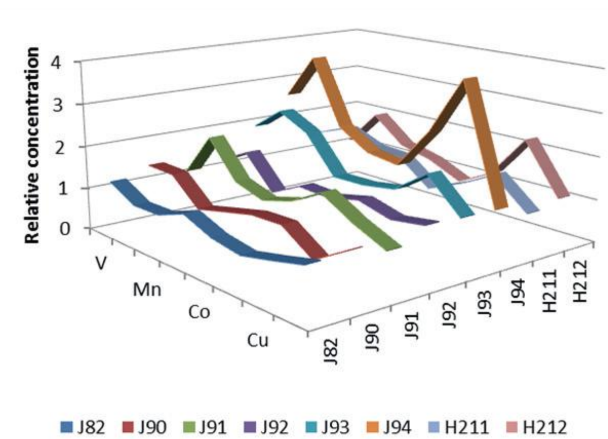


***Fig. 4.*** Variation in concentrations of selected trace elements relative to unenriched seafloor sediments along a transect from Whale Island, off the Bay of Plenty coast (station J82), to White Island (station J94), and thence the seafloor to the northeast of White Island (stations H211 and H212). [Compiled from data in *N.Z. DSIR Bulletin* **1977**, *218*, 123 (fig. 1) and 124 (table 1).]


***Fig. 5.*** ***Left:*** Engraving after a drawing by John Henry Fuseli. From Erasmus Darwin, The Temple of Nature, or, The Origin of Society (London, 1803); an image widely used in many different types of publications since the poem was published, (https://nz.pinterest.com/pin/170362798376606849/ , accessed v18 February 2017). ***Right:*** Photograph of a portrait of Erasmus Darwin 1731-1802 that hangs in Erasmus Darwin House, Lichfield, Staffordshire, England (http://www.erasmusdarwin.org/, accessed 16 February 2017).

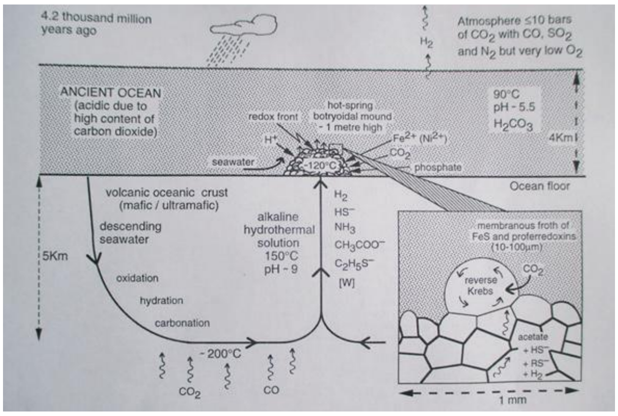


***Fig. 6.*** Model for the emergence of life on the ocean floor at a submarine alkaline hot spring, 4.2 billion years ago. The Krebs cycle in the inset part of the diagram is also known as the citric acid cycle or tricarboxylic acid cycle [Reproduced from *Journal of the Geological Society of London* **1997**, *154*, 379, (fig. 1).]

cently received renewed attention,[24] and was described in a more populist style in *Live Science:*

“Authors of the new theory argue the environmental conditions in porous hydrothermal vents — where heated, mineral-laden seawater spews from cracks in the ocean crust — created a gradient in positively charged protons that served as a "battery" to fuel the creation of organic molecules and proto-cells.

Later, primitive cellular pumps gradually evolved the ability to use a different type of gradient — the difference in sodium particles inside and outside the cell — as a battery to power the construction of complex molecules like proteins. And, voilà, the proto-cells could leave the deep-sea hydrothermal vents.

" ‘A coupling of proton gradients and sodium gradients may have played a major role in the origin of life. This is really cool, novel stuff,’ Jan Amend, a researcher at the University of Southern California, who was not involved in the study, wrote in an email to *LiveScience*. The study reflects the increasingly popular idea that a simple, everyday source of power, not a rare occurrence like a lightning strike, could have provided the power to initially create life, he said.”[25]

From a biological stand-point, recent work on the Last Universal Common Ancestor (LUCA) has reached the conclusion that “LUCA inhabited a geochemically active environment rich in $H_2$, $CO_2$ and iron. The data support the theory of an autotrophic origin of life involving the Wood–Ljungdahl pathway in a hydrothermal setting.”[26,27] A more populist website uses this recent paper to assert, “We’ve been wrong about the origins of life for 90 years.”[28]

Even from this very selective account, chemistry at the margins of the tectonic plates appears to have been integral to the development of life on this planet, and, were technology to improve, might yet provide a feedstock of metals for its future.

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# Book Review: *A Tale of Seven Scientists and a New Philosophy of Science*, by Eric Scerri


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There are numerous themes at play in Eric Scerri's *A tale of Seven Scientists….*[1] Scerri's earlier books about the development of the periodic table[2] are heroic in character,[3] charting the success of the big players in simplifying chemical complexity into what is now an instantly recognisable visual summary of chemical properties of the elements and interpretations of underlying physical behaviour of the atoms' constituents – the Periodic Table. In his latest book, Scerri focuses on seven 'little people', to use his own phrase. For five of these people the 'pivotal person' (pp. xxv-xxvi) is Niels Bohr; while for the other two, the 'pivotal person' is Dimitri Mendeleev (Table 1).

Chapters 2 – 8 provide for each of the little people a synopsis of their lives and a discussion of their influence on the thinking of the day. They are of variable format and length, the latter seeming to be as much a function of Scerri's interpretation of the extent of their interaction with (where it occurred) and influence on or by the relevant 'pivotal person'. As I read these biographical chapters, I developed an image of these lesser scientists as orbiting around their respective pivotal person: with those closer to the centre having a more pervasive influence on the science involved, or at least on Scerri's interpretation of the science.

Having read these chapters, I gained the impression that of the seven 'little people', Edmund Stoner and Charles Janet had been the most influential, an impression confirmed by my empirical measures of impact in Table 1. As Scerri freely admits, there are many other 'little people' he could have chosen, and the book does indeed refer to many others. If these were included, the image of 'little people' orbiting around a 'pivotal person' would become more of a smear of influence: more like a cloud of electronic charge rather than discrete electrons about the nucleus of an atom, if you will.

Of course, in a book devoted to the 'little people', some attention also has to be paid to the 'pivotal persons', in this case Bohr and Mendeleev. Scerri does this well and it is confirmed by Table 2 and Fig. 1, in which a nice balance between the work of all the researchers in *A Tale…* – both 'little' and 'pivotal' – can be inferred from the similar number of entries in the index that relate to each scientist and their work. This is very different from the distribution of index entries about the scientists and their work in Scerri's other histories of the Periodic Table (*The*

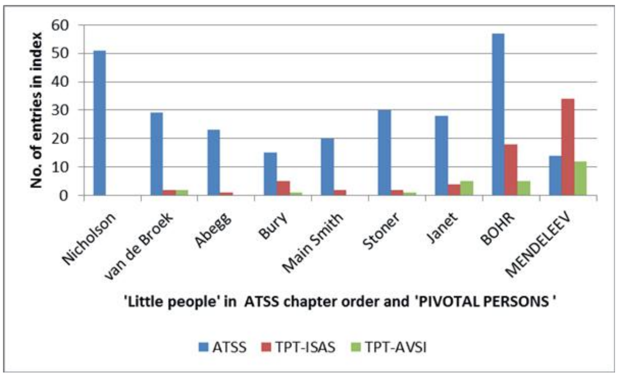


***Fig. 1.*** Index entries for 'little people' and their 'pivotal persons' in *A Tale of Seven Scientists* (ATSS), and a comparison with index entries for two other histories of the Periodic Table written by Eric Scerri.

***Table 1***. The 'little people' in Eric Scerri's *A Tale of Seven Scientists*.

| Discipline | **"Little people"** *Name* *(birth-death)* | *Years for which research is cited in chapter endnotes* | **Measures** *Inferred Influence** [rank] | *Inferred Impact of research†* [rank] | Theme of investigation / "Pivotal person" |
|---|---|---|---|---|---|
| Physics | John Nicholson (1881-1955) | 1911-1912, 9 articles (*n6*,‡ 1911; *n9*, 1911; *n13*, 1911 [3 articles], 1912 [3 articles]; *n14*, 1912) | 28 [2] | 3.1 [7] | Electronic configuration / Bohr |
| Physics | Edmund Stoner¶ (1899 -1968) | 1924-1925, 2 articles (*n16*, 1924; *n18, n19*, 1924; *n33, n34*, 1925) | 32 [1] | 16 [1] | Electronic configuration / Bohr |
| Chemistry | John D. Main Smith¶ § | 1923-1927, 4 articles (*n3*, 1923; *n6 ,n7*, 1924; *n8, n9*, 1927; *n18*, 1925 | 14 [7] | 3.5 [6] | Electronic configuration / Bohr |
| Chemistry | Charles Bury (1890-1968) | 1921, 3 articles (*n25*, 1921; *n29*, 1921; *n34*, 1921) | 24 [3] | 8.0 [3=] | Electronic configuration / Bohr |
| Chemistry | Richard Abegg** (1869-1910) | 1899-1904, 2 articles (*n6*, 1899;** *n17*, 1904) | 16 [6] | 8.0 [3=] | Arrangement of elements in Periodic Table / Mendeleev |
| Inter-disciplinary | Anton van den Broek†† (1870-1926) | 1907-1913, 5 articles (*n3*, 1907; *n4*, 1911; *n5*, 1911; *n13*, 1913; *n15*, 1913) | 22 [4=] | 4.4 [5] | Arrangement of elements in Periodic Table / Mendeleev |
| Inter-disciplinary | Charles Janet (1849-1932) | 1927-1930, 2 articles (*n5*, 1927; *n8*, 1930) | 22 [4=] | 11 [2] | Arrangement of elements in Periodic Table / Mendeleev |

* A measure of the influence of the work on Scerri's thinking is the number of pages in the relevant chapter of *A Tale...*

† A measure of the impact of the work is the ratio of the length of the chapter to the number of papers by the author that are explicitly cited.

‡ '*n6*' denotes the endnote number to the chapter; in this case the 6th endnote in the chapter on Nicholson.

¶ In *Tales…*, Scerri describes in some detail the priority disputes between eminent scientists, by also discussing the dispute between two of the 'little people' – Stoner and Main Smith, he suggests that this activity is perhaps more pervasive in science that might be commonly thought.

§ Scerri attributes the lack of attention given to Main Smith's articles to their publication in the little known journal *Chemistry and Industry*. This is despite his 'comprehensive' 1924 book *Chemistry and Atomic Structure*.

**Scerri does not cite the article but it appears to be: Abegg, R.; Bödlander, G., *Z Anorg. Chem.*, **1899**, *20*, 453-496; cited in Mingos, M.P. (ed.) *The Chemical Bond 1, 100 Years Old and Getting Stronger*, Springer: Switzerland, 2016

†† Despite having articles published in *Nature*, the lack of attention given to van den Broek's contribution is attributed (by Scerri) to his being an 'outsider' to the disciplines normally researching the Periodic Table.

***Table 2***. Comparison of index entries in three of Eric Scerri's books related to the Periodic Table.

| **Theme** | **Researcher** | **No. of index entries in *A Tale of Seven Scientists… (ATSS)*** | | **No. of index entries in *The Periodic Table – Its Story and Its Significance (TPT-ISAS)*** | | **No. of index entries in *The Periodic Table – A Very Short Introduction (TPT-AVSI)*** | |
|---|---|---|---|---|---|---|---|
| | | No. | Relative to pivot | No. | Relative to pivot | No. | Relative to pivot |
| Electronic configuration | Pivot | | | | | | |
| | Bohr (1920-1923)* | 57 | 1.0 | 18 | 1.0 | 5 | 1.0 |
| | *Little people*† | | | | | | |
| | Nicholson (1911-1912) | 51 | 0.90 | 0 | 0 | 0 | 0 |
| | Stoner (1924-1925) | 30 | 0.53 | 2 | 0.11 | 1 | 0.2 |
| | Main Smith (1923-1927) | 20 | 0.35 | 2 | 0.11 | 0 | 0 |
| | Bury (1921) | 15 | 0.26 | 5 | 0.28 | 1 | 0.2 |
| Arrangement of chemical elements in Periodic Table | *Pivot* | | | | | | |
| | MENDELEEV (1869)‡ | 14 | 1.0 | 34 | 1.0 | 12 | 1.0 |
| | *Little people* | | | | | | |
| | Abegg (1899-1904) | 23 | 1.64 | 1 | 0.03 | 0 | 0 |
| | Van den Broek (1907-1913) | 29 | 2.07 | 2 | 0.06 | 2 | 0.17 |
| | Janet¶ (1927-1930) | 28 | 2.00 | 4 | 0.12 | 4 | 0.33 |

*Inferred from: Nielsen, J.R., (ed.) *Volume 4: The Periodic System (1920-1923). Niels Bohr Collected Works*. Elsevier: Amsterdam, 2008.

† Date ranges for research by the 'little people' as shown in Table 1.

‡ Mendeleev, D. *Zeitschrift für Chemie* **1869**, *12*, 405-406.

¶ Includes entries related to 'left-step' variations of the Periodic Table, which Janet developed.


***Fig. 2.*** Von Tempsky and his forest rangers. New Zealand Illustrated Magazine, 01 March 1900. (Alexander Turnbull Library, Wellington: http://natlib.govt.nz/records/2663973).

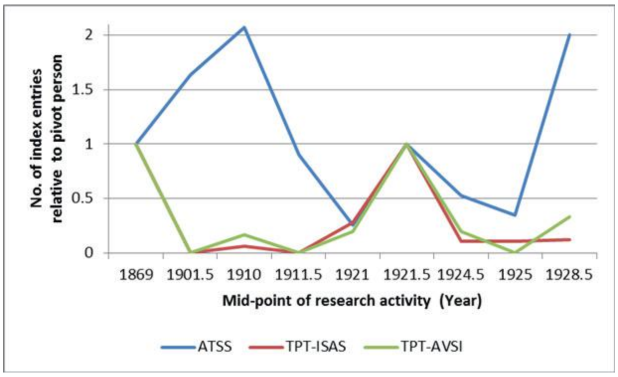


***Fig. 3.*** Ratios of index entries for 'little people' relative to the appropriate 'pivotal person' versus mid-point of research activity. The plot for *A Tale of Seven Scientists* (blue line, ATSS) is very different from those for Scerri's other histories (red line, TPT-ISAS; green line, TPT-AVSI). These latter two lines are reminiscent of plots that suggest successive 'revolutions' in science (see text).

*Periodic Table – Its Story and its Significance* and *The Periodic Table – A Very Short Introduction*) which concentrate on the major 'players'. These latter two books are akin to the portrayal of science in museums, textbooks and classrooms as a "stately progression of breakthroughs and discoveries, inspirational geniuses and long march out of the darkness of ignorance into the light of knowledge".[4] Scerri's *A Tale of Seven Scientists* is, thus, very different from the more usual histories: highlighting the importance of mistakes to the progress of science, and reminding us that science is no different from any other human endeavour: complex, messy, and punctuated with success and disappointments. In reading this part of *A Tale…*, I was reminded of the comparison between Watson's account of the structure of DNA in *The Double Helix*[5] – essentially a quest,[6] and later accounts of the discovery that make more of the contributions of that discovery's 'little people', viz., Maurice Wilkins[7] and Rosalind Franklin.[8]

In a chapter that Scerri says is 'bringing it all together', he uses Merton's views of priority disputes[9] as driven by the need for reputation of the scientists involved and recognition of their achievement to observe (p. 179):

"Whereas the image of scientists is one of the disinterested pursuit of scientific knowledge for the sake of humanity, the reality is frequently one of harsh disputes, accusations of plagiarism, and all-out wars between leading scientists."

Scerri asserts that this behaviour, so similar to that of most other human endeavours, is evidence of "an evolutionary struggle between competing members of a species". Add to this the 'little people' in the background of science whose discoveries and activities struggle for at least some recognition (and/or funds), and the conduct of scientific research appears akin to one of those war scenes, where the foot-soldiers are sent into battle to their deaths by their commanding officer, who will later receive the accolades (Fig. 2).

This final chapter justifies the last part of the book's title: *… and a New Philosophy of Science*. Here, Scerri develops his analogy of the conduct of science to biological evolution, and uses it to cast doubts on whether science is appropriately portrayed as revolutionary.[10] I found it interesting to plot the relative data on Table 2 against the mid-point of research activity of both the 'little people' and the 'pivotal persons'. This diagram – Fig. 3 – shows a variable trend in the relative data for *A Tale…*, but two peaks for Scerri's more traditional history books. It occurred to me that the plots for the latter could be interpreted as periods of 'normal science' between peaks of activity, reminiscent of the trends seen in citations of 'revolutionary' papers relating to the development of the theory of plate tectonics.[11] Perhaps the difference between revolutionary and organic science comes down to whether the story is written in a way that excludes or includes the 'little people'.

Of course, debate about the applicability of Kuhn's ideas on scientific revolutions[10] is hardly new; indeed, Scerri cites several examples. However, although I considered that Scerri labours the point a bit too hard, by the end of the book, I felt that he had made a reasonable argument to at least justify his personal preference in this regard. In fact, 'personal' is a theme of this book: not only does the last chapter describe the development of Scerri's own philosophy of science, but it links back to twenty pages of 'Biographical Background' and ten pages of 'Introduction', also written from a personal perspective, and including a blog, which includes others' personal perspectives.[12] Time will tell whether in the philosophy of science Scerri is one of the 'little people' or a 'pivotal person'.

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# What is happening in Europe – the political ramifications of Brexit on the European patent system

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In the July 2014 Patent prose article we considered plans to set up a unitary European patent and the problems being encountered back then. The latest problem, that few saw coming, is Brexit.

## The background

Presently, you can file a single European patent application at the European Patent Office that covers any one or more European Patent Convention (EPC) member states. This application is examined centrally rather than having separate examination in different European countries, potentially saving time, effort and money. Once the European Patent Office decides that an application is allowable, you still have to go through formalities in each of the European member states that you want protection in. The result is a separate national patent in each selected European country. Due to the costs associated with the unbundling of the European patent into national patents and ongoing renewal fees, many European patents only become effective in 3 to 5 countries out of a possible 38.

However, as we talked about in our previous article, there has been a long running proposal to set up a unitary European patent which would mean a single patent could cover multiple EPC member states.

## What now?

The existing European Patent regime involving the unbundling of a European patent into separate national patents is separate from the agreements and membership of the European Union (EU). Brexit is the UK's exit from the European Union, not the EPC. The problem is that the unitary patent system is being implemented by the EU. Consequently, while Brexit will have no or little direct impact on the ability to use European patents to obtain protection in the UK, the likelihood of being able to use the unitary patent system in the future to cover the UK is less clear.

So what will happen if the unitary European patent goes ahead? The UK would be unlikely to be a part of it as it currently stands because it is exclusively for EU countries. However, while the UK is still in the EU, they are still part of the process.

As part of the unitary European Patent system, a Unified Patent Court also needs to be set up. A patent that covers a number of countries also needs to be enforced (i.e. suing a party that infringes the patent) or invalidated centrally, which means having a court with jurisdiction over all the countries. Prior to Brexit, the plans for the Unified Patent Court were advanced. An agreement on the structure of the new court was signed by 25 EU states on 19 February 2013. But, in order for the agreement to go into force it still needed to be ratified by at least 13 states, including France, Germany and, significantly, the UK. The plan also included having a division of the Court that dealt with chemical-/pharma-related patents located in London.

In November last year the UK intellectual property minister, Baroness Lucy Neville-Rolfe, indicated that the UK would go ahead and ratify the agreement on the Unified Patent Court in order to enable the plan to move ahead. Then, once the UK started the process to leave the EU, they could withdraw from the system or negotiate a way to continue to be part of it.

The present uncertainty stems from when the UK will start the process to leave the EU, whether they will want to negotiate to be part of the unitary European patent and whether it is even legally possible for a non-EU country to be party to the Unified Patent Court.

There has also been comment that a unitary European patent that does not include the UK will be less attractive. Will the other members of the EU still want to go ahead with the unitary European patent without the UK?

For the time being there are no conclusive answers to any of these questions and with the UK and the EU engaged in tough negotiations on their future relationship, there presently seems little political will to lay their cards on the table.

We will keep you updated if there are any further developments.

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact:

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# Dates of note

## APRIL

**23** ***Johannes Fibiger***, the Danish pathologist who received the 1926 Nobel Prize for Physiology or Medicine for the discovery of the *Spiroptera carcinoma* and induced cancer in laboratory animals for the first time, was born this day 150 years ago in 1867.

In 1827, 21-year old ***William Rowan Hamilton*** presented his *Theory of Systems of Rays* to the Royal Irish Academy in Dublin. It proved to be a single function that brought together mechanics, optics and mathematics and led to the wave theory of light.

**24** ***Jean Charles Marignac***, the Swiss chemist who made many precise determinations of atomic weights and suggested the possibility of isotopes and the packing fraction of nuclei, was born this day 200 years ago.

**25** ***John Chipman***, the American physical chemist and metallurgist who studied the role of oxygen in iron and steelmaking, was born in 1897.

In 1957, an experimental sodium reactor (SRE) began self-sustaining nuclear fission with sodium at 175°C in the core; by the 12$^{th}$ of the month it was providing electricity commercially.

**26** ***Michael Smith***, the British-born Canadian biochemist who won the 1993 Nobel Prize for Chemistry (with Mullis) for the development of oligonucleotide-based site-directed mutagenesis that enabled researchers to introduce specific mutations into genes, was born in 1932.

***Alfred Krupp***, the German manufacturer of steel and armaments died in 1887.

***Torunn Garin***, the Norwegian chemical engineer who helped develop aspartame sweetener as a sugar substitute as an employee of General Foods and subsequently became senior laboratory manager, died in 2002.

**28** This day in 1932 saw the first vaccine against yellow fever for human immunisation announced.

**29** ***Wallace Hume Carothers***, the American chemist who developed nylon in 1935, died in 1937.

In 1997, the worldwide Chemical Weapons Convention took effect after being signed by 88 countries, but excluding Russia.

**30** In 1897, at the Royal Institution Friday Evening Discourse, ***Joseph John Thomson*** announced the existence of ***electrons*** telling his audience that earlier in the year, he had made a surprising discovery - a particle a thousand times smaller than the atom.

## MAY

**1** ***Rufus Porter***, the American editor and inventor who put out the first issue of *Scientific American* in August 1845, was born in 1792, 225 years ago.

***John Glover***, the English chemist who developed the Glover Tower to reclaim useful chemicals during the manufacture of sulfuric acid, then the most important industrial chemical, died in 1902.

**2** ***Heinrich Gustav Magnus***, the German chemist and physicist who discovered the Magnus effect (the lift force produced by a rotating cylinder that gives for example, the curve to a curve ball) and is noted for the first platino-ammonium complex, his green salt $[Pt(NH_3)_4][PtCl_4]$), was born in 1802.

***Abraham (Pineo) Gesner***, the Canadian chemist and geologist who pioneered the extraction of kerosene (paraffin - which he also named) by dry distilling asphalt rock, was born in 1797.

***August Wilhelm von Hofmann***, the German chemist and inaugural professor of chemistry at the Royal College of Chemistry in London whose research on aniline helped lay the basis of the aniline dye industry, died in 1892.

This day in 1892 saw an industrial method for the production of calcium carbide discovered. By chance ***Thomas L. Wilson*** found a hard crystalline solid that gave off a gas when dropped in water that burned with a bright, smoky flame. It was shown to be calcium carbide and acetylene and the discovery eventually led to the formation of Union Carbide Company.

**4** ***Edward Calvin Kendall***, the American biochemist who (with Reichstein) won the 1950 Nobel Prize for Physiology or Medicine for research on the structure and biological effects of adrenal cortex hormones, died in 1972.

**5** ***Joseph Bienaimé Caventou***, the French chemist noted for research in partnership with Pierre-Joseph Pelletier into vegetable bases and the resulting contributions of alkaloid chemistry to medicine, died in 1877.

**7** The American Medical Association was established this day in 1847.

**9** ***Manfred Eigen***, the German physicist and biochemist who shared the 1967 Nobel Prize in Chemistry (with Norrish and Porter) for studies of extremely fast chemical reactions, has his 90$^{th}$ birthday today.

**10** The theory of valence was announced by Sir Edward Frankland in 1852.

**11** The B.F. Goodrich Company (Akron, Ohio) announced the development of a tubeless tyre this day in 1947.

**12** ***Jean-Baptiste Boussingault***, the French agricultural chemist who identified the biological nitrogen cycle, died in 1887.

**14** ***Mikhail Semyonovich Tswett***, the Russian botanist and father of chromatography who provided us with adsorption chromatography by extracting plant pigments from leaves with ether and alcohol and passing the resulting solution through a column of calcium carbonate, was born in 1872.

**16** Sir ***Frederick Gowland Hopkins***, the English biochemist who won the 1929 Nobel Prize for Physiology or Medicine (with Eijkman) for discovery of the essential nutrient factors now known as vitamins, died this day in 1947.

**17** ***Odd Hassel***, the Norwegian physical chemist who shared (with Barton) the 1969 Nobel Prize for Chemistry for work establishing conformational analysis, was born in 1897.

**18** Glass was engraved for the first time in Toulouse, France this day in 1787.

**19** ***John Jacob Abel***, the American biochemist and pharmacologist who made important contributions to the modern understanding of the endocrine glands and was the first full-time professor of pharmacology in the US (John Hopkins University), was born in 1857.

**20** Marie Curie was presented with a gram of radium worth $100,000 at the White House in Washington, DC, this day in 1921.

**22** ***George A. Olah***, the Hungarian-American chemist and recipient of the 1994 Nobel Prize for Chemistry for his 1960s work that isolated the positively charged, electron-deficient carbocations, woud have had his 90th birthday today, he dies on 8 March 2017.

***Herbert C. Brown***, the English-born American chemist and father of organoboranes who received the 1979 Nobel Prize for Chemistry (with Wittig), was born in 1912.

**23** ***Tom Bacon***, the English mechanical engineer who pioneered the modern hydrogen-oxygen fuel cell, died this day 25 years ago.

**26** ***Julius Stieglitz***, the American chemist whose research of molecular rearrangements and stereochemistry helped lay the foundations of physical organic chemistry, was born in 1897.

***Ernest Solvay***, the Belgian father of the Solvay process to produce sodium carbonate, died in 1922.

**27** ***Kasimir Fajans***, the Polish-American physical chemist who discovered the radioactive displacement law simultaneously with Soddy and found several elements that are created through nuclear disintegration, was born in 1887.

**28** ***Paul Émile Lecoq de Boisbaudran***, the French chemist who improved the spectroscopic methods developed by Kirchhoff and discovered gallium (1875), samarium (1880), and dysprosium (1886), died in 1912.

**29** ***Philippe Lebon***, the French engineer, chemist, and inventor of illuminating gas, was born this day in 1767, 350 years ago.

**30** ***Julius Axelrod***, the American biochemist and pharmacologist who investigated the formation of noradrenaline, discovered and isolated the enzyme he called catechol-o-methyl transferase, and received the 1970 Nobel Prize for Physiology or Medicine (with Katz and von Euler), was born in 1912.

**31** ***Richard Julius Petri***, the German inventor of the Petri dish, was born in 1852.

## JUNE

**1** ***René-Just Haüy***, the French mineralogist and founder of crystallography as a science by discovering the geometrical law of crystallisation, died in 1822.

***Richard Kirwan***, the Irish chemist whose *Elements of Mineralogy* was the first English systematic treatment of the subject, died in 1812.

**2** ***Claire Cameron Patterson***, the American geochemist and first to precisely measure the age of the earth (4.55 billion years), was born in 1922.

**3** ***Nils Gabriel Sefström***, the Swedish chemist who discovered the element vanadium, was born in 1787.

**4** ***Leslie H. Lampitt***, the English analytical chemist and food scientist who founded the largest (3000 sq. ft.) food laboratory in Europe for J. Lyons & Co. in 1919 and applied science to food production, died in 1957.

***Heinrich Otto Wieland***, the German chemist who won the 1927 Nobel Prize for Chemistry for his work on steroids in which he provided the structure of the bile acids, was born in 1877.

The Pasteur Institute was founded in Paris in 1887.

A process for making vaseline was patented by Robert Chesebrough in 1872. This English-born American chemist made it from the residue of petroleum distillation left in the still after all the oil had vaporised. Distillation by heat under vacuum and filtration through bone-black gives good quality vaseline. The patent claims uses in currying, stuffing and oiling all kinds of leather with the finest grade adapted as glycerine cream for chapped hands.

**5** The first personal computer, the Apple II, went on sale this day in 1977.

**6** In 1902, Prof ***James Dewar*** demonstrated to the Prince and Princess of Wales solid air and then a jet of liquid air raising to about 2 m.

**7** In 1637, ***René Descartes***' book *Discourse on Method of Rightly Conducting the Reason, and Seeking Truth in the Sciences* was published. It was a major work in science and mathematics as it led to logic, geometry and algebra holding utter certainty and it ushered in the scientific revolution of Galileo and Newton.

**10** It is 65 years since DuPont registered Mylar® as a trademark for the extraordinarily strong polyester film that grew out of the development of Dacron®.

**11** ***Carl von Linde***, the German chemist and engineer who invented mechanical refrigeration and tested it in a Munich brewery, was born in 1842, 175 years ago today.

***Carl Remigius Fresenius***, the German analytical chemist known for devising a method for the systematic identification and separation of individual metal and non-metal ions, died in 1897.

**14** ***John Ulric Nef***, the Swiss-American chemist who showed that carbon can have a valency of two as well as four, was born in 1862.

**16** ***Georg Wittig***, the German chemist noted for the organophosphorus reaction of ylides named after him, the Wittig reaction, and who won the 1979 Nobel Prize for Chemistry (with Brown), was born in 1897.

**17** Sir ***William Crookes***, the English physicist and chemist who discovered thallium, was born in 1832.

**18** ***Dudley R. Herschbach***, the American chemist who pioneered the use of molecular beams in the study of chemical reactions and shared the 1986 Nobel Prize in chemistry (with Lee and Polanyi), was born in 1932.

**19** Sir ***Cyril Norman Hinshelwood***, the English physical chemist who studied the details of reaction rates and mechanisms and, in particular, the combination of hydrogen and oxygen, and for which he shared the 1956 Nobel Prize for Chemistry (with Semyonov), was born in 1897.

**20** ***Erwin Chargaff***, the Austro-Hungarian biochemist who discovered the number of guanine and cytosine units and those of adenine and thymine in DNA to be the same, hinting at the base pair makeup of DNA. He also showed that the relative amounts of the four bases varies from one species to another. He died 15 years ago.

***James Mason Crafts***, the American chemist who with Friedel discovered the Friedel-Crafts reaction in 1877, died 100 years ago today.

**21** ***Louis-Jacques Thenard***, the French author of the influential 1813 four-volume *Treatise on Chemistry* who isolated boron (with Gay-Lussac) and hydrogen peroxide (1818), and produced the cobalt-based pigment Thenard's blue that is stable at high temperatures and used in porcelain, died in 1857.

**25** ***William H. Stein***, the American biochemist who was a co-winner of the 1972 Nobel Prize for Chemistry (with Moore and Anfinsen) for studies on the connection between chemical structure and catalytic activity of the active centre of ribonuclease, was born in 1911.

**28** ***F. Sherwood Rowland***, the Armenian chemist who (with Molina and Crutzen) shared the 1995 Nobel Prize for Chemistry on the depletion of the Earth's ozone layer, was born in 1927.

***Bertram Eugene Warren***, the American crystallographer who helped understand crystalline and noncrystalline materials and the transition from amorphous to crystallinity, was born in 1902.

***Wilhelm Hisinger,*** the Sweedish mineralogist who (with Berzelius) isolated cerium, died in 1852.

## JULY

**3** ***Pierre Berthier***, the French mineralogist who discovered bauxite in March 1821, was born in 1782.

**4** ***Albrecht Kossel***, the German biochemist and 1910 Nobel Prize winner for Physiology or Medicine for studies leading to the understanding of the chemistry of nucleic acids and proteins, died in 1927.

**10** ***Kurt Alder***, the German chemist and recipient (with Diels) of the 1950 Nobel Prize for Chemistry for their 1928 diene synthesis or ***Diels-Alder reaction***, was born in 1902.

**11** ***William Gregor***, the English clergyman, mineralogist and chemist who discovered titanium, died 100 years ago today.

**13** ***Henry Edward Armstrong***, the English organic chemist whose major research was in substitution reactions of naphthalene (see this *Journal,* **2015,** *79*, 157-160), died in 1937.

**14** Sir ***William Henry Perkin***, the English chemist and father of the synthetic dye industry following his discovery of aniline purple, died in 1907.

This day in 1867 saw Alfred Nobel first demonstrate dynamite at a quarry in Redhill, Surrey.

**15** This is the day in 1662 that the Royal Society received its Royal Charter from King Charles II.

**16** This day 150 years ago (1867) saw reinforced concrete patented by Frenchman Joseph Monier.

**17** Sir ***Frederick Abel***, the English chemist, military explosives specialist, and who invented cordite with Sir James Dewar, was born in 1827.

**18** ***Roald Hoffmann***, the Polish-born American and co-recipient (Fukui) of the Nobel Prize for Chemistry in 1981 for independent studies of reaction mechanisms, has his 80$^{th}$ birthday today.

**19** ***Pierre-Joseph Pelletier***, the Frenchman whose research with Caventou into vegetable bases and the subsequent alkaloid chemistry and its importance to medicine, died in 1842, 175 years ago.

**20** ***Gerd Binnig***, the German physicist and co-inventor (with Rohrer) of the scanning tunnelling microscope, was born 70 years ago.

***Tadeus Reichstein***, the Swiss chemist and recipient of the 1950 Nobel Prize for Physiology or Medicine (with Hench and Kendall) for his isolation of the first four active hormones from the adrenal cortex, the first synthesis of one of them, and the proof of their steroid nature, was born in 1897.