

Volume 77, No.4, October 2013

Articles and Features

- 113 Sands of time: Silica stardust in meteorites
Ilsa Cooke
- 115 Report on the 45th International Chemistry Olympiad competition
Suzanne Boniface
- 116 HOTAIR: Can we make sense of this anti-sense RNA?
Jeremy Ralston
- 120 A golden era in modern chemistry
James R. Wright
- 126 The importance of trace metal chemistry in understanding ocean processes
Rob Middag
- 130 Linking anthropogenic climate change and stratospheric ozone depletion
Laura E. Revell
- 136 Some unremembered chemists: John William Draper (1811-1882)
Brian Halton
- 142 Obituary: Robert John (Robin) Ferrier (1932-2013)

Other Columns

106	Comment from the President	135	New Zealand Science Scene
107	NZIC July News	141	Grants and Awards
112	NZIC Conference Update	143	Patent Proze
119	Chemistry in the News	144	Dates of Note
125	Conference Calendar	147	Author Index
129	NZIC AGM Notice	148	Subject Index

Advertisers

Inside front cover	Merck
Inside back cover	New Zealand Institute of Chemistry

Cover

Front cover: T.A. Rector (University of Alaska Anchorage) and H. Schweiker (WIYN and NOAO/AURA/NSF). The image shows part of a large supernova remnant called the Cygnus Loop. It is located about 1,500 light-years from Earth. Astronomers estimate the supernova explosion that produced the nebula occurred between 5,000 to 10,000 years ago. The illustration relates to the article by Cooke (page 113).

Comment from the President

I spent the morning of Sunday 25 August at the Canterbury-Westland Science & Technology Fair, helping judge the many student exhibits. It is always wonderful to see so many young people enthusiastically engaging in hands on, curiosity driven science. It is unfortunate, however, to see how few Year 12 and 13 exhibits there are in spite of the often quite substantial prizes up for grabs. I think there is an opportunity here for those of us in the tertiary and industry sectors to get alongside schools and support students with additional advice and perhaps access to equipment. Some sage advice at the right time could easily lift a good project to a great, prize-winning project. There may even be the opportunity for students to gain achievement standard credits *via* scientific investigation achievement standards if schools and the tertiary sector work together on this.

My presidential talk this year focused on the importance of communicating science and making a stand against pseudoscience, so I have been absolutely delighted to see the efforts of our Waikato colleagues in correcting some of the misinformation being circulated about fluoridation (<http://www.sciencemediacentre.co.nz/2013/08/23/anti-fluoride-campaigner-tries-to-sideline-waikato-chemists/>). I applaud the Waikato group for being proactive in circulating a letter of support for fluoridation amongst the scientific and professional communities.

Sir Peter Gluckman is correct when he states that many of the issues around fluoridation are value judgements (<http://www.pmcsa.org.nz/blog/what-is-in-the-water/>). However, this does not negate the fact that to make good value judgements the underlying scientific information needs to be clear and correct. Consequently, it is important that we challenge pseudoscience and misinformation where we can. And from what I have seen in the media, the opponents of fluoridation are not averse to using pseudoscience and misinformation to promote their views. I know that for some scientists it is difficult to step outside the comfortable and familiar walls of our laboratories to communicate with the public, but it is vital that we do so. The consequences of a world where people cannot distinguish between science and pseudoscience is frightening, although it can provide for some humour as well (see: <http://www.youtube.com/watch?v=HMGIbOGu8q0>).

At our recent Council meeting NZIC membership fees were discussed and it has been suggested that some members (those with grants that need spending, for example) might find it useful to pay membership fees for several years at a time. If anyone is interested in this option could you let me know and we can see about setting it up for members.

Also, I have been asked to remind those of you who publish in the area of chemical physics that the NZIC receives



funding from the journal *Physical Chemistry Chemical Physics*, the amount of which depends on the number of New Zealand-based authors who publish in this journal. As this journal also has a relatively high impact factor, I would like to encourage members to consider submitting appropriate papers to *Physical Chemistry Chemical Physics*.

The August Council meeting also included selection of this year's winners of the Easterfield Medal, the Maurice Wilkins Centre award, the Industrial & Applied Chemistry prize and the Denis Hogan Chemical Education award. This year many talented people were nominated for awards, which made our selection panel's job extremely challenging. Congratulations to those who won awards, and to those who didn't – your achievements still impressed the members of the selection panel: there was close competition in several categories.

This issue of *Chemistry in New Zealand* will be the last for Dr Peter Hodder as scientific editor. I'd like to take this opportunity to thank Peter for all his hard work. The co-ordination of multiple authors and copy cannot be the easiest thing to manage, but Peter has done it extremely well.

As the October issue is the last for 2013, this is my last "Comment from the President". I hope I will see many of you in Wellington at the 2013 NZIC conference – the programme so far looks excellent, thanks to the Wellington team's hard work. It has been an enjoyable time as president, supported by a dedicated council team, and by Richard Rendle, our Honorary General Secretary, and I have enjoyed meeting members on my visits to all the Branches this year.

Michael Edmonds
NZIC President

New Zealand Institute of Chemistry

supporting chemical sciences

October News

NZIC PRIZE WINNERS 2013

Congratulations to all 2013 NZIC prize winners.

Easterfield Medal: *James Crowley*, Otago

Maurice Wilkins Centre Prize for Chemical Science: *Robin Smith*, Otago

Shimadzu Prize for Applied and Industrial Chemistry: *Nigel Perry*, Otago

ABA Books Denis Hogan Prize for Chemical Education: *Duncan Smith*, St Pauls Collegiate School Hamilton

BRANCH NEWS

AUCKLAND

School of Chemical Sciences, University of Auckland

On 12 June the School hosted its fifth Annual Research Showcase. Dr *Ji-anyong Jin* and his committee did an outstanding job and we were all treated to a wonderful day of chemistry. All of our PhD students gave professional and exciting presentations of their work, whether in a poster or oral format. We are also very fortunate to have the wine scientists as members of SCS. The wine they chose was superb and our wine science students were very knowledgeable and professional. Dr *Lance Gravatt* was the keynote lecturer, and he gave a brilliant talk on the importance of vaccines. The Auckland NZIC committee is an enthusiastic and generous sponsor of this event.

The Branch annual dinner was at the Four Seasons Restaurant, AUT University, on 30 September where our members met and had a lovely dinner and chat.

Congratulations to Dr *Michael Schmitz* for landing the FOS Professional Development award. He used it to attend the Asia-Pacific NMR

symposium in Brisbane. Also, Dr *Geoff Waterhouse* – with his collaborators – was awarded a FMHS FRDF grant of \$159,903 for the project *Novel polymer implant for on-demand ocular drug delivery*; he was also awarded a Japan Society for the Promotion of Science (JSPS) fellowship to undertake research at Tokushima University. The fellowship is based around the project *TaON materials for photocatalytic water splitting*, which will further strengthen his group's existing expertise in the area of H₂ production from water and bio-fuels. Associate Prof *Cather Simpson* and Professor *David Williams* were successful in obtaining a Vice Chancellor's Strategic Development Fund grant for a project entitled *Lighting the Future: the University of Auckland Science Scholars Programme*. This initiative aims to engage about 100 top science students in an enriching programme. She is also the recipient of the 2013 National Tertiary Teaching Excellence Award. Congratulations to Shengpu Gao who won the best Poster Prize at the first Meeting of the Asia-Oceania Sonochemical Society, held at the School of Chemistry of The University of Melbourne. Congratulations also to Anis Arzami who won the third Poster Prize at the NZIFST Conference held in Hastings. Both Shengpu and Anis are PhD students in Associate Prof *Yacine Hemar's* Group. Dr *Duncan McGillivray* was awarded a CLear scholarship that provides a \$2,500 grant-in-aid to help him lighten his workload while he invests time and energy studying towards a PG-Cert in Academic Practice. Professor *Margot Skinner* was made a Fellow of the New Zealand Institute of Food Science and Technology.

We were fortunate to have many visitors who give brilliant presentations. Professor Dame *Carol Robinson*, Professor of Chemistry, at the University of Oxford gave a seminar titled *Rare gases to ribosomes*. Professor *David O'Hagan*, School of Chem-

istry, Centre for Biomolecular Sciences, University of St Andrews gave a lecture on the synthesis and properties of alicyclic chains and rings that contain runs of vicinal C-F bonds. Professor *Paul Burn*, Head and co-director of the Centre for Organic Photonics & Electronics (COPE) at The University of Queensland gave a lecture on *Deep Blue Phosphorescence for OLED lighting and displays*. Dr *Wessel Du Toit*, Department of Viticulture and Oenology, Stellenbosch University, South Africa, gave a talk on *Oxidative versus reductive handling of Sauvignon blanc grapes and wine*. Dr *Bruno Therrien*, Institute of Chemistry, University of Neuchâtel, Switzerland gave a talk on *Drug Delivery by Water-Soluble Organometallic Cage*. Dr *Norbert Jux*, from the Department of Chemistry & Pharmacy, Friedrich-Alexander-University of Erlangen-Nuremberg, Germany spoke on *Functionalised Porphyrins*.

The New Zealand Institute for Advanced Study (NZIAS), Massey University Auckland

Al Nielson has just been promoted to the professorial level. In July, Al attended the 20th European Conference on Organometallic Chemistry at St Andrews, Scotland, where he delivered an oral presentation and two posters. He then moved on to the second European Inorganic Chemistry Conference in Jerusalem, Israel, where he delivered two invited oral presentations and chaired one of the conference sessions. *Elke Pahl* and *Peter Schwerdtfeger* gave invited talks at the sixth Asian-Pacific Conference for Theoretical and Computational Chemistry in Gyeongju (Korea). The recent *Angewandte Chemie* paper entitled *Evidence for Low-Temperature Melting of Mercury owing to Relativity* has received major attention in the international press (not much in New Zealand though). A very good and easy-to-understand video by

Brady Haran (former BBC science journalist and now independent film maker) explaining why mercury is liquid at room temperature has just been uploaded on Youtube. It contains a nice explanation about relativistic effects and how these influence the melting behaviour of mercury, see <http://www.youtube.com/watch?v=NtnsHtYYKf0>

CANTERBURY

University of Canterbury

Chemistry and Fine Arts exhibition

The collaborative communication project between the Department of Chemistry and various departments in the Faculty of Arts culminated on 30 May with the most successful gallery opening this year, with more than 100 people attending. The CHEM 212/BCIM 212 class and students from the School of Fine Arts collaborated to produce a piece of art that communicated a scientific concept. The science students selected and explained a phenomenon to students enrolled in Design and Sculpture courses, who then produced a tangible piece of art. Students from the Postgraduate Diploma in Art Curation then organised and assembled the exhibition, complete with a catalogue that provided the scientific context for each piece of work, explained for both scientists and non-scientists. The exhibition remained open until 14 June.

Visitors

Dr *Peter Surman* from Douglas Pharmaceuticals visited the Department for a week in May as part of the FutureIntech VIP scheme. Peter spent a great deal of time speaking to undergraduate and postgraduate students about the skills required in the pharmaceutical industry, highlighting the skills that employers look for in graduates at all levels. Peter also spent time talking to academics from Chemistry, Chemical and Process Engineering, and Biological Sciences about the fundamental science being carried out at UC that complements the applied science of the pharmaceutical industry. Peter said, "Skills learned by postgraduates in research and publication are keenly sought by us as these people have the po-

tential to initiate new projects and to produce technical reports to the publishable standard required to support our international regulatory applications. UC is a top class university and very strong in the physical sciences and engineering. It has been great to learn about projects underway at the MacDiarmid Institute and Callaghan Innovation. There is mutual interest to continue to explore areas where Douglas and UC can collaborate on research topics and student development."

Dr *Sally Gaw* returned from an Erskine trip to the UK in May. During the six-week trip she visited Environmental Science Departments at Lancaster University, the University of York, the University of East Anglia and Plymouth University. A key issue Sally picked up on was the increased focus for all of the universities on the employability of their students. Employability initiatives being introduced include industry placements and modules focusing on employability/career skills. Other common agenda items for the departments visited were improving mathematics skills and reducing the amount of summative assessment.

Erskine Fellow Prof *Andy Phillips* visited the department for six weeks (July – August). Andy completed his PhD at Canterbury in 1999, then took up an academic position at the University of Colorado in 2001. Then he moved to Yale University, where he is currently a professor of Chemistry. Andy's research interests are the chemistry and biology of natural products, methods and strategies for complex molecule synthesis, and new approaches to the discovery of biologically active small-molecules.

MANAWATU

Landcare Research, Palmerston North

Benny Theng and wife, Judy, have returned from Brazil, where they attended the 15th International Clay Conference in Rio de Janeiro (7-11 July, 2013). On the way back to New Zealand, they spent two happy weeks with son, Andrew, in Vail, Colorado. Of the 300 participants at the conference, the majority were from Latin

America. Benny did not meet another 'kiwi' at the conference, reflecting the low profile of clay mineralogy in New Zealand as well as the tight control on overseas travel. By the same token, there were fewer delegates from Australia, the EU, Japan and China than usual. Benny is also pleased to report that the pre-conference short course (of 12 lectures) he gave on *The chemistry of clay-polymer reactions* was well received.

Massey University, Institute of Fundamental Sciences

Congratulations to Prof *Simon Hall* who has become the new Head for the Institute of Fundamental Sciences. Simon will be in charge of staff contributing to nine majors within the BSc programme. He commenced his new duties on 1 September.

In August the Fundamental Sciences Students Association (FUSSTA) held their first annual ball, which proved to be a great night for all involved.

Paul Plieger has been made a Fellow of the NZIC. The Plieger group expects new PhD candidate *Matthew Price* on 1 November. Matthew will be working on aluminium and boron complexes for LED applications.

Ashley Way has been awarded a Massey University Doctoral Scholarship, and will commence her studies towards a PhD under the supervision of *Mark Waterland* in November.

Recent talks at Massey have included *Jianyong Jin* from the University of Auckland who spoke about polymer chemistry, *Bruno Therrien* from the University of Neuchâtel who talked about organometallic cages as photosensitizer carriers, and *Jérôme Pelloux* from Université de Picardie who talked about PME/PMEI-mediated changes in pectins. In addition to these talks, *Helen Hsu* and *Nyree Parker* gave talks on their PhD work.

OTAGO

Dr *Michael Edmonds* visited Dunedin in July to attend the ChemEd conference and also gave his NZIC President's address, *Chemistry — an antidote to pseudoscientific thinking?*, generating much discussion during the question session afterwards.

The Otago Branch ran a student essay competition mid-year, with the winners awarded cash prizes and their articles published in this issue of *Chemistry in New Zealand*. The 1st and 2nd place prize winners for the inaugural competition were **James Wright** (PhD student, Department of Chemistry) with his essay *A Golden era in modern chemistry*, and **Jeremy Ralston** (MSc student, Biochemistry) writing about *HOTAIR: can we make sense of this anti-sense RNA?*

University of Otago, Department of Chemistry

Jim McQuillan was recognised by the Royal Society of Chemistry for his contribution to the development of Surface Enhanced Raman Spectroscopy (SERS). On the 40th anniversary of the discovery of this highly-sensitive analytical technique by Jim, Martin Fleischmann and Patrick Hendra, the RSC awarded a National Chemical Landmark plaque to the University of Southampton Chemistry Department where the ground-breaking experiments were undertaken.

Russell Frew, currently on secondment to the International Atomic Energy Agency in Vienna, returned to Dunedin in July to present his Inaugural Professorial Lecture, *Stable isotope deltas: using nature's tiny signatures to make connections in food and forensics*.

Funded by a Royal Society International Exchanges Grant awarded jointly with **James Crowley**, Ai-Lan Lee from the Institute of Chemical Sciences, Heriot-Watt University, Edinburgh was a visitor in the Department in late July. In addition to meetings with staff and students, Dr Lee gave a seminar that discussed her research into the development of gold- and palladium-catalysed reactions.

The Department welcomed **Jenny Lyburn** as a technician working alongside **Ian Stewart** in the running and maintenance of instrumentation such as mass spectrometry, HPLC and NMR.

Honours graduate **Ilsa Cooke** received a Fulbright Award that will allow her to undertake PhD studies at



Professors Patrick Hendra and Jim McQuillan at the National Chemical Landmark plaque unveiling, University of Southampton, 24 July 2013

the University of Virginia in Charlottesville. Ilsa will join the group led by Eric Herbst and Karin Oberg specialising in the chemistry of interstellar clouds and in planetary atmospheres. Before leaving, Ilsa wrote an article for this issue on *Sands of Time: Silica Stardust in Meteorites*. The PhD dissertation of **Angela Kaltenbach** has been placed on the Division of Sciences list of exceptional PhD theses. Angela was supervised by Claudine Stirling for work on *Uranium isotopic analysis of terrestrial and extra-terrestrial samples*. PhD student in the Jameson group, **Matthias Fellner** received third prize in the poster competition at the Queenstown Molecular Biology Meeting Redox in August.

Staff in the Plant Extract Research Unit are involved in several exciting projects with “core” funding from Plant & Food Research, including work on mānuka honey production, analogues of a new class of plant growth hormones, rapid methods for sensing disease in apples and grapes, and applying the new Fujita X-ray method to New Zealand natural products. On a smaller scale, the “Peruvian potatoes” team also had a win in a science quiz, fundraising for the 2014 NZ International Science Festival (<http://www.scifest.org.nz/>). Staff – **Catherine Sansom**, **John van Klink** and **Nigel Perry** – and students – **Oliver Watkins**, **David Richards** and **Daniel Killeen** – combined their knowledge on topics ranging from

chocolate for dementia to Star Wars esoterica. But the game-breaker was their topical limerick:

*There once was a lab out at Invermay,
But AgResearch leaders were old
and fey.*

“We don’t need science.”

“Costs too much in compliance.”

So they moved all the staff, faraway.

WAIKATO

Current NZIC President, Dr **Michael Edmonds** visited recently and gave a most entertaining talk on *Chemistry — an antidote to pseudoscientific thinking?*, which was greatly appreciated by the audience.

Analytical Chemistry Competition 2013

This annual event was held on at the University of Waikato in June. A total of 22 teams of four students each from the wider Waikato/Bay of Plenty region competed in the event. The task was to analyse a sample of $\text{BaCl}_2 \cdot n\text{H}_2\text{O}$ using a gravimetric procedure for Ba^{2+} and a volumetric method for Cl^- . This allowed the value of ‘n’ to be calculated in the empirical formula by difference. This proved to be a challenging analytical task, but those who did well, did very well; and the top place-getters were very close in the marks they received.

The competition allowed enthusiastic Year 13 chemists to spend a day in the University laboratories working



The winners of the 1st prize in the Analytical Chemistry competition, from left: Jack Treloar, Geoff Wilkin, David Lloyd, Samuel McCabe.

on an experiment that would be beyond the resources of their schools. Rivalry was fierce but the main emphasis was on enjoying the experience and meeting students from other schools.

Results were: 1st Prize: Hamilton Boys' High School (David Lloyd, Samuel McCabe, Jack Treloar, Geoff Wilkin); 2nd Prize: Pukekohe High School (Alan Blakemore, Olivia Pointon, Tim Rensen, Jemma Simmonds); 3rd Prize: Mount Maunganui College (Jonathon Gumbley, Haylem Rayner, Lucie Thyne, Zach Tombleson); 4th Prize: Aquinas College (Guy Bennett, Daniel Hughes, Stanley O'Toole, Phoebe Scherer); 5th Prize: Otumoetai College (Lucas de Rijk, Emma Dwight, Ben Houlton, Katie Wilson).

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

University of Waikato

Megan Grainger has just returned from six weeks at The University of Missoula in Montana, working with Emeritus Prof Richard Field on production of a model that will predict the ideal environment for the chemical conversion that occurs in mānuka honey resulting in the unique mānuka factor (UMF).

Retirement of Professor Alistair Wilkins

Alistair Wilkins retired from the Chemistry Department at the end of August 2013 after thirty eight years of service. He arrived in 1974 as a PhD graduate of Otago University and proceeded to establish himself as an excellent researcher in natural products chemistry and in organic environmental analysis. Over the years, Alistair has been involved in many research areas, including algal toxins, lichens, honey, saponins, metabolites responsible for animal diseases and mycotoxins. More recently, he carried out extensive analyses on environmental samples associated with the grounding of the *Rena* on Astro-labe Reef in Tauranga.

At Waikato, Alistair was the NMR guru and, in fact, very much the expert on almost any instrument in the Department! Alistair had a long-standing secondment relationship with the Veterinary Institute at the University of Oslo in Norway, where he would spend three months a year "playing" on the NMR spectrometer (now a 600 MHz cryoprobe instrument) to his heart's content and generating many results. He was also involved in many other fruitful collaborations with scientists at institutions such as AgResearch and the Cawthron Institute.

As many people commented at his retirement function, Alistair would

always drop everything to help you. He was very generous with his time and seemed to have virtually limitless energy and enthusiasm for both his teaching and research. At the function, the students presented Alistair with a scrapbook of memories of his time at Waikato; he was also presented with a model Bedford truck, a larger version of which he used to deliver bread for his holiday job as a student! **Wendy Jackson** also made an "environmental sampling" cake, complete with miniature farm animals and pins to mark sampling sites! We wish Alistair all the best with his retirement but expect to see him in one capacity or another for a while yet!



The amazing "environmental sampling" cake made by branch secretary Wendy Jackson to mark Alistair's retirement.



Alistair at his retirement function

WELLINGTON

Both the Branch and the SCPS were saddened to learn of the death of Emeritus Professor **Robin Ferrier** on July 11, one of New Zealand's internationally recognised chemists. Robin's distinguished career in Carbohydrate Chemistry stemmed from early academic work at Birkbeck

College of London University that evolved at Victoria from his arrival in late in 1970 as Professor of Organic Chemistry. During his time here, he conducted leading-edge research and taught many students who have gone on to have successful careers. He is remembered through the annual Ferrier Lectureship which was established in 2012. A full obituary appears elsewhere in this issue.

The first of two June Branch meetings saw NZIC President *Michael Edmonds* deliver his presidential address on 5 June. *Chemistry – an antidote to pseudoscientific thinking?* provided members and guests with the necessary wake-up call on the plethora of bad advertising that ranges from downright incorrect science to that which uses all the right words around something that is blatantly incorrect. Michael's use of examples of complaints to the standards authorities from his own efforts served to illustrate just how much one individual can do and how much more most of us should be doing. The second meeting that month was the Wellington Branch's major outreach effort for the year. It was the *NZIC Matariki Fireworks Display* and consisted of a family-friendly lecture-display of fireworks by *Anthony Lealand* of Firework Professionals Ltd, given in two Sunday shows in Victoria's Rutherford House (venue for the NZIC conference later in the year). The mid-afternoon session was a sell-out, with the 300-seat lecture theatre full. Anthony outlined the chemistry and history of fireworks, told the audience how fireworks are made and illustrated this with 15 live pyrotechnic demonstrations, noting that aluminium, once a wonder material that only the richest people could afford, is now a key component of white light production in fireworks. Anthony started his company some 35 years ago in Christchurch and has developed it to the extent that the business now delivers firework shows all over the South Pacific. It has performed in international competitions and manufactures fireworks for theatrical and special effect use in theatres and air shows throughout New Zealand. The finale was a most memorable end to the excellent event. Although the repeat performance that evening did

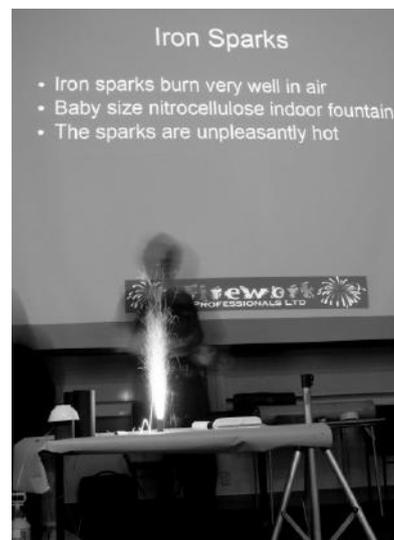
not fill the theatre, over 200 people were there. Well done Wellington!

Victoria University – SCPS

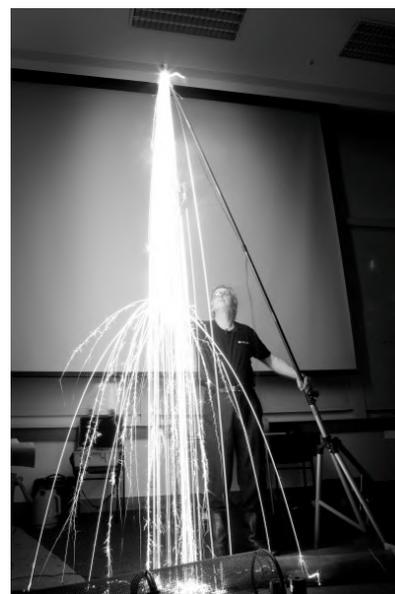
Dr *Jonathan Halpert* took up the recently advertised position of Lecturer in Physical Chemistry on 1 October. He gained his PhD from MIT and was based at the Cavendish Lab of Cambridge University prior to joining the School. His expertise in semiconductor-nanocrystal synthesis and characterisation as well as device fabrication fits neatly into the school research's profile.

Prof *John Spencer* recently spent two months at the University of York working with Prof Duncan Bruce, a plenary lecturer at the Hamilton NZIC Conference. He performed joint work on metallomesogens. York has a very strong liquid crystal group and some exciting young organometallic chemists with whom John had very useful interactions. He was also interested to see the way in which teaching was conducted at York and how they handled large numbers of undergraduates through an extensive laboratory programme.

"How much should chemists trust molecular orbitals?" asked Dr *Deb Crittenden* (Chemistry Department, Canterbury University) in her lecture to the School in mid-June. Pointing out that molecular orbitals are widely used in all fields of chemistry to predict the behaviour of electrons in molecules, she outlined the well-known qualitative variants of molecular orbital theory including crystal field theory, frontier orbital theory, the valence shell electron pair repulsion model with orbital hybridization, and Walsh diagrams. Noting that these models are widely and constructively used to explain molecular shapes, bonding patterns and reactivity of many molecules and complexes, she discussed the breakdown of these. Thus, she asked, "as hydrogen dissociates, should the electrons remain in the σ -bonding orbital? Does it make sense to define a σ -bonding orbital once the nuclei are so far apart they are essentially the centres of free atoms?" How can the molecular energy be quantitatively calculated for all choices of bond length? Her presentation went on to outline a simple



- Iron Sparks**
- Iron sparks burn very well in air
 - Baby size nitrocellulose indoor fountain
 - The sparks are unpleasantly hot



Chemistry of fireworks

but effective method for determining when it is necessary to move beyond the simple molecular orbital picture, and how to go about this in a robust and reliable way, particularly for large molecules, clusters and complexes.

Prof *Norbert Jux* (Friedrich-Alexander-Universität, Erlangen-Nürnberg) visited the School in late June to explore his overlapping interest with various staff members. His seminar

Functionalised Porphyrins, about these pigments of life, attracted a good audience and showed just why they are Nature's choice of dyes for solar energy harvesting and processing as well as for numerous oxidative transformations in the respiratory chain. Both of these highly sophisticated sequences generate a cyclic regeneration of carbon dioxide on the one side, and oxygen on the other that is driven by light. Fascinated by these actions, the Jux group has explored the field and given some insights into porphyrin chemistry. The synthesis and characterisation of tetrapyrroles with a high number of reactive sites, and the manipulation of them – generating a variety of highly functionalized porphyrins, such as octacationic and hexadeca-anionic (metallo) porphyrins – were explained. These were followed by a detailed view on the coordination chemistry of a porphyrin crown-ether conjugate, and then photovoltaic devices based on the layer-by-layer deposition technique with highly charged porphyrins and carbon-based nanotubes, and graphene.

July saw the visit of Dr Leigh Aldous (University of New South Wales, Sydney). He completed his PhD in Chemistry & Chemical Engineering at the Queen's University of Belfast in 2007, under Prof Hardacre. Post-doctoral study at Oxford University was followed by his appointment to



Very keen PhD students at the fifth School of Chemical Sciences Showcase.

the NSW lectureship, where he is Programme Coordinator of the BSc Nanotechnology course. Dr. Aldous' research focuses upon electrochemistry in ionic liquids, as well as electrochemistry and electroanalysis. His lecture *Ionic liquids at interfaces, such as electrodes and macadamia nut shells* provided insight on the widespread availability of ionic liquids and their use as new, unique solvents. As non-volatile, non-flammable, inherently conductive electrolytes, their potential applications are immense and he described five examples of looking at ionic liquids at interfaces, primarily but not exclusively by electrochemistry.

Prof *Andy Phillips* (Yale University) visited Wellington in early August during his Canterbury Erskine Fellowship to meet colleagues and

deliver his inspiring seminar *New Directions in Chemistry to Impact Novel Therapeutics*. He briefly described his group's contributions to new highly efficient tandem reactions and their applications in synthesis of complex natural product targets. Most of the talk was about the on-going work in discovery of new chemicals for therapeutics, based on protein interactions. Their design of new chemical structures is accomplished by careful examination of the protein interactions with other biochemical scaffolds, augmented with computation. Mass spectrometric analysis of protein complexes then provides a method for analysis of the binding of the chemicals to the proteins. Thus, he described the challenges of discovering small molecules that affect transcription factors, protein-protein interactions, and lncRNAs.

NZIC 2013 Conference Update

The organisation for the forthcoming NZIC conference in Wellington is proceeding well and is certainly rapidly increasing in pace! With the plenary speakers well under control, focus has shifted to the other aspects of the meeting including the conference excursions, invited speakers and the logistical aspects of the meeting like catering, poster boards etc. All in all, things are shaping up well.

Make sure that all of you that are attending the conference monitor the website (www.chemistryconference.org.nz) as up-to-date information regarding the speakers, venue, and, most importantly, the timetable will be uploaded as

soon as is practicable. Remember also that delegates are responsible for organising their own accommodation and should do so as soon as possible. Te Puni Village at the Kelburn campus is offering a discounted rate for conference delegates and is an attractive option, albeit a 25 min walk from the conference venue. Other hostels and hotels are available closer to Rutherford House as well.

As always, do not hesitate to contact the conference organising committee with any questions or queries (email: robert.keyzers@vuw.ac.nz). We look forward to welcoming you all to Wellington in December!

Sands of time: Silica stardust in meteorites

Ilsa Cooke

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Keywords: *presolar grains, nucleosynthesis, oxide-silicates, isotopic signatures*

It has become a common and poetic notion that we are the children of stars. Indeed, the atoms in our bodies were formed by nuclear reactions in the dying cores of suns. Our solar system formed about 4.55 billion years ago from the collapse of a giant cloud of gas and dust that came from dying stars predating our own sun. What resulted was a giant, rotating disc that caused mass to collect in the centre and form our sun. What could have caused the gravitational collapse that formed our solar system? A nearby supernova explosion could have done it; perhaps even the same supernova that flooded the presolar cloud with gas and dust. I have heard professed that we are “all made of stardust”. However, our early solar system was a hostile place; so hostile, that half a century ago it was believed that “stardust” could not have survived. Stardust, or presolar grains as they are scientifically known, are tiny time capsules; remnants of a time before our solar system. The tiny fraction of presolar dust that did survive became trapped in primitive meteorites. Presolar grains are relics of a variety of stars including novae, supernovae and red giants. They offer the opportunity to study nucleosynthetic processes of different stars and their contributions to the presolar dust population of our solar system. A grain the size of a speck of dust can provide more detail about stellar processes than even our most powerful telescopes.

Presolar Grains in Meteorites

Presolar grains are formed from the nucleosynthetic products of stars, which survived the collapse of the presolar cloud and became trapped in primitive meteorites (Fig. 1). The first presolar grains discovered were nanodiamonds in 1987.¹ Since then, scientists have found grains of more than ten different minerals in primitive meteorites. Abundant presolar minerals include diamond, silicon carbide, graphite, corundum, spinel and silicates.

Presolar grains are of the order of nanometres to several micrometers in size. They are identified by their unusual, “alien” compositions, that differ from the material in which they are embedded. The grains are isolated from the bulk meteorite by a series of acid and oxidising reagent treatments, which dissolve ~99% of the rock’s silicates and organic materials.² The grains of interest are then removed from the residue by colloidal or density separation. Since their discovery, several thousand presolar grains have been analysed, each contributing vital information about the stars that gave birth to our solar system.³

The Legacy of the Stars: Red Giants and Supernovae

Giant stars are steadily pumping dust into our solar system. Thus, it is no surprise that the majority of known presolar grains appear to have condensed from the nucleosynthetic products of giant stars.

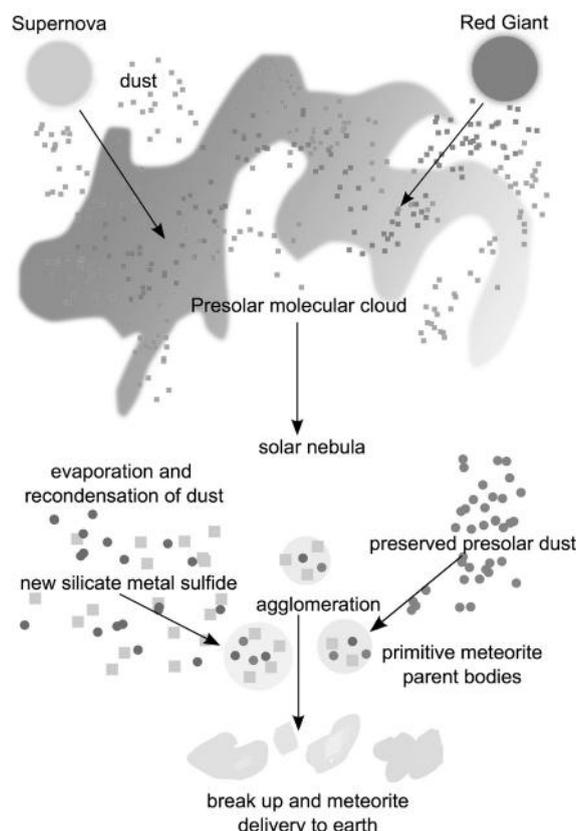


Fig. 1. Before our solar system began, dying giant stars such as red giants and supernovae produced dust grains that were ejected into the presolar cloud. A tiny amount of the original stardust survived the formation of our early solar system. This stardust became trapped, along with new silicate material, in the parent bodies of primitive meteorites. Some of these meteorites were delivered to earth where the presolar stardust may be extracted and analysed. Adapted from Lodders & Amari (reference 3).

Stars have a life cycle that can be tracked in terms of their temperature and brightness. Giant stars occur in the late stages of stellar evolution. Red giants originate from dwarf stars with masses of 1 – 8 times that of our sun. For most of its life a star will burn hydrogen (H) to helium (He) in its core. Once the H is exhausted, the He core contracts and increases in temperature, igniting H-burning in an envelope around the He-core. This causes the radius of the star to expand and the star moves on to the red giant branch (RGB) phase. During the RGB stage, He-burning and nuclear reactions in the core create carbon (C) and oxygen (O), resulting in a C- and O-rich core. Once the He is exhausted, the star enters the asymptotic giant branch (AGB) phase. Each of these giant stars produces different types of presolar grains with characteristic compositions. Presolar grains from AGB and red giant stars are the most abundant and most widely studied of all known stardust.

Massive stars, greater than eight times the mass of our sun, end their lives in spectacular stellar explosions (supernovae), spewing their nucleosynthetic products into space. After the production of carbon and oxygen, massive stars are able to sustain further nucleosynthetic reactions, forming neon, silicon and sulfur, among other elements, terminating at nickel. Before a supernova explosion, the star consists of onion-like layers of different elements that are a result of nuclear reactions at varying temperatures (Fig. 2). The temperature of the star increases toward the core, so different elements exist in zones from the core to the surface. These zones are named after the dominant element present: nickel (Ni), silicon/sulfur (Si/S), oxygen-rich zones: oxygen/silicon (O/Si), oxygen/neon (O/Ne) and oxygen/carbon (O/C), helium/carbon (He/C) and helium/neon (He/Ne) zones surrounded by an H-envelope. Within these zones, the atoms that make up different presolar minerals are formed.

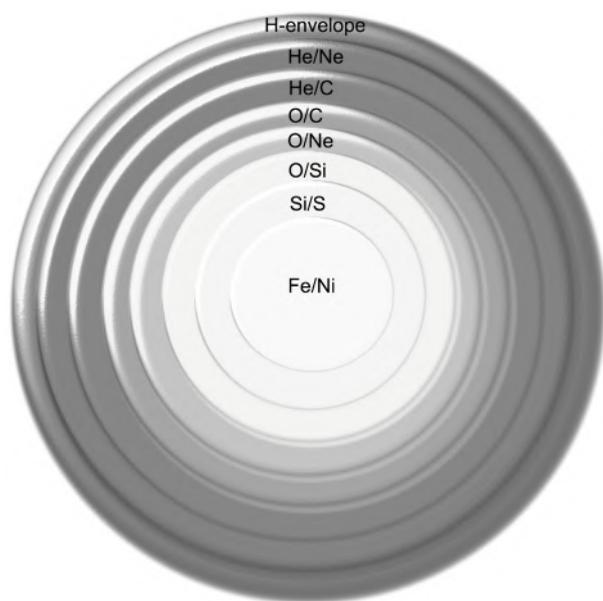


Fig. 2. Onion model depicting the layers of a supernova before its explosion. Nuclear fusion reactions result in layers of elements of increasing mass towards the core where the star is hottest. Theoretical models can be used to predict in which layers particular presolar minerals could form.

Stellar Fingerprints: the Importance of Isotopes

Presolar grains have different “fingerprints” from those formed after the birth of our solar system. These fingerprints come in the form of very tiny differences in the masses of the elements that make up the grains. Grains from ancient stars have highly unusual isotopic signatures that cannot be explained by any processes occurring in our solar system.³ Furthermore, different stars can produce different proportions of isotopes. This means that isotopes, and the characteristic signature they impart on presolar grains, are the key to unlocking secrets of our early solar system.

Oxygen isotopes are a key identifier of presolar grains. A classification system was developed to characterise oxide-silicate grains into four groups based on their oxygen isotopic composition.⁴ These four groups (Fig. 3) reflect

the different stellar origins or nucleosynthetic processes that may have produced the grains.⁵

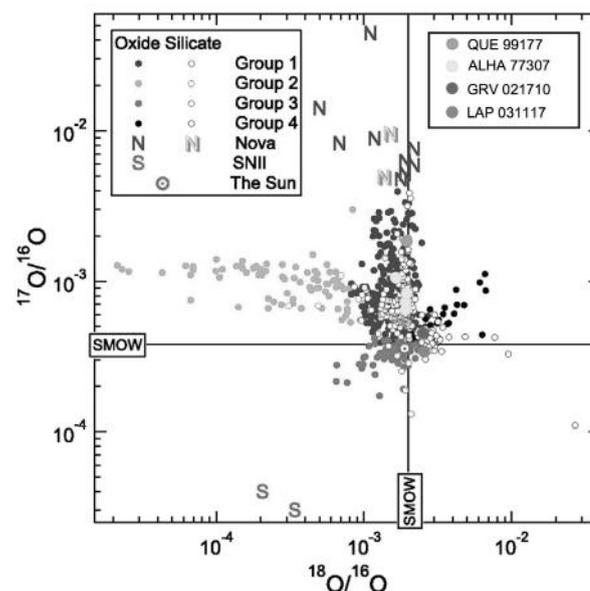


Fig. 3. A three-isotope plot displaying oxygen isotopic compositions of presolar oxide-silicate grains and their classification into four groups. SMOW (standard mean ocean water) oxygen isotopic composition is historically used to represent the solar system average. The silica grains thought to come from supernovae (GRV 021710 and LAP 031117) plot with the Group 4 oxide grains. The silica grains from QUE 99177 and ALHA 77307 are also plotted and fall amongst the group 1 grains. These grains are believed to have originated from AGB or red giant stars (adapted from Davis (ref. 5)).

Presolar Sand, the Mythical Condensate

One mineral we are all familiar with is silicon dioxide (silica, SiO_2), or “sand”. Initially, thermodynamic calculations predicted that silica would not condense in stellar environments. From these models, it was expected that silicon would be completely consumed by forming magnesium and iron rich silicates. In fact, presolar sand was dubbed the “mythical condensate” by researchers at the University of Washington in St Louis. Much to their surprise, presolar silica grains were discovered by researchers at the very same university. In 2009, Christine Floss and Frank Stadermann discovered the first silica grain in a primitive meteorite QUE 99177.⁶ Within the next year, four more such grains were found in ALHA 77307.⁷ However, all of these grains were enriched in ^{17}O relative to the solar abundance and had close to solar $^{18}\text{O}/^{16}\text{O}$ ratios (Fig. 3). This oxygen isotope fingerprint indicates that these grains probably originated from a red giant or AGB star. Not long after this discovery, graduate students in Christine Floss’ group discovered two more silica grains in primitive Antarctic meteorites LaPaz 031117 and Grove Mountains 021710.⁸ These grains were unusual. Their oxygen isotopic composition was different from those discovered in QUE 99177 and ALHA 77307. These grains were enriched in ^{18}O and had subsolar $^{17}\text{O}/^{16}\text{O}$, meaning they must have been formed in core-collapse supernovae (Fig. 3). In fact, the oxygen isotopic signatures of both grains were so similar that they were probably produced in the same supernova explosion; perhaps even the same

supernova that was thought to trigger the collapse of the presolar cloud and form our solar system.

Calculations had suggested that the oxygen isotopic composition of many Group 4 oxide and silicate grains would result from mixing of ^{16}O -rich material from the O-rich layers with material from the He/C zone and the H envelope.⁹ It was suggested that silica might originate from inner O and Si/S layers of supernovae. If silica grains do condense in the O-rich layers, the grains should exhibit large excesses in ^{16}O . However, the grains identified in LAP 031117 and Grove Mountains 021710 had excess ^{18}O . The ^{18}O enrichment in these grains could be reproduced by mixing small amounts of material from the O-rich inner zones and the ^{18}O rich He/C zones with large amounts of material from the hydrogen envelope. In fact, most presolar oxide and silicate grains from supernovae have shown excesses in ^{18}O instead of ^{16}O , much like these silica grains; the reason for the discrepancy remains unclear.

Perhaps we are not all made of stardust, but true stardust does exist — trapped within primitive meteorites: pure samples of stars. The presolar silica grains discovered at the University of Washington in St Louis are a snapshot

of a supernova. Whether they are from a supernova that caused the formation of our solar system, our planet and ultimately the star children that inhabit it, we should take with a grain of sand.

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Report on the 45th International Chemistry Olympiad competition

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The 45th International Chemistry Olympiad competition was held in Moscow on 15–24 July 2013 at the Moscow State University. It was opened by the Russian Deputy Prime Minister of Social Affairs, Olga Golodets. With up to four students from each country, there were 291 students representing 74 countries, and there were another three countries observing. The New Zealand team was represented by Feng (Frank) Zhou (Macleans College), Scott Huang (Rangitoto College), Ka Yin Keniel Yao (Macleans College), and Xin Yi (Cindy) Ou (Mt Roskill Grammar). The mentors were Dr Owen Curnow (University of Canterbury) and Dr Andrew (Buck) Rogers (St Peter's College). The New Zealand team made a three-day stopover in Hong Kong on the way to Moscow to break up the long travel and to prepare for the competition.

For the competition, the students were challenged by a very difficult five-hour theory exam; the average mark for all students was under 50%. The material covered was similar to the preparatory problems and included such topics as the absorption of gases on graphene, the decomposition of methane hydrates, and the biochemistry of archaea. The five-hour practical exam was slightly easier, although only one of our students managed to finish it. In addition to some titrations, there was a challenging series of viscosity measurements to determine the molecular mass of polymer samples. In the end, the New



Team photo, from left to right: Frank Zhou, Scott Huang, Keniel Yao, Cindy Ou.

Zealand team achieved one silver medal (Frank) and three bronze medals, with Scott's being the highest ranked bronze medal of the competition. This was an outstanding result; although countries aren't ranked in any way, our performance was similar to that of the Australians and British and ahead of the Canadians and Irish. Most of the gold medals were taken by Asian countries as well as the former Soviet states. The students especially valued the opportunity to meet with students from so many other countries.

HOTAIR: Can we make sense of this anti-sense RNA?

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Keywords: long non-coding RNA, cancer prognosis, modular functionality

Introduction

The essential information flow from DNA to RNA to protein is fundamental to biochemistry. However, the function of RNA is not restricted to the task of providing messenger RNA for protein synthesis. Indeed, many further functions are provided by RNA that are not translated. Examples of these non-coding RNAs (ncRNA) are: transfer RNA, which presents the ribosome with each amino acid to be included in the construction of proteins; ribosomal RNA, which contributes significantly to the structure and function of the ribosome; and other ncRNA such as silencing RNA (siRNA) and micro RNA (miRNA), which can regulate the translation of messenger RNA. Apart from ribosomal RNA, these examples of ncRNA have a length of less than 200 nucleotides.

Long non-coding RNA (lncRNA) can be defined as non-coding RNA greater than 200 nucleotides¹. Examples of lncRNA are HOTAIR, p21, H19 and BANCER, involved respectively in the following: cancer outcomes,² translation inhibition,³ inhibition of apoptosis in gastric cancer⁴ and melanoma cell migration.⁵ A brief summary of some types of RNA and their respective function is presented in Fig. 1.

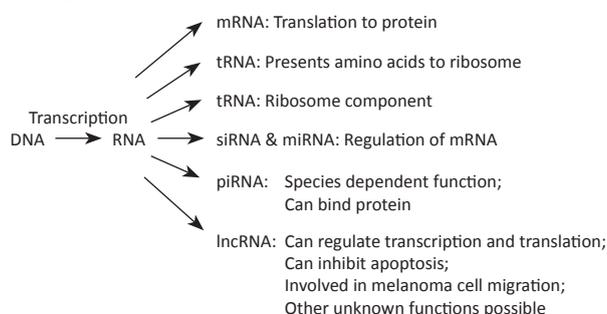


Fig. 1. Some RNA types and a brief description of their function.

lncRNA such as HOTAIR have been identified and associated with multiple types of cancer. Studies of HOTAIR provide valuable insight of the significance of lncRNA, and demonstrate the activity of functional domains that provide protein binding capacity resulting in altered transcriptional activity. This importance encourages the consideration of HOTAIR and other lncRNA as candidates for potential biomarkers and drug targets.

Identification of HOTAIR

HOTAIR (*HOX* antisense intergenic RNA) is a 2158 base pair lncRNA,² discovered in a study published in 2007.⁶ This included determining whether differential transcription of *HOX* genes is caused by ncRNA forming distinct chromatin domains. HOTAIR was selected as a prospective causal factor as it is located on the boundary between

chromatin domains which produce differential expression of genes either side of the boundary. Depletion of HOTAIR with siRNA caused much higher transcription of *HOXD* on chromosome 2, whilst having little effect on the region of origin of HOTAIR, *HOXC* from chromosome 12.

Importance of HOTAIR

The importance of HOTAIR is shown by associations between multiple cancers and expression of HOTAIR. Breast cancer metastatic samples showed increased HOTAIR by factors of hundreds to almost two thousand in comparison to non-cancerous samples.⁷ Primary breast tumours also showed high HOTAIR expression, as almost 33% showed a 125 fold increase in HOTAIR.⁷ Correlations between the liver cancer hepatocellular carcinoma (HCC) and HOTAIR have also been studied, with results indicating that HOTAIR levels could be used to contribute a prognostic factor in this disease. Of particular interest were samples taken from patients who had received a liver transplant, as transplant recipients with recurrence of HCC also had high levels of HOTAIR, whilst those without recurrence had low levels of HOTAIR.⁸ Colorectal cancer (CRC) has also been studied with respect to HOTAIR: HOTAIR levels were found to be higher in CRC tissues than tissues without cancer.⁹ Poor prognosis was also associated with high levels of HOTAIR in CRC tissues.⁹ In concordance with these correlations, HOTAIR has also been found to be expressed at higher levels in human pancreatic tumours than non-tumour tissue, is a negative prognostic factor for pancreatic cancer and has been identified as a possible target for intervention.² These associations of HOTAIR with different types of cancer are summarised in Table 1.

In addition to associations with cancer, and as a lncRNA which has functions proven by knockdown,^{7,8} HOTAIR now provides a platform for further understanding the structure-based characteristics which provide these functions.

Structural Considerations

It has been suggested that as the function of HOTAIR includes an interaction with PRC2, it may be beneficial to consider whether this structural feature is also present in other lncRNA which may be achieved through computational comparative genomics.¹⁰

However, this identification of structures in new ncRNAs may be difficult if a comparison is made by sequence alone, as other research has shown that lncRNA function can be conserved within a domain that does not conserve primary sequence.¹¹ In addition to this consideration of sequence identity between HOTAIR and other lncRNA,

Table 1. Summary of HOTAIR associations with a selection of cancer types.

Disease Analysed	Sample Type	Negative Control	Outcome of Association with HOTAIR	Reference
Breast Cancer Metastases	Breast Cancer Metastases	Non-Cancerous Samples	Cancerous samples increased HOTAIR by factors of 100x to almost 2000x	7
Primary Breast Cancer Tumour	Primary Breast Cancer Tumour	Non-Cancerous Samples	Almost 33% showed increase of 125x	7
Liver Cancer Hepatocellular Carcinoma	Transplant Recipients	Transplant Recipients	High levels of HOTAIR in recurring patients, low levels without recurrence	8
	Tissue with Recurrence	Tissue without Recurrence		
Colorectal Cancer	Colorectal Cancer Tissue	Colorectal Non-Cancerous Tissue	Higher levels of HOTAIR in cancerous tissues. Poor prognosis in Colorectal Cancer tissue with high levels of HOTAIR	9
Pancreatic Cancer	Pancreatic Cancer Tissue	Pancreatic Non-Cancerous Tissue	Higher levels of HOTAIR in cancerous tissues, HOTAIR is possible prognostic factor	2

the sequence conservation of HOTAIR can also be considered between species. An example is exon 1 (shown in Fig. 2) which has a similar RNA secondary structural prediction in humans and cows.

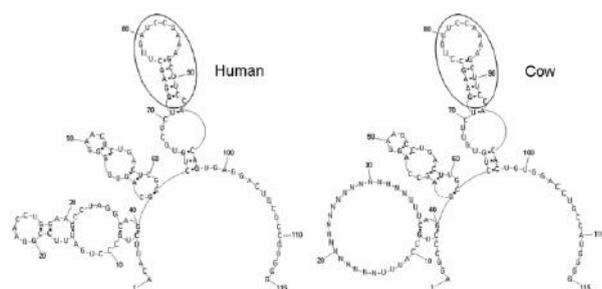


Fig. 2. PMmulti structural predictions of the 5' exon 1 of HOTAIR in human and cow. Circled are regions that have similar structural predictions with Mfold.¹⁰

At least two functional domains have been found in HOTAIR. At the 5' end exon 1 contains a sequence that binds PRC2 (at the Suz12 subunit of PRC2). At the 3' end domain B of exon 6 contains a sequence that binds LSD1.¹⁰ Remarkably, these regions have been found to be highly conserved in sequence and structure within ten mammals.¹⁰ Other regions of HOTAIR showed low conservation of sequence. This indicates the importance of those conserved regions as their consistent sequence provides the necessary structural basis for its function.

Functions of HOTAIR

When the 5' exon 1 of HOTAIR binds PRC2, and the 3' exon 6 binds LSD1 the functional effect of these interactions involves the in *trans* methylation and demethylation of histones, namely H3K27 methylation by PRC2 and demethylation of H3K4me2 by LSD1.¹² Although the finding of HOTAIR was unique in terms of in *trans* activity, within the functional context of lncRNA, 20% of lncRNAs have also been found to have a chromatin modifying function.¹³ As HOTAIR binds both PRC2 and LSD1 this provides a link, hence acting as a molecular scaffold.¹² The resulting function of this scaffold interaction is the epigenetic modification of chromatin, which consequently regulates gene expression by silencing *HOXD* genes.⁶

Identified regulated genes include the transcription factors *HOXD8-11*.⁶ Expression of *HOXD* genes has been found to be associated with the anatomical location of cells in which they are expressed as well as differentiation, hence matching differentiation of a cell with the site it is located.¹⁴ *HOXD8*, for example, is expressed only in the trunk and proximal regions of the leg.¹⁴ HOTAIR is expressed preferentially at different locations, such as at the foreskin but not the lung.⁶ Hence, HOTAIR epigenetically regulates cell differentiation at specific locations.

As described previously, HOTAIR has a strong association with cancer. Therefore, it is possible that HOTAIR could be targeted as either a biomarker or therapeutic for cancer. Because of this importance, furthering an understanding of the relationship between structure and function of HOTAIR could provide useful information.

Modular Functions

In addition to the functionality of HOTAIR shown thus far, further interactive capacity is possible. Modular regulatory principles, as described with respect to lncRNA,¹⁵ suggest that modular functional domains of lncRNA could perform activities such as binding to RNA or DNA, as well as the PRC2 and LSD1 proteins found to bind HOTAIR. Consequently, the function of HOTAIR may extend beyond the previously identified interactions. The activities of these domains may occur independently of each other. These modular regulatory principles appear to apply to HOTAIR, as the two 5' and 3' domains respectively bind PRC2 and LSD1 independently. This was shown by deletion mutants in which nucleotides 1 – 300 were shown to bind PRC2, and nucleotides 1500 – 2146 bound to LSD1.¹² Further HOTAIR domains may be possible, such as an interaction with histones, which could consequently enable the H3K27 or H3K4me2 methylation and demethylation respectively.

This modular approach to understanding HOTAIR could have further utility by comparing secondary and tertiary structures of identified HOTAIR functional domains with unknown domains of other lncRNAs. This would also

place HOTAIR information in the context of other functional lncRNA domains. Modular functionality could then be more accurately understood, with possible benefits such as increasing the specificity of therapeutic drugs that target domains of HOTAIR. Another possible advantage arising from considering functional domains of HOTAIR could be knowledge of a domain that potentially forms the basis for designing a HOTAIR activity assay as a biomarker. Establishing a library of modular domains may also enable analysis of conserved nucleotides necessary for a specific function. This could allow diagnosis of diseases, and also hopefully form the basis for a successful therapeutic response.

If an active site necessary for the function of HOTAIR is identified within a modular domain, it may be beneficial to target this active site with an antagonist. A possible oversight of the modular approach could mistakenly be made if the functions of the lncRNA were assumed to be limited to individual domains. For example, two domains may each have an individual function, but these domains could also have an additional combined function. Another possibility would be if there was a switch mechanism in the lncRNA. Then a loss of function mutation in a domain other than the switch that is involved in the switch activity may appear to assign the function solely to this non-switch domain. Actually the switch region would also be a functional domain that could remain unidentified by loss of function mutations. Hence, when considering modular domains, a possible pitfall could be a false perception of accepting a simplified version of an actually more complex lncRNA function. A eukaryotic example of ncRNA that has a switch region binding to the coenzyme thiamine pyrophosphate (TPP) is the TPP riboswitch.^{16,17}

HOTAIR in Relation to Pancreatic Cancer

In a 2012 study,² some conclusions were made regarding the association of HOTAIR with pancreatic cancer. Firstly, HOTAIR was found to be a negative prognostic factor for pancreatic cancer, as comparative HOTAIR expression in normal pancreas and pancreatic tumours was found to be significantly increased in tumour samples. Patients with tumours that had spread from the pancreas to the regional lymph nodes also had increased levels of HOTAIR. Similarly, samples from patients with tumours that extended beyond the pancreas, when compared with tumours only in the pancreas, showed increased HOTAIR. A Kaplan-Meier plot showed significantly shorter survival times for patients with high HOTAIR expression compared with low HOTAIR. The combination of these results, all of which show HOTAIR as a negative prognosis factor for pancreatic cancer, is useful, as it demonstrates the importance of HOTAIR with respect to pancreatic cancer. Despite this success, the majority of these increased levels of HOTAIR within the tumour, primary lymph node and extended tumour remained within the span of the negative control results. This means that HOTAIR as a biomarker for these outcomes does not appear to provide a definitive answer.

Secondly, this study indicated that HOTAIR is pro-oncogenic. This was shown by overexpression of HOTAIR,

resulting in significantly increased cell growth in one of two pancreatic cell lines. In addition, cell growth was significantly reduced upon knockdown of HOTAIR in two other pancreatic cell lines. Results from gene set enrichment analysis also indicate potential for pro-oncogenic HOTAIR activity, as it was shown to regulate genes with the function of cell proliferation and cell cycle progression. Cell invasion was also decreased with knockdown of HOTAIR, and apoptosis was increased upon knockdown of HOTAIR in two pancreatic cell lines.

Thirdly, the genes regulated by HOTAIR in pancreatic cancer cell lines were concluded to be significantly different from those regulated in breast cancer cell lines. However, this aspect of the study only considered gene expression of Panc1 and MDA-MB-231, one example each respectively of pancreatic and breast cancer cell lines. It would be interesting to repeat this with different cell lines of each cancer type, as considerable variation has been shown in the results of other experiments within this study, which considered more diverse samples of cancer cell lines.

Although the gene regulation effects of HOTAIR have been shown to be dependent on an interaction with PRC2, this study also showed that some regulated HOTAIR genes are independent of PRC2. This finding was achieved by comparing mRNA expression with each of HOTAIR knockdown and EZH2 (a subunit of PRC2) knockdown, with results of significant induction of selected tumour suppression genes and no significant induction of the same genes, respectively. As HOTAIR has been shown previously to also bind LSD1, a further experiment that could be of interest is to replace the knockdown of EZH2 with knockdown of LSD1. If the regulation of these tumour suppression genes were found to be independent of LSD1, this could suggest either direct regulation by HOTAIR, or another regulatory binding partner of HOTAIR exists, or either of PRC2 or LSD1 may be sufficient to regulate these genes. This could be checked by a double knockdown of PRC2 (via EZH2) and LSD1, to determine if this gene regulation can occur with neither present.

Discussion

The results from these studies encourage the consideration of HOTAIR as a biomarker or a targeted response to pancreatic cancer. Although HOTAIR has been shown to be overexpressed in the Panc1 and L3.6pL pancreatic cancer cell lines, it could also be of interest to determine how well these particular cell lines represent the general population with pancreatic cancer. This is because there is considerable variation in HOTAIR levels from other cell lines, so it would be useful to determine whether this variation is also present in a broader range of pancreatic cancer cell lines which would better represent pancreatic cancer patients.

In future research, it may also be of interest to attempt identification of further structural details of HOTAIR, such as possible methylation of adenosines that could alter function. These types of post-transcriptional modification are often found in regions of functionality¹⁸ which may benefit the identification of further modular regulatory

domains within HOTAIR. Also, as HOTAIR may interact not only with the proteins PRC2 and LSD1 but possibly also with RNA, identifying these possible interactions could provide further understanding of HOTAIR interactions. As lncRNA has been described as having scaffold characteristics, it may be possible that speculative RNA interacting with HOTAIR may also interact with either or both of PRC2 and LSD1. Therefore, any RNA binding to these proteins could be tested for also having interactions with HOTAIR. As we traverse the unknown characteristics of HOTAIR, we progress in the direction of making sense of this anti-sense.

Acknowledgements

Thanks to Dr Chris Brown for his inspiring, thoughtful teaching of lncRNA; Dr Harold Bernhardt for an abundance of enthusiastic, insightful discussion; and everyone from the Tate lab for helping it all precipitate.

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Chemistry in the News

Discovery of a new marine-derived anthrax antibiotic

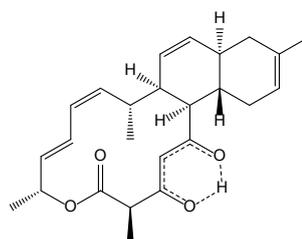
Anthea Lees

A new potent, anthrax antibiotic named Anthracimycin has been discovered, which is also active against methicillin-resistant *Staphylococcus aureus*. The new discovery was made in sediments off the coast of California and the antibiotic was isolated from the deep sea bacteria *Streptomyces* sp. The bacteria culture extracts showed activity against *Bacillus anthracis* (which is the spore-forming bacteria that causes anthrax) as well as activity against methicillin-resistant *Staphylococcus aureus*.

Anthrax is a human infectious disease spread by aerosol dispersion and in modern times has been used as a bio-terrorism weapon. In 2001 the US postal service had an anthrax scare, whereby letters were deliberately sent that contained powdered *Bacillus anthracis* spores. This resulted in a number of anthrax infections and five deaths. Anthrax can also be passed to humans through the handling of infected livestock. Although vaccines are currently being developed, they are, as yet, unavailable, so the discovery of this new antibiotic is very important.

Anthracimycin has a molecular formula of $C_{25}H_{32}O_4$ and is a polyketide antibiotic. 1D and 2D NMR studies showed the presence of a lactone-macrolide linkage and

the structure and absolute configurations surrounding the asymmetric carbon centres were established by X-ray crystallography.



Structure of Anthracimycin

The discovery was made by researchers at the Scripps Institute of Oceanography, University of California and their team leader Prof. William Fenical, commented, "The real importance of this work is that anthracimycin has a new and unique chemical structure. The discovery of truly new chemical compounds is quite rare. This discovery adds to many previous discoveries that show that marine bacteria are genetically and chemically unique." The results were published in *Angew. Chem. Int. Ed.* **2013**, *52*, 7822-7824.

A golden era in modern chemistry

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Keywords: *chemotherapeutics, arthritis, anti-cancer, homogeneous catalysis, gold*

Introduction

Gold (Au), the 79th element of the periodic table, has been valued since the beginning of recorded history. The initial usage of gold was probably ornamental, owing to its superior malleability, and evidence of its use can be traced as far back as the Bronze Age (ca. 5000 BC).¹ One of the most famous historical examples is the mask and sarcophagus of the young Egyptian pharaoh Tutankhamen (Fig. 1a), dated 1323 BC, which was made almost entirely of gold.

This fondness for gold is attributed to its resistance to oxidation, and its malleability. Gold is often found in its pure form, and historically this was mainly in rivers and streams. Its desirable characteristic colour inspired the element's name – 'Aurum' which when translated from Latin means 'shining dawn'. Other civilisations have similar references to gold as well. For example, the Incas referred to gold as 'the tears of the sun', and the Greeks thought of gold as a dense combination of water and sunlight.

The first valuation of gold can be dated back as far back as 3100 BC, in the first Egyptian dynasty, where its founder Menes equated one part of gold to two and a half parts silver. However, the use of gold as a universal form of currency didn't eventuate until ca. 600 BC when Lydian merchants produced the first gold coins (Fig. 1b).² This preceded Greek coinage, which was eventually adopted by the Roman Empire and the rest is history. Gold's resilience to oxidation made it ideal for this purpose.

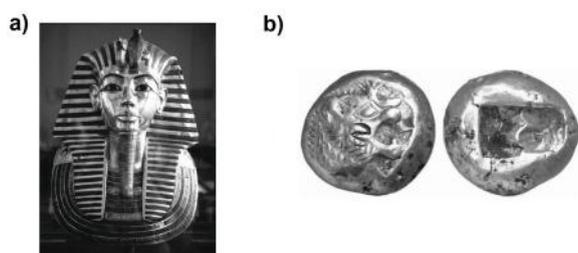


Fig. 1. a) The mask of the Pharaoh Tutankhamen, b) examples of early coins created by Lydian merchants from the 6th Century B.C.

Gold was sought after throughout early history not only for the purposes listed above, but also for religious reasons. Gold is mentioned throughout the Christian Bible (e.g., Genesis 2:10-12) and even further back to mythological times. For example, in Greek mythology the god Zeus presented himself to a woman in the form of a shower of gold. This resulted in the birth of the hero Perseus who goes on to kill the evil Medusa.³ The association of gold with the gods gave gold a divine status in ancient times: a way of communicating with the gods. It was even considered to be a link to immortality.

In the Middle Ages, this quest for immortality was at the core of western alchemy. The biggest and probably best known goal of alchemy was to produce the Philosopher's stone – a substance believed to be an elixir of life for achieving immortality, with the ability to turn any base metal into pure gold. Eventually, in the 17th and 18th centuries, alchemy declined. Robert Boyle's scientific method, led famous chemists Antoine Lavoisier and John Dalton to disprove the alchemical notion of the five fundamental elements. This was the birth of modern day chemistry.

The current use of gold in synthetic chemistry most often involves the use of its oxidised species Au(I) and Au(III), synthetically prepared from the strong acid aqua regia.⁴ Access to these species has enabled a paradigm shift of the metal's once perceived inertness. As a result, the understanding of the metal's properties and applications has been a rapidly growing topic in recent times.

The rest of this article describes and explains two main paths gold is now taking in chemistry: the development of chemotherapeutic agents, and the very recent and once thought improbable application to homogeneous catalysis.

Gold Chemotherapeutics

Although alchemists used gold in the treatment of a variety of illnesses, there was no scientific evidence for such activity until the late 1800s,⁵ when Robert Koch showed that the gold salt $K[Au(CN)_2]$ prevented the growth of bacteria (bacteriostasis). Since then gold has been included in realms of heavy metal therapy.

Rheumatoid Arthritis

In the 1930s Forestier showed that gold salts could be effective in the treatment of rheumatoid arthritis. Some of the drugs used in this trial, namely gold sodium thiomalate (Myochrysine, Fig. 2a) and gold thioglucose (Solganal) in the US and sodium bis(thiosulfato)gold(I) and sodium thiopropanolsulfate-S-gold(I) in Europe are still in clinical use today. The introduction of auranofin (Fig. 2b) in 1985 provided an oral alternative; however, the effectiveness is far less than the above intramuscularly administered drugs. The mechanism of action was not very well understood for a long time, but Stephen L. De Wall and co-workers have carried out experiments to suggest that square planar heavy metals [including Au(III)] can facilitate peptide release from MHC (II) proteins – proteins essential for normal immune function, and prevent an autoimmune response that causes the symptoms of rheumatoid arthritis.^{6,7} They also postulated that the Au(I) compounds used for rheumatoid arthritis are prodrugs and provide *in vitro* evidence for its intracellular oxidation via

hypochlorite release (OCl⁻) from macrophages in the synovial fluid of joints.

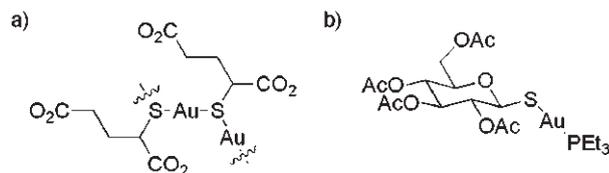


Fig. 2. The chemical structures of a) the polymeric aurathioma-late and b) auranofin.

With administration of many heavy metal compounds, there are side effects. Side-effects which result in discontinuation are experienced by 35% of patients. Along with rashes that can develop into severe dermatitis, mouth, tongue and laryngeal ulcers can also appear, as well as mild-to-severe kidney damage. Long term use of gold drugs can also cause chrysiasis – a dermatological condition that results in an irreversible discolouration of the skin to a gray-purple or gray-blue colour. In conjunction with these side effects, and the drug's latent effectiveness of 4-6 months, this class of drugs has been superseded in the treatment of rheumatoid arthritis.

Cancer

Investigations into the antitumour properties of gold compounds began in the mid-1970s.⁸ Reasons for this included the fact that gold(III) compounds have a *d*⁸ electron configuration, and are isoelectronic to platinum, adopting a square planar geometry that could possibly mimic the coordination mode of cisplatin – the most widely used heavy metal-based drug for the treatment of cancer. Other reasons for investigation were the fact that these drugs (from rheumatoid arthritis research) suppress the immune response and are therefore anti-inflammatory, and that studies showed that there was no increased risk of other diseases using gold compounds.

One of the first to be investigated was auranofin (*vide supra*) and results from studies on mouse tumour models showed *in vitro* inhibition of DNA and RNA replication, and therefore protein synthesis.⁹ The P-Au(I)-S arrangement was considered essential for activity, and so development was concentrated on making modifications to the phosphine groups to impart solubility and also to modify the thiolates to incorporate biologically active thiols. These have proven successful against human leukaemia, with greater *in vitro* activity than cisplatin.

Unfortunately, although promising *in vitro*, *in vivo* they were practically inactive owing to cysteine thiols on the surface of proteins readily displacing the thio-glucopyranoside moiety, deactivating the complex. Au(III) compounds at this time were also promising *in vitro*, but were not stable because of the reducing environment of cells. It is safe to say that initial studies were discouraging.

In the late 1980s, the beginnings of a new class of thiol-free compounds emerged with the synthesis of the mononuclear bis-diphenylphosphinoethane (dppe) Au(I) complex by Sadler's group (Fig. 3a).¹⁰ This compound was not only active *in vivo*, but the *in vitro*

results showed that this class of compounds worked by a mechanism different from both auranofin and cisplatin, possibly owing to stability *in vivo* against ubiquitous thiols. Unfortunately, the solubility of this compound was very low in water (<1 μg mL⁻¹) and the activity was less than that of cisplatin. Berners-Price and coworkers have since developed a more water-soluble version of this compound that is selective for cancer breast cells over healthy cells (Fig. 3b).¹¹

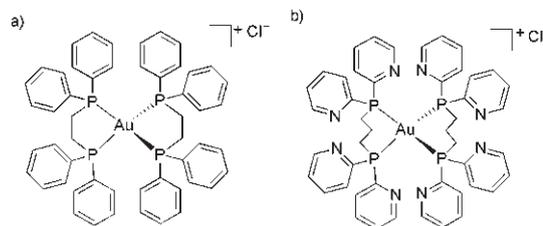


Fig. 3. Tetrahedral Au(I) complexes showing a) [Au(dppe)₂]Cl and b) the cancer cell-selective [Au(d2pypp)₂]Cl complex.

Hard donor polydentate ligands in gold(III) complexes were used to combat the instability *in vivo* (Fig. 4). In general, these compounds were highly cytotoxic with IC₅₀ values in the low μM/nM range. Of interest was that these complexes could kill cells that cisplatin could not; thus, like the Au(I) compounds, this suggested a different mode of action.

The Berners-Price group were able to provide insight into this unknown mode of action by using *N*-heterocyclic carbenes (NHCs, Fig. 5).¹² These ligands have similar properties to phosphines, they are easier to modify with different substituents (allowing tunability), but, more importantly, they form more stable complexes. The group synthesised a variety of lipophilic cationic dinuclear bisbidentate NHC complexes (e.g., Fig. 5a), with the rationale of exploiting the negative membrane potential of the mitochondrial membrane (which is elevated in cancer cells) for entry into the mitochondria. The results of *in vitro* testing showed that they induced mitochondrial membrane permeabilisation (MMP), which plays a key

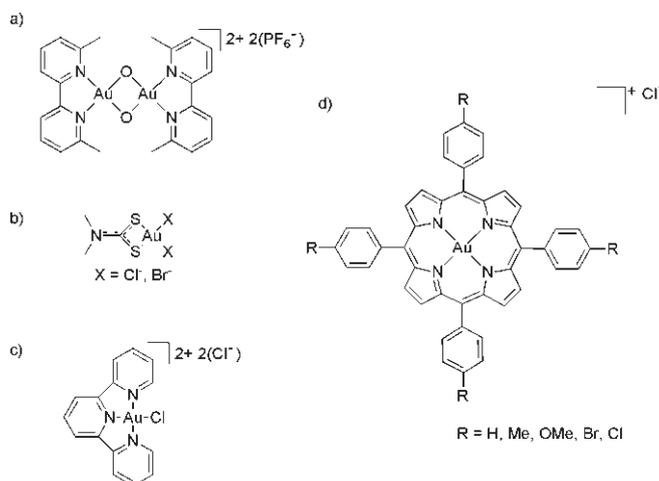


Fig. 4. Examples of gold(III) complexes with antitumour activity: a) an oxo-bridged dinuclear bis(bipyridine) complex, b) dithiocarbamate complexes, c) a gold(III) terpyridine complex and d) porphyrin complexes.

role in apoptosis, whilst also providing evidence for enzyme inhibition.

Another example is a mononuclear (amino-NHC)AuCl complex (Fig. 5b), which was shown to have a greater antiproliferative effect than cisplatin, with cellular selectivity for a particular glioblastoma line (U-87 MG).¹³ Also interesting was that the activity of the complex was based on a DNA-dependent mechanism, in contrast to evidence gathered on many other Au compounds that involved accumulation in mitochondria followed by enzyme inhibition (DNA-independent).

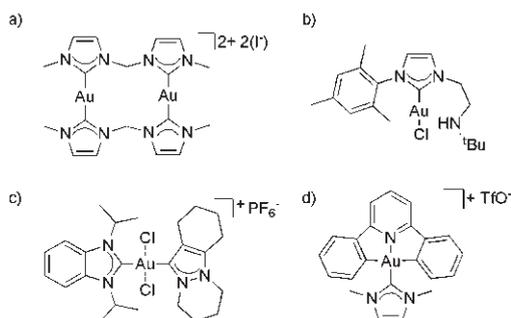


Fig. 5. Examples of successful NHC-based Au complexes tested for anticancer activity: a) a bis(diNHC) dinuclear cationic species, b) a amino-NHC neutral gold chloride complex, c) a heteroleptic Au(I or III) cationic complex, and d) a NHC gold(III) C^NC tridentate cationic complex.

There are also examples of Au(III) NHC drugs based on cyclometallated C^NC tridentate ligands, whereby the NHC ligand is auxiliary in the remaining coordination site (Fig. 5d).¹⁴ These compounds were tested in a variety of cell lines, and over 80% of them possessed a higher activity than cisplatin. The mechanism by which these compounds act is proposed to be caused by binding to topoisomerase-linked DNA, which leads to DNA cleavage and eventually apoptosis.

There are now a variety of NHC-based Au complexes that have been studied for their antitumour properties. Activities for these complexes vary significantly, but most are comparable to cisplatin,^{15,16} if not better.^{13,14,17-19}

One of the main modes of action for gold(I) compounds, and one of the main targets when testing gold compounds, is inhibition of the selenoenzyme thioredoxin reductase (TrxR). Normally this enzyme is involved in regulating cellular redox; however, in malignant cells it is involved in apoptosis, cell proliferation and metastasis, and is up-regulated in some cancers. For the lipophilic cationic gold complexes, they rapidly accumulate into the mitochondria, and selectively inhibit the enzyme (Fig. 6). This in turn causes an increase in oxidised thioredoxin (Trx2) and peroxide levels which stimulates MMP, allowing these species to diffuse into the cytosol where the hydrogen peroxide oxidises cytosolic thioredoxin (Trx1). Oxidised thioredoxin then activates apoptotic pathways leading to cell death.

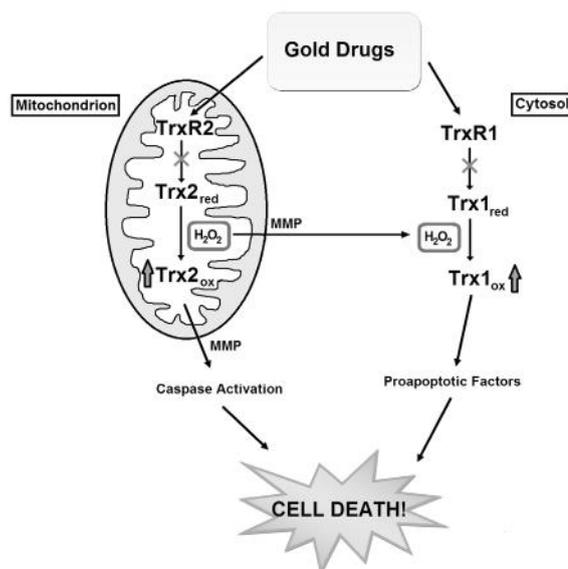


Fig. 6. A simplified mechanism of action of gold(I) antitumour agents via inhibition of thioredoxin reductase (adapted from ref. 20).

Gold(I) Catalysis

The Rise of Homogeneous Gold Catalysis

The idea of gold having chemical activity was long thought improbable owing to its well-established inert nature and its resistance to oxidation – properties which had led to gold's application in dentistry, jewellery and currency. Therefore, any use in catalysis was also considered improbable: a quote by Hubert Schmidbaur in the mid-1990s (translated by Nugent)²¹ reflects this:

The general doctrine appears to have been that gold, in contrast to its neighbor element on the periodic table, platinum, in neither the homogeneous nor the heterogeneous phase, exhibits activity that is in any way satisfactory. Gold was considered to be 'catalytically dead'

Nugent mentions that this misconception of inertness provided the first hints towards gold activity. In the 1970s de Meijere and co-workers were interested in the thermal conversion of diademane to triquinacene (Scheme 1).²² The investigation involved making a heat flow reactor, which was lined with metallic gold for its heat conductivity. However, when the reaction was carried out, instead of synthesizing the desired product, they produced snoutene. Further investigations led to the synthesis of a gold(I) complex (dicyclopentadiene gold chloride), which performed the conversion to snoutene at room temperature, strongly supporting the notion that the lining of the reactor was acting non-innocently.



Scheme 1. The initial discovery of gold's catalytic ability. Using a glass reactor, the expected retrocyclisation product triquinacene was isolated; with a gold lined reactor, the unprecedented product snoutene was produced.

The first reports of homogeneous catalysis emerged in the 1980s by the Utimoto group, employing a chiral ferrocenylphosphine gold(I) complex to catalyse the aldol reaction between aldehydes and enolates. Although they achieved high yields for this reaction, the reaction lacked selectivity (between *cis* and *trans* isomers) and the *cis* isomer had poor enantiomeric purity.

Although there have been several reports of gold(III) catalysis in the 1990s,²³⁻²⁵ these catalysts had low turnover numbers owing to the propensity to reduce to Au(0), and were performed at high temperatures. There was also evidence of Au(I) being more catalytically active than the trivalent analogue Au(III), but all the reactions involved the presence of acid.

A seminal report of Teles and co-workers showed an example of LAu(I)Cl catalysts (where L = arsenes, phosphines and phosphites) in the alcohol addition to alkynes, where the turnover numbers achieved were greatly improved (5000 for L = PPh₃).²⁶ Teles also noted that although electron-withdrawing ligands improved the catalytic activity, the stability of the catalyst suffered. This publication was the first that gained consensus for the idea that gold was chemically active. Since this report, the rate of publication has increased exponentially, with over 200 publications submitted solely on homogeneous gold catalysis in 2010.²¹ As significantly more work has been conducted with gold(I) catalysts, this will be the focus of the next section.

Reactivity of Gold(I) Catalysts

Gold catalysts act as carbophilic π -Lewis acids – i.e., they are particularly selective in coordinating to carbon-carbon π -bonds, namely alkynes, alkenes and allenes (Fig. 7).

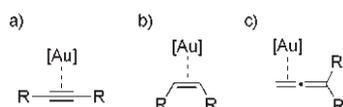


Fig. 7. Gold catalysts, [Au], activate alkynes (a), alkenes (b) and allenes (c).

The catalysts must be activated to cationic gold(I) species (Fig. 8), which traditionally involves abstraction of a halide *via* silver metathesis. Once activated, the catalyst coordinates in an η^2 fashion, activating the unsaturated bond to attack by nucleophiles such as oxygen, nitrogen, sulphur, and even carbon. Once the nucleophile attacks, the catalyst is now more strongly σ -bound to allow any further transformation of the substrate to occur. The final

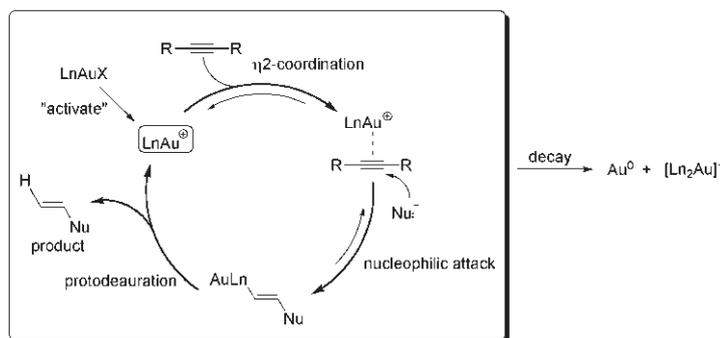


Fig. 8. The general gold(I) catalytic cycle.

step, protodeauration, is the recycling step, whereby the catalyst is substituted by a proton, allowing reaction of other substrate molecules.

This unique mode of reactivity of gold(I) has opened access to a variety of reactions that can be carried out under much milder conditions than previously reported. Unlike other heavy metals, gold(I) does not cycle between oxidation states during the catalytic cycle, and so it remains a soft Lewis acid for the entire reaction, allowing reactions that previously had to be carried out under harsh conditions to be carried out under much milder conditions, often in higher yields.

The Development of Gold(I) Catalysts

Initially, the gold(I) compounds tested consisted of phosphine ligated compounds of the formula (PR₃)AuCl. Phosphine ligands were already ubiquitous at the time gold(I) catalysis came about and were already successful as ligands in other heavy metal catalysis owing to their high σ -donor strength and poor π -back donation. This made the catalysts more stable than with related Werner-type complexes (*N*, *O* donors), allowing higher turnover numbers. There are now a variety of commercially available phosphine ligated Au(I) catalysts available (Fig. 9).

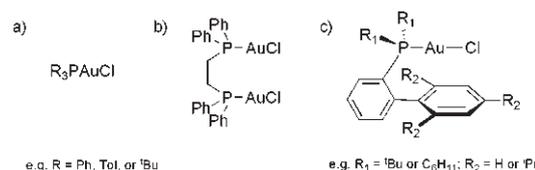
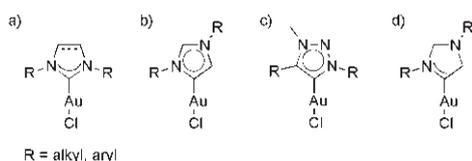


Fig. 9. Common commercially available phosphine-based gold(I) catalysts. One type of phosphine-based Au(I) catalyst to note is the range of biphenyl phosphine complexes (c) developed by Antonio Echavarren (see reference 27). The active catalyst is supposedly, in part, stabilised by a metal-arene interaction between the metal center and the phenyl ring. It is now widely used as a catalyst.

At the time this class of catalysts were developed, NHCs were well established in the literature. These ligands have a greater σ -donor strength than phosphines, are relatively easily synthesised, and their complexes were more stable. The most common of the NHCs are the 'Arduengo' imidazol-2-ylidenes (Fig. 10a) which vary with different *N*-substituents.²⁸ The catalysts with the most practical NHCs are those with sterically-hindering groups at these sites, which not only stabilize the free carbenes during synthesis, but also help shield the gold by any incoming destabilizing species in solution.

In practice, NHCs are usually synthesised with identical substituents, as the symmetric species are more trivial to synthesise than the non-symmetric analogues. Additionally, the extent of σ -donation is limited by the proximity of the two heteroatoms to the donor centre. Because of this, efforts have been made to move the heteroatoms to more remote locations of the heterocycles. Example of these so-called abnormal/mesoionic carbenes (MICs) are the isomeric imidazol-4-ylidenes (Fig. 10b)²⁹ and the 1,2,3-triazol-5-ylidenes (Fig. 10c).³⁰ The advantage of



R = alkyl, aryl

Fig. 10. a) The Arduengo-type imidazole-2-ylidene NHC complex, b) the isostructural mesoionic imidazol-4-ylidene complex, c) the 1,2,3-triazolylidene complex and d) the saturated imidazol-4-ylidene complex.

triazolylidenes, aside from the strong σ -donation is that they are more synthetically trivial owing to the copper-catalysed azide-alkyne cycloaddition reaction (CuAAC), and so have a more accessible range of tunability. To push the σ -donation even further, research has been undertaken into making saturated analogues of these complexes (Fig. 10d).³¹

As mentioned in the previous section, the activation of gold catalysts usually requires adding a silver salt to abstract the halide co-ligand. Recent studies have shown that in some cases the silver species (also a group 11 metal) can act non-innocently and partake in the reaction. Determining whether these reactions are completely gold catalysed is not necessarily trivial. To avoid the use of silver altogether, the idea of using labile ligands was adopted. The best example of this is work by Gagosz and co-workers, who synthesised the triphenylphosphinegold(I) triflimidate catalyst.³² The triflimidate coligand (NTf_2^-) is labile enough to create the active species in solution, owing to its weakly coordinating nature. A variety of triflimidate analogues of the gold phosphines are now commercially available (Fig. 11).

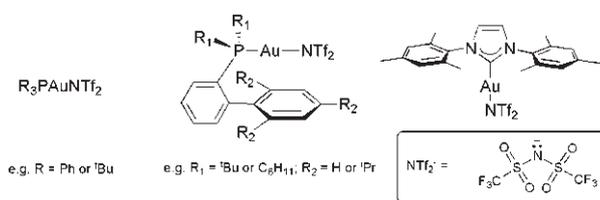


Fig. 11. A selection of new ‘silver-free’ triflimidate gold complexes now available.

There has been interest in the synthesis of multinuclear gold(I) catalysts for two reasons. The first reason is because of the higher gold content per mole of compound and increasing potency. The second reason is recent evidence of dinuclear participation or “dual activity” of gold species, owing to the isolation of dinuclear gold-substrate intermediates, supported by theoretical calculations. The Nolan and Toste groups have studied these in some detail (Fig. 12).³³⁻³⁵

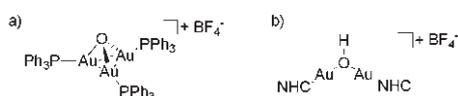
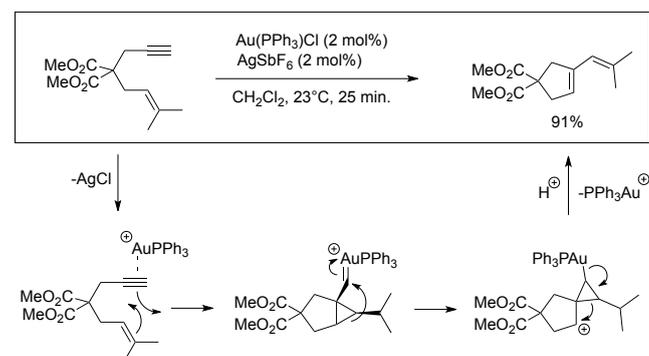


Fig. 12. Multinuclear complexes created by (a) Toste and (b) Nolan.

These catalysts function by the dissociation of an LAu^+ fragment in an equilibrium process, generating the active species. Nolan’s catalyst when dissociated can impart

Lewis acidity (LAu^+) and Brønsted acidity (LAu-OH) concertedly.

Along with the development of gold catalysts, gold-catalysed reactions are constantly being developed. There is now a plethora of gold-catalysed reactions that exist, with a few benchmark reactions to which these novel catalysts are subjected. One common example is the intramolecular enyne cycloisomerisation which typically rearranges 1,6-enynes via 5-*exo*-dig or 6-*endo*-dig pathways (Scheme 2).³⁶



Scheme 2. Proposed mechanism for the gold(I)-catalysed cycloisomerisation of 1,6-enynes (see reference 36).

Conclusion

Gold has had a huge influence on the development of human civilization. Its physical properties prompted its use in currency as a universal form of exchange, and aesthetically we have long appreciated gold. Its inferred divine status stimulated alchemical quests that led to the development of chemistry. Even within this field, gold has emerged as a unique transition metal at the forefront of antitumor therapy, and has recently given rise to a new mode of homogeneous catalysis. Gold catalysts not only act differently from other late transition metals, but offer access to new and unique chemical transformations. The extent of catalyst development in such a short period of time indicates a desire to explore gold’s full potential. The fact that research into gold chemistry is still being carried out shows us that, even after five millennia, gold still has more to offer.

Acknowledgement

The author thanks the Department of Chemistry, University of Otago for funding a PhD Scholarship.

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Conference Calendar

ISE Satellite Student Regional Symposium on Electrochemistry & 19th Australian and New Zealand Electrochemistry Symposium

Dates: 25 – 26 November 2013

Venue: Commonwealth Scientific and Industrial Research Organisation CSIRO, Clayton, Melbourne.

The meeting will be a forum for the presentation and discussion of research on all aspects of electrochemistry. The symposium will feature lectures by two renowned international experts and the Electrochemistry Division's 2013 Bond medallist:

Deadline for early-bird registration (reduced fee): 15 October 2013.

See: <https://www.raci.org.au/events/category/electrochemistry-division>

2013 NZIC Conference

Dates: 1 – 5 December 2013

Venue: Victoria University of Wellington, Rutherford House, Pipitea Campus, Wellington

Plenary Speakers: The six plenary speakers that have accepted our invitation to present are: Pieter Dorrestein (Scaggs Institute/UCSD; Analytical Chemistry), Ben Davis (Oxford; Organic Chemistry), Jim Watkins (U. Massachusetts; Materials/Industrial Chemistry), Tina Overton (Hull; Education), Jeff Tallon (Callaghan Innovation; Physical Chemistry), and Philip Power (University of California, Davis).

See: <http://www.nzic.org.nz/conferences.html>

Oz carbon 2013

Dates: 1 – 3 December 2013

Venue: Graduate House, The University of Melbourne, Australia

You are invited to gather with fellow carbon scientists and technologists to hear about, discuss and debate the latest developments in the rapidly moving carbon field. This meeting will consider carbon materials ranging all the way from traditional activated carbon through to more modern nanoporous carbons and beyond to glassy carbons, amorphous carbon, diamond, carbon nanotubes, graphene, carbon black etc. The meeting will span from materials aspects of carbon through to its applications, and will cover both experimental and theoretical aspects.

This meeting is to be held from late-afternoon of Sunday 1 December to mid-afternoon of Tuesday 3 December 2013. The programme will feature a number of tutorial sessions lead by invited experts that focus on highly topical areas.

Deadlines: 22 November 2013 – final date for acceptance of registration (late registrations will be accepted at the meeting).

See: www.ozcarbon2013.net/

The importance of trace metal chemistry in understanding ocean processes

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Keywords: *trace metals, manganese, phosphate, phytoplankton*

More than 70% of the Earth's surface consists of oceans. The oceans contain a multitude of life, are important as a source of food and play an important role in our global climate. Within oceans, trace elements are important regulators of ocean processes, including marine ecosystem dynamics and carbon cycling. The role of iron, for instance, is well known as a limiting micronutrient of phytoplankton (the base of the food chain) growth in the surface ocean.^{1,2} Other trace elements, such as zinc and lead³ whose distributions have been significantly impacted by human activity, are harmful to the natural and human environment owing to their toxicity at high concentrations. Through their effect on phytoplankton growth, trace metals affect the amount of atmospheric CO₂ sequestered in the deep ocean via the biological pump, thereby affecting global climate.¹ In addition, much of what is known about past ocean conditions, and therefore about the processes driving global climate change, is derived from trace element and isotope patterns recorded in marine deposits.

Since the mid-1970s, marine chemists have gained a first-order understanding of the concentrations, distributions, and chemical behaviour of trace metals in seawater. Important factors initiating this leap in knowledge were major advances in modern analytical chemistry and instrumentation. Along with the development of highly sensitive analytical techniques came a recognition and appreciation of the importance of handling contamination issues by using clean techniques during all phases of sampling and analysis (Fig. 1). This is necessary owing to low concentrations of trace metals in seawater relative to the ubiquity of metals on a ship or in a laboratory (e.g., dust, rust, paint with copper and zinc antifouling agents, brass fittings, galvanized material). As a result, seawater concentrations of most trace metals have now been accurately determined in at least some parts of the oceans, and their oceanic distributions have been found to be consistent with oceanographic processes.



Fig. 1. *Left:* The all-titanium 'Titan' Ultra-Clean sampling system for trace metals coming on deck after a deep deployment in the Mediterranean Sea aboard RV *Pelagia*. The vessel and sampling system are owned by the Royal Netherlands Institute for Sea Research. Otago researchers were participating as collaborators on this GEOTRACES expedition. *Right:* The author taking subsamples for trace metals inside the 'cleanroom van' that houses the Titan sampling system. The air supply for this van is filtered to ensure it contains negligible amounts of dust that is a source of contamination for trace metals.

The concentrations and distributions of trace metals in seawater are controlled by a combination of sources, sinks and internal cycling. External sources of trace metals include rivers, wind-blown dust from arid and semi-arid regions of the continents, and hydrothermal vents at mid-ocean ridges. Processes removing trace metals from seawater include active biological uptake as well as passive scavenging onto either living or non-living particulate material. These particles sink towards the sea floor: the ultimate sink of trace metals is generally burial in marine sediments. However, while settling towards the sea floor or in the superficial sediments, a proportion of these particles will be broken down by bacteria and the metals released again. The various sources and sinks as well as the internal cycling are superimposed on the general circulation and mixing of the oceans, resulting in the characteristic oceanographic distributions of each trace metal. One of the first examples of accurately measured concentrations was for the trace-metal cadmium (Cd).^{4,6} These early studies demonstrated that dissolved Cd in the ocean follows a pattern similar to that of the nutrients nitrate and phosphate that fuel phytoplankton growth. These were surprising results, as Cd was known as a toxic metal. It has now been shown by laboratory studies that Cd is used as a metal co-factor in the carbonic anhydrase enzyme.⁷ It has been shown to be able to substitute for Zn and a separate Cd-specific carbonic anhydrase enzyme has been identified in diatom algae.⁸

Prior to 2010, most of the data for full depth vertical profiles of trace metals in seawater was from papers published in the 1980s and 1990s. Most of the profiles were from either the North Pacific or North Atlantic. There was a paucity of vertical profiles from the South Atlantic and South Pacific. In the mid-2000s, it was argued that a new trace metal programme needed to be in place in order to provide appropriate global coverage of the concentrations of trace metals. Much of the impetus for such a program came from the recognition of Fe as an important micronutrient influencing global biogeochemical cycles in the oceans^{1,9,10} and the potential role of other trace metals such as zinc (Zn). As a result, the international GEOTRACES programme (www.geotraces.org) was formed, that aims to identify processes and quantify fluxes that control the distributions of trace elements and their isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions. One goal of GEOTRACES is to determine global ocean distributions of selected trace elements and isotopes (TEIs)

– including their concentration, chemical speciation and physical form – and to evaluate the sources, sinks, and internal cycling of these species to characterise more completely the physical, chemical and biological processes regulating their distributions. These measurements are needed to both initiate and verify models and to identify processes not contained in existing models. Major field efforts involving zonal and meridional transects have recently taken place and more are planned during the rest of this decade by several nations.

One of the first GEOTRACES expeditions was during the International Polar Year aboard RV *Polarstern* during expedition ANT XXIV/3 (10 February 2008 – 16 April 2008) from Cape Town (South Africa) to Punta Arenas (Chile; Fig. 2). One parameter of interest was dissolved manganese (Mn). Dissolved manganese occurs in a small concentration range in the open ocean, with surface concentrations between 0.1 and 25 nmol L⁻¹ and generally low and quite uniform concentrations in the deep ocean.^{11,12} Concentrations of dissolved manganese ([Mn]) are typically elevated in the surface layer of most ocean regions and are the result of photoreduction of Mn oxides¹³ and atmospheric input.^{11,14} However, in the Southern Ocean the surface [Mn] is known to be very low,^{15,16} most likely owing to very limited input in combination with active removal by the Antarctic algal community.^{17,18,19}

Several Fe fertilization experiments^{20,21} have shown that Fe and light are key factors limiting the growth of phytoplankton in the Southern Ocean. Since phytoplankton is the base of the food chain, in essence all life is limited by the availability of light and Fe in the Southern Ocean. Dissolved Mn has also been suggested to be potentially (co-)limiting.¹⁵ This has been shown in labora-

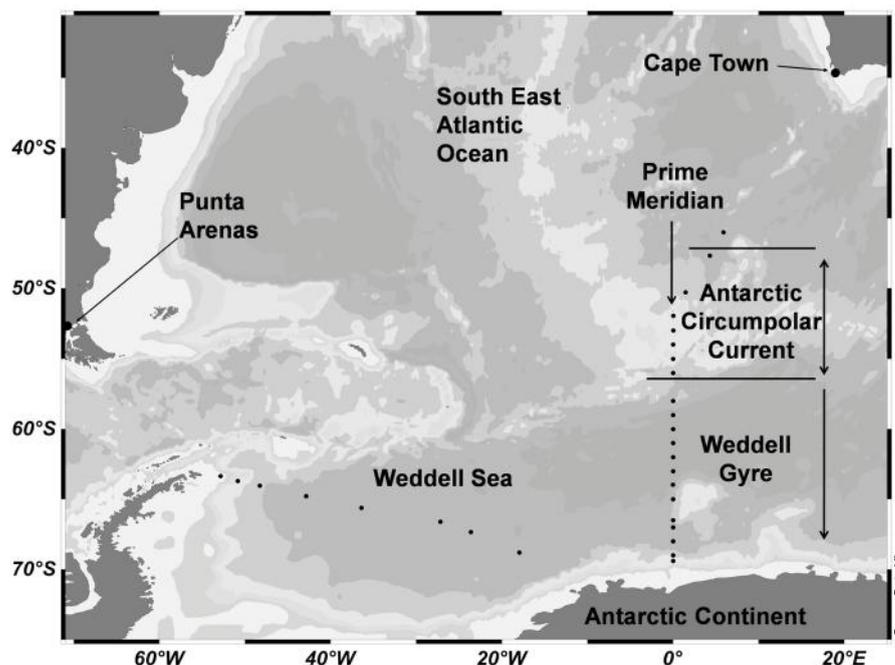


Fig. 2. Chart of the Atlantic sector of the Southern Ocean with sampling station positions along the Prime Meridian and in the Weddell Sea. Samples were collected aboard RV *Polarstern* during GEOTRACES expedition ANT XXIV/3 (10 February 2008 – 16 April 2008) from Cape Town, South Africa to Punta Arenas, Chile. This expedition was during the International Polar Year.

tory experiments²² and to some extent in the field,^{23,24} but a positive response to Mn addition is not always observed.^{23,25,26} This indicates that in some parts of the Southern Ocean the ambient [Mn] is in adequate supply, *i.e.*, not limiting. Manganese is an essential nutrient needed for various biological processes in cells, most notably photosynthesis.^{13,27} Additionally, Mn is also essential in the superoxide dismutase (SOD) enzymes of marine diatoms,^{22,28} especially under Fe-limiting circumstances. Under Fe-limiting conditions, more Reactive Oxygen Species (ROS) are formed, such as superoxide and hydroxyl radicals. The ROS are highly reactive and therefore destructive for the cell and must be destroyed by SOD at the site of production. The depletion of Mn in constant proportion to the depletion of phosphate, which has been observed in the surface waters of the Southern Ocean,^{18,19} confirms Mn is indeed an essential element. The slope of the Mn-PO₄ relation in the surface ocean (Fig. 3) equals the dissolved $\Delta\text{Mn}:\Delta\text{PO}_4$ (disappearance ratio) owing to biological uptake, assuming relatively uniform Mn and PO₄ concentrations before biological uptake in summer. This slope can be taken as representative for the Mn:PO₄ uptake ratio and, thus, the cellular Mn:PO₄ ratio of the phytoplankton, if both Mn and PO₄ are taken up into plankton cells. The PO₄ depletion is caused by actual uptake,²¹⁻²⁵ but for Mn one could question whether it is actual uptake or mere adsorption on the outside of plankton cells. If it is actual Mn uptake, the $\Delta\text{Mn}:\Delta\text{PO}_4$ must closely resemble the known Mn:PO₄ ratio of phytoplankton. Indeed, the observed $\Delta\text{Mn}:\Delta\text{PO}_4$ matches the value of $\sim 0.4 \times 10^{-3} \text{ mol mol}^{-1}$ identified by Bruland *et al.*²⁹ for the Mn:PO₄ composition of phytoplankton from multiple studies, supporting the hypothesis that the Mn depletion is due to actual uptake rather than adsorption. The observed ratio is lower than the value of $\sim 1 \times 10^{-3} \text{ mol mol}^{-1}$ reported by Kuss and Kremling³⁰ for an individual study, indicating there is spread in the ratio between different regions and phytoplankton communities. Consistent with this notion, there appears to be a trend of increasing $\Delta\text{Mn}:\Delta\text{PO}_4$ from north to south based on observations in the Southern Ocean.^{18,19} It was suggested that the $\Delta\text{Mn}:\Delta\text{PO}_4$ could be related to the ambient dissolved Fe availability, as the need for Mn by diatoms, the dominant phytoplankton class, increases under decreasing Fe concentrations.^{18,19} Similarly, a decrease was previously observed in the cellular Mn:P ratio for diatoms from $0.42 \times 10^{-3} \text{ mol mol}^{-1}$ to $0.22 \times 10^{-3} \text{ mol mol}^{-1}$ after Fe addition in the Pacific sector of the Southern Ocean.³¹ Plotting the $\Delta\text{Mn}:\Delta\text{PO}_4$ (dissolved Mn and PO₄ measurements) and the Mn:P ratio for diatoms from the Pacific sector of the Southern Ocean *vs.* the dissolved Fe concentrations (Fig. 4) does indeed result in a significant correlation ($p = 0.001$). This increase of the Mn:PO₄ ratio with decreasing Fe concentrations is consistent with the hypothesis of elevated Mn requirement of the diatom dominated phytoplankton community under low Fe conditions.¹⁸ The extremely low surface concentration of Mn in the surface layer of the Southern Ocean,^{18,19} in combination with the low concentrations of Fe, would potentially be limiting to the diatom community. Supplying diatoms with only additional Fe would alleviate only part of this co-limitation, as Mn is still needed in photosynthesis and SOD, even if there is ample Fe. Manganese, together with

the effects of Fe and light limitation, might have the potential to control life in parts of the Southern Ocean,¹⁹ but this will need to be verified in future studies.

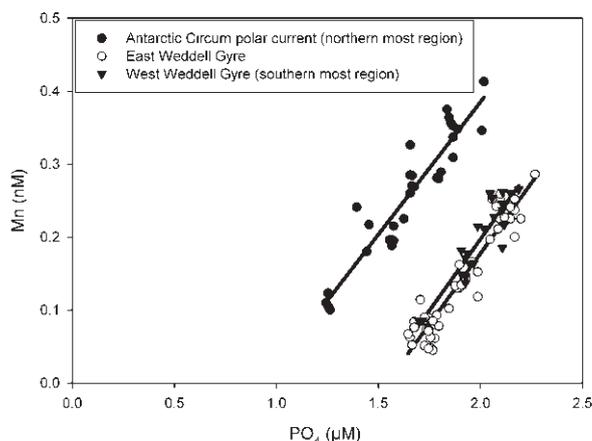


Fig. 3. Surface concentrations of dissolved Mn (nM) vs. surface concentrations of PO₄ (µM). The slope of the relationship increases from north to south (0.36; 0.39 and 0.40 nM/µM respectively, adapted from refs. 18 and 19).

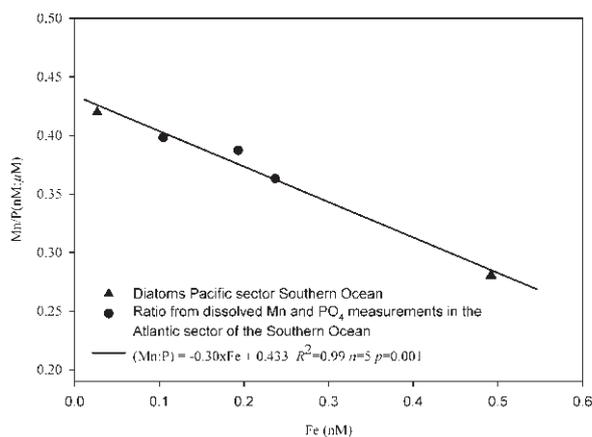


Fig. 4. The Mn:PO₄ ratio plotted vs. the ambient Fe concentrations. Figure adapted from ref. 19. The Mn:PO₄ ratio in phytoplankton appears to increase when ambient Fe concentrations decrease, indicating an increased need for Mn under low Fe conditions.

The effect of trace metal and light availability on Antarctic phytoplankton and therefore the entire ecosystem will be further investigated during the 2014-2015 summer season in a collaborative project. This project is being led by Professor Arrigo from Stanford University and scientists from the University of Otago have been invited to join for the sampling and analysis of trace metals. Other on-going trace metal research at Otago includes participation in the Mediterranean and Black Sea GEOTRACES expeditions and trace metal levels in New Zealand shell fish (see <http://neon.otago.ac.nz/chemistry/contacts/profile/rm>).

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NZIC Annual General Meeting

The NZIC AGM will take place at Rutherford House, Victoria University of Wellington, on Tuesday 3 December 2013 at 4.30pm

Agenda

1. Apologies
2. Minutes of the previous AGM held Dunedin on 22 November 2012
3. Matters arising
4. Financial Report including audited accounts
5. Election of Officers:
 - i. President
 - ii. 1st Vice-President
 - iii. 2nd Vice-President
 - iv. Treasurer
 - v. Honorary General Secretary
6. Appointment of auditor
7. Other Business

Nominations for officer positions close with the Hon. Gen. Sec. (rendle@xtra.co.nz) on 10 November 2013.

Linking anthropogenic climate change and stratospheric ozone depletion

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Keywords: *Antarctic ozone hole, carbon dioxide, climate change, Montreal Protocol, methane, nitrous oxide, ozone*

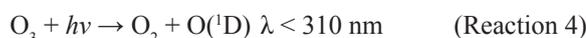
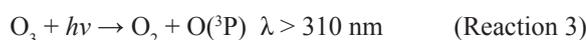
Global climate change and the Antarctic ozone hole are two well-known examples of how anthropogenic activities can alter the physical and chemical properties of the atmosphere, with significant consequences for life at Earth's surface. However, global climate change and stratospheric ozone depletion are not independent of one another. For example, common anthropogenic greenhouse gases such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) participate indirectly in stratospheric ozone chemistry. Furthermore, the halogen-containing gases that lead to the formation of the Antarctic ozone hole are also greenhouse gases with large global-warming potentials. This article reviews the links between global climate change and ozone depletion; in particular the effects that CO₂, CH₄ and N₂O are expected to have on stratospheric ozone through the 21st century.

Stratospheric ozone

The region of the atmosphere approximately 10 – 50 km above Earth's surface is called the stratosphere, contains around 90% of atmospheric ozone, and is commonly referred to as “the ozone layer”. The remaining ~10% of atmospheric ozone is found in the troposphere (0 – 10 km above Earth's surface), and is produced as a result of human activities such as fossil fuel combustion and subsequent reactions between hydrocarbon and nitrogen oxide gases. Stratospheric ozone absorbs solar UV-B radiation (280–320 nm), which is harmful to terrestrial organisms in that it can cause skin cancer, eye disease and DNA damage. While stratospheric ozone is beneficial to life on Earth's surface, tropospheric ozone is detrimental: it is an air pollutant and contributes (for example) towards respiratory problems in humans.¹ More information about the composition and properties of the atmosphere is given in textbooks.^{2–4}

Stratospheric ozone is produced and destroyed in a series of reactions known as the Chapman cycle, first proposed by Sidney Chapman in 1930.⁵ The cycle begins with photolysis of molecular oxygen (by absorption of a solar photon of energy $h\nu$) to produce two oxygen atoms (Reaction 1). Atomic oxygen then undergoes a three-body reaction with O₂ (Reaction 2), in what is the dominant ozone production process in the stratosphere. (The molecule M, which is nearly always O₂ or N₂, is unaffected during the reaction, but carries away excess kinetic energy that would otherwise cause the ozone to fragment back to O and O₂). Ozone can be photolysed by Reaction 3, producing atomic oxygen either in its ground state (O(³P), referred to hereafter as O), or in an energetic metastable excited state (O(¹D)), depending on the wavelength of the incident photon (Reaction 4). Although it is short-lived, O(¹D) is highly reactive and is present in sufficient con-

centration to play a crucial role in the chemistry of the upper stratosphere. It is deactivated to ground state atomic oxygen via molecular collisions (Reaction 5). Finally, in the last step of the Chapman cycle, atomic oxygen and ozone react to produce O₂ (Reaction 6).



Reactions 2 and 6 are strongly temperature-dependent, and are central to changes in ozone abundances anticipated through the 21st century, as will be discussed later.

Halocarbons, the Antarctic ozone hole and Montreal Protocol

By the 1970s, a class of compounds called halocarbons was in widespread use in industry for applications such as refrigerants and aerosol propellants. Halocarbon applications took advantage of the compounds' low toxicity and low reactivity. However, because of their low reactivity, it was theorized that they would survive for long enough to pass up to the stratosphere where they could undergo UV photolysis, thus releasing chlorine and bromine atoms and leading to accelerated ozone destruction.⁶

In 1985, ozone measurements indicating a substantial decrease in average amounts of ozone in the Antarctic atmosphere in October were published.⁷ This phenomenon, now commonly referred to as “the ozone hole,” is caused by chlorine- and bromine-catalysed chemical cycles.^{8–10} The processes leading to the formation of the ozone hole are not reviewed here, but overviews are available.^{3,11}

In response to widespread concern about the impacts of halocarbons on the ozone layer, a protocol was designed to phase-out chlorine- and bromine-containing ozone-depleting substances. Called the Montreal Protocol for Substances that Deplete the Ozone Layer, it was signed in 1987 and has now been ratified by all United Nations member countries. Subsequent amendments and adjustments to the protocol mean that concentrations of stratospheric chlorine and bromine are now decreasing.¹¹

As well as benefitting the ozone layer, the Montreal Protocol has had a substantially beneficial impact on Earth's climate, since most ozone-depleting substances are also

greenhouse gases with large global-warming potentials.¹² A greenhouse gas's global-warming potential is measured as the global-mean radiative forcing¹³ resulting from a 1 kg emission of that gas, relative to the radiative forcing resulting from a 1 kg emission of CO₂, and integrated over a 100-year time period. The 100-year global-warming potentials for CO₂, CH₄ and N₂O are 1, 25 and 298, respectively. In contrast, common halocarbons such as CFC-11, CFC-12 and halon-1301 have huge 100-year global warming potentials — 4750, 10900 and 7140, respectively.¹⁴

21st century ozone and CO₂

Owing in part to the phase-out of halocarbons under the Montreal Protocol, stratospheric ozone abundances are projected to increase through the 21st century, as shown in Fig. 1.¹⁵ The lines in Fig. 1 represent results from different chemistry-climate models. Briefly, chemistry-climate models consist of a general circulation model (that describes the way in which the atmosphere circulates and contributes to changes in climate) coupled to an atmospheric chemistry model; they are currently the best tool available for simulating the long-term evolution of the global atmosphere.¹⁶ It is apparent from Fig. 1 that total column ozone¹⁷ is projected to increase to greater amounts than those observed in 1960, prior to abundances of stratospheric chlorine and bromine becoming elevated. This is primarily due to the influence of increasing CO₂ concentrations cooling the stratosphere, as will now be discussed.

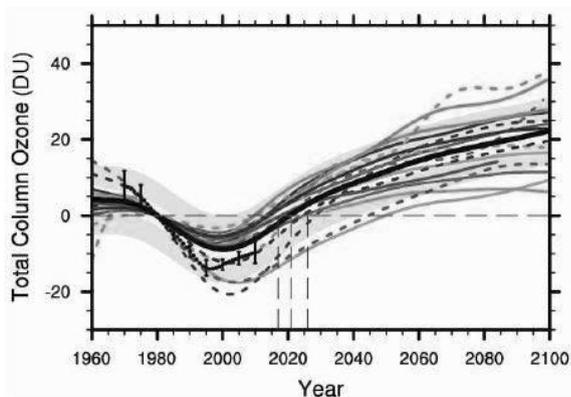


Fig. 1. Chemistry-climate model projections of annual-mean total column ozone at northern midlatitudes (35–60°N). The various traces represent projections from different chemistry-climate models (Eyring, Fahey & Waugh, reference 16), and the thick black line shows the multi-model mean. The series of dots with error bars between 1970 and 2010 are observations, calculated from ground-based and satellite ozone measurements. All traces have been adjusted to the 1980 baseline (reproduced from ref. 15).

Although increasing greenhouse gas concentrations lead to warming of the troposphere, they lead to cooling of the stratosphere. This is because greenhouse gases in the stratosphere emit heat to space, and the cooling effect exceeds the absorption of infrared radiation in the stratosphere. The absorption of infrared radiation in the stratosphere is decreasing because increasing amounts of greenhouse gases in the troposphere trap infrared radiation lower down in the stratosphere. The net effect is cool-

ing.¹⁸ Because key reactions in the Chapman cycle are temperature-dependent, a cooling stratosphere is projected to lead to increased ozone abundances.^{19,20} The rate of Reaction 2 actually increases with decreasing temperature, thus producing more ozone. Concurrently, Reaction 6 slows with decreasing temperature, and therefore ozone loss by this reaction diminishes.

Chemistry-climate models project that stratospheric ozone will increase in all regions of the atmosphere through the 21st century, with the exception of in the tropical lower stratosphere.¹⁵ Here, ozone is affected by changes in stratospheric circulation. The overall meridional (north-south) circulation is called the Brewer-Dobson circulation. This is the process by which air from the tropical troposphere ascends into the stratosphere, is subsequently transported towards the poles and descends in middle and polar latitudes.²¹ It is by this mechanism that chlorine compounds, historically produced from halocarbons (which were predominantly emitted in the Northern Hemisphere), were transported to the Antarctic stratosphere and thus led to the development of the Antarctic ozone hole.^{7,9,22}

It is thought that increasing sea-surface temperatures (attributed to global warming) through the 21st century will lead to a strengthening of the Brewer-Dobson circulation.^{23,24} A strengthening Brewer-Dobson circulation would result in enhanced transport of gases to polar latitudes, and would shorten the residence times of chemical constituents in the stratosphere, which would affect the lifetimes of long-lived greenhouse gases.²⁵ Going back to the case of projected decreases in tropical lower stratospheric ozone through the 21st century, the effect of a strengthening Brewer-Dobson circulation is that less time would be available for ozone to form in rising parcels of air.²⁶

Greenhouse gases (predominantly CO₂) lead to cooling of the stratosphere and warming sea-surface temperatures. Stratospheric cooling affects ozone through changes in the reaction rates of the Chapman cycle; while increasing sea-surface temperatures are thought to lead to strengthening of the Brewer-Dobson circulation, which has implications for ozone abundances. Following CO₂, the two most important anthropogenic greenhouse gases controlled by the Kyoto Protocol are CH₄ and N₂O. While the effects of CO₂ on ozone are somewhat indirect, CH₄ and N₂O affect ozone directly via chemical processes. The chemistry of these gases in relation to ozone depletion will be discussed in the following sections.

The effect of CH₄ on stratospheric ozone

The concentration of atmospheric CH₄ has increased from 700 ppb to around 1800 ppb since pre-industrial times.^{4,27} CH₄ is produced by methanogenic bacteria which grow in low-oxygen environments and cause the fermentation of cellulose and other organic material in (for example) wetlands, and in the rumina of cows and sheep. As well as agriculture, other anthropogenic sources include landfills and biomass burning.²⁸

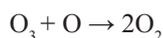
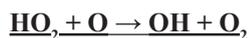
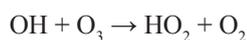
In the stratosphere, CH₄ undergoes oxidation with ener-

getic oxygen atoms to produce an OH radical (Reaction 7).

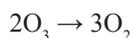
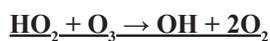
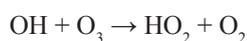


OH is highly reactive and rapidly interconverts to H atoms and HO₂ radicals.³ Collectively, H, OH and HO₂ are referred to as the HO_x family, and participate in catalytic cycles (such as cycles I and II shown below; rate-determining steps are in bold), which lead to loss of odd-oxygen (O + O(¹D) + O₃) species:

Cycle I:



Cycle II:



Cycle I is the dominant HO_x-induced mechanism for ozone loss in the upper stratosphere, where UV radiation is more intense and abundances of O are large. In the lower atmosphere where there is the greatest concentration of O₃ relative to O, cycle II is the dominant HO_x-induced ozone loss process.

The main process for removal of HO_x radicals is formation of water vapour via Reaction 8:



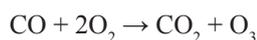
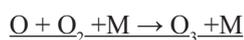
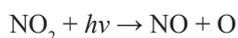
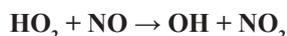
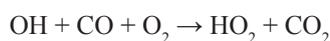
Water vapour cools the stratosphere, which, in turn, increases ozone abundances. Therefore, CH₄ can have both a positive (via increase of water) and negative (owing to cycles I and II) effect on ozone abundances.

Chemistry-climate model studies have shown that the overall effect of increasing CH₄ is to increase total column ozone.^{29, 30} As well as the cooling effect achieved from the production of water vapour, two further pathways serve to increase ozone abundances. Firstly, CH₄ decreases Cl abundances via Reaction 9, thus slowing chlorine-catalyzed ozone loss cycles.



Secondly, HO_x radicals lead to production of tropospheric ozone via cycle III.^{31, 32}

Cycle III:



My research colleagues and I have investigated whether the relationship between CH₄ and ozone (and N₂O and ozone), is linear or otherwise.³³ Figure 2a shows that stratospheric column ozone increases as the CH₄ concentration increases. Stratospheric column ozone decreases as N₂O concentrations increase, shown in Fig. 2b. Furthermore, there is a quasi-linear relationship between the CH₄ and N₂O concentrations and the stratospheric column ozone abundance.

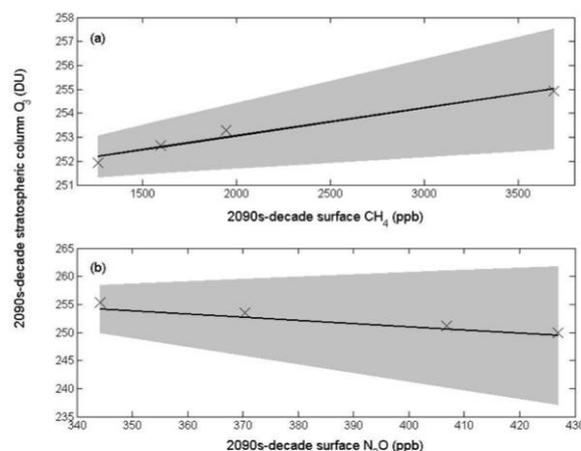


Fig. 2. (a) Global-mean stratospheric (1-100 hPa) column ozone (Dobson units) in the 2090s decade vs. global-mean CH₄ surface concentration in the 2090s decade. The crosses represent results from four chemistry-climate model simulations, where the only parameter changing between each simulation was the CH₄ concentration scenario. A simple linear regression model was fitted (represented by the black line), and the grey shaded region indicates the 95% confidence interval for the slope and intercept of the regression model. (b) As for (a), but for these simulations the same CH₄ concentration scenario was used, and a different N₂O concentration scenario was applied (both parts of the diagram are adapted from ref. 33).

The effect of N₂O on stratospheric ozone

N₂O is produced from microbial activity in tropical soils and the oceans, and as a result of anthropogenic activities such as agriculture – particularly the use of nitrogen-based fertilizers. The concentration of N₂O in Earth's atmosphere has increased from 276 ppb to 322 ppb since pre-industrial times, and is projected to continue increasing through the 21st century.²⁷

N₂O is sufficiently stable to migrate to the stratosphere, where around 90% of it is destroyed via photolysis (Reaction 10):



The rest is destroyed by oxidation (Reactions 11, 12);³



Reaction 12 is an extremely significant pathway for stratospheric ozone, since it produces NO and is the major source of stratospheric nitrogen oxides (NO_x = NO + NO₂). NO_x radicals participate in a number of ozone-depleting catalytic cycles, of which cycle IV dominates.³⁴ The projected rate of the ozone-depleting NO_x cycles through the 21st century, as simulated by a chemistry-climate

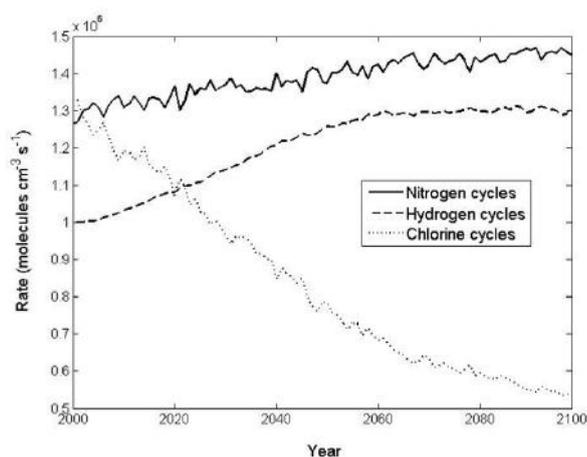
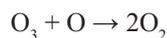


Fig. 3. Global-mean rates of the ozone-depleting NO_x , HO_x and chlorine cycles at 2 hPa (~ 40 km) in the 21st century, as simulated by a chemistry-climate model (adapted from the results presented in ref. 36).

mate model, is shown in Fig. 3, together with the rates of the ozone-depleting HO_x and chlorine cycles.

Cycle IV:



Although chlorofluorocarbon production has been phased out under the Montreal Protocol, chlorofluorocarbons are still the dominant ozone-depleting substance owing to their long stratospheric lifetime. However, of the ozone-depleting substances currently emitted, N_2O emissions dominate.³⁵ The effect of N_2O on stratospheric ozone through the 21st century is moderated by a number of factors, such as interference from other greenhouse gases and climate change effects; for example stratospheric cooling and the increasing strength of the Brewer-Dobson circulation. A strengthening Brewer-Dobson circulation shortens the lifetimes of some chemical constituents, as discussed earlier. This means that nitrogen species are projected to be removed from the atmosphere at a faster rate, therefore slowing the NO_x -induced ozone loss cycles.²⁵

As the stratosphere cools, the dominant ozone-depleting NO_x cycle, cycle IV, is projected to slow for two reasons:³⁶

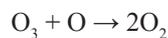
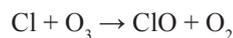
1. The first step of cycle IV is highly temperature-dependent and is projected to slow as the stratosphere cools. Therefore, the ratio of NO_2/NO decreases and less NO_2 is available for the rate-determining step of cycle IV.
2. Because Reaction 2 of the Chapman cycle is highly temperature-dependent and is projected to speed up as the stratosphere cools, the ratio of O/O_3 decreases and less O is available for the rate-determining step of cycle IV.

NO_x species react with chlorine species, leading to a slowing of NO_x chemistry, for example by Reaction 13:³⁵



ClO also reacts with O in catalytic cycle V, which is analogous to cycles I and IV:

Cycle V:



ClO and HO_2 compete with NO_2 for O in the upper stratosphere, and therefore slow the $\text{NO}_2 + \text{O}$ reaction (Cycle IV).³⁶ Ozone-depleting chlorine chemistry will be of decreasing importance through the 21st century following the phase-out of halocarbon emissions, as shown in Fig. 3. However, if CH_4 emissions continue to increase through the 21st century, then so will the rate of HO_x -induced ozone loss in the upper stratosphere (also shown in Fig. 3).

There are numerous ways in which the effects of N_2O and CH_4 on ozone are altered by the chemical and physical environment of the stratosphere, as discussed above. The key message here is that the entire physical and chemical environment of the stratosphere must be taken into account when assessing the effect of a single species. And, despite the many factors discussed above that are projected to ameliorate the effect of N_2O on ozone, the conclusions of Ravishankara *et al.* do not change,³⁵ of all the substances currently emitted, N_2O is the most important substance for ozone depletion this century.

Could widespread biofuels production and consumption have an impact on stratospheric ozone?

Concerns were first raised in 2008 over potential detrimental effects to the climate if the production and consumption of first-generation biofuels (those produced from vegetable oil, sugar or starch) were to become widespread.³⁷ Biofuels are often considered carbon-neutral, because plants remove CO_2 from the air by photosynthesis, and CO_2 is released when the biomass is burnt. However nitrogen-based fertilizers are applied to the crops used to produce biofuels, and therefore any CO_2 reduction achieved (by using biofuels in place of fossil fuels) could be countered by a subsequent increase in N_2O emissions.³⁷ Furthermore, as mentioned earlier, while the 100-year global warming potential for CO_2 is 1, for N_2O it is 298.¹⁴

As well as offsetting climate change mitigation measures, an increase in N_2O emissions from increased biofuels consumption could potentially be damaging to the ozone layer. Using a chemistry-climate model, my research colleagues and I simulated the evolution of the stratosphere through the 21st century under a “biofuels” scenario, in which N_2O emissions increased and CO_2 emissions decreased.³⁸ As shown in Fig. 1, ozone abundances are generally expected to increase through the 21st century. However under the biofuels scenario ozone decreased slightly between 2000-2100, for the following reasons:

1. A smaller growth in CO_2 emissions was used in the biofuels scenario compared with the control scenario,

to represent reduced fossil fuel burning. As a result, the stratosphere cooled less through the 21st century, and so temperature-dependent Chapman chemistry was not altered to favour increased ozone abundances.

- The biofuels scenario used a large growth in N₂O emissions compared with the control scenario, to represent increased application of nitrogen-based fertilizer. This resulted in enhanced NO_x-induced ozone loss in the stratosphere.

The effects of biofuels are crop-dependent,³⁷ and second-generation biofuels show promise in transitioning the regions where they are grown from net sources to net sinks for greenhouse gases.³⁹ In terms of climate policy, the conclusions drawn from our work suggest that if future attempts are made to mitigate CO₂ emissions, then N₂O emissions must also be addressed,³⁸ the combination of reduced stratospheric cooling and increased NO_x-induced ozone depletion could be damaging to the ozone layer.

Summary

This article has discussed the effects that the three dominant anthropogenic greenhouse gases have on stratospheric ozone. CO₂ predominantly affects ozone by cooling the stratosphere, which changes temperature-dependent reaction rates and is projected to lead to an overall increase in ozone abundances. CH₄ leads to ozone destruction in the upper atmosphere (through the production of HO_x radicals), but, overall, leads to an increase in the ozone abundance. Despite this, it hardly needs to be said that CO₂ and CH₄ should not be viewed as policy alternatives for protecting the ozone layer owing to their harmful effect on other areas of the climate system. Now that the halocarbons have been phased out, N₂O is the most important substance for ozone depletion in the 21st century, although its impact on ozone is moderated by other greenhouse gases; shown, for example, by the study on potential impacts of biofuels on the ozone layer.

CO₂, CH₄ and N₂O will play important roles in determining stratospheric ozone abundances this century; however the model projections discussed here are based (and can only be based) on current knowledge. Unprecedented changes in the atmosphere have occurred in the past as a consequence of anthropogenic activities (for example, the Antarctic ozone hole), and could well occur in the future. It is vital that we understand the effects of human activities on atmospheric processes and composition, and their consequences for the rest of the Earth system.

Acknowledgement

Thanks to Bryce Williamson for helpful discussions and suggestions on writing this article.

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New Zealand Science Scene

Fluoridation of drinking water

Anthea Lees

Hamilton City Council spent four days in June of this year looking at submissions, for and against, the continued fluoridation of their water supply, which has been occurring since the 1960s. They voted on June 5th, by a 7-1 majority, to remove fluoride from the city's water supply. The Council members heard arguments from both sides of the debate and decided to halt addition of fluoride to their water supply as soon as their current stocks ran out. It is thought that through this decision, the Council will make savings of \$48,000 per annum. Deputy Mayor Gordon Chesterman said he was not satisfied fluoridation had achieved benefits "beyond reasonable doubt". He argued that the government should be doing more to minimise the consumption of high sugar food and drinks which lead to increased tooth decay.

Twenty three of the sixty seven current New Zealand councils still continue to add fluoride to their water supply, but Hamilton have joined the likes of Dunedin, Tauranga, Central Hawke's Bay, New Plymouth, Whanganui, Rotorua, Whangarei, Timaru, Nelson, Greymouth and Napier, who have all decided to remove or reduce, fluoridation.

During the debate the pro-fluoride team argued that removal of fluoride would result in an increase in tooth cavities, dental decay and increased dental bills which would greatly affect the lower socio-economic members of the community. The anti-fluoride team blamed the sugary food industry for an increase in dental problems and argued that people would eat more sugary foods if they felt their teeth were protected by drinking fluorinated water.

In New Zealand fluoride levels in natural water are very low and so fluoride has been traditionally added to the water supplies. Other parts of the world have natural levels



Fig.1. Picture of sodium fluoride tablets (picture taken from Wikimedia.org)

of fluoride in their water which can reach above 4 mg/L and this level is still thought to be safe for human consumption. In New Zealand 0.7-1.0 mg/L is the level used for the fluoridation of water and this level is thought to provide the beneficial health effects of reduced cavities.

The World Health Organization, World Dental Federation and the International Association for Dental Research all agree that "universal access to fluoride for dental health is part of the basic human right to health".

Toothpastes and fluoride tablets are also available sources of fluoride but this fluoride is limited as it does not provide a constant small dose throughout the day, which fluoride in water provides.

In New Zealand, fluoride for water treatment is supplied as sodium fluoride (NaF), sodium silico fluoride (Na_2SiF_6) or the most commonly used form which is sodium hydro-fluorosilicic acid (H_2SiF_6).

Fluoridated water is thought to prevent tooth decay as the tooth enamel hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is replaced by fluoroapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$, which is more resistant to acid attack.

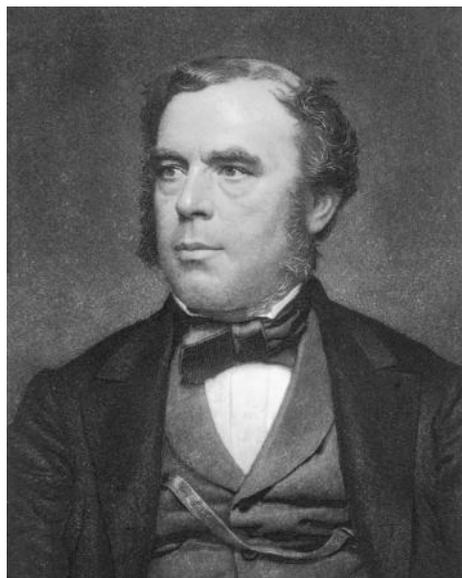
Some unremembered chemists

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.

John William Draper (1811-1882)

Brian Halton

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(email: brian.halton@vuw.ac.nz)



John William Draper, 1811-1882

Anyone familiar with photochemical phenomena should be aware of the name 'Draper', as it is enshrined in the first law of photochemistry – the Grotthuss-Draper law. These two 19th century scientists recognised that for light to produce an effect upon matter it must first be absorbed. Although Theodor von Grotthuss (1785-1822) proposed the law first in 1817, he gained more recognition for his electrochemical work and his idea that charge is not transported by the movement of particles but by the breaking and reformation of bonds – the Grotthuss mechanism. This was the first essentially correct concept for charge transport in electrolytes, and is still valid for charge transport in water; the current proton hopping mechanism is a modified version of the original. However, it was Draper who gave substance to the proposal that light needs to be absorbed before it can impact on matter. This he independently recognized in 1842. He trained as a chemist and physician who conducted investigations and wrote on chemistry, physics, botany, physiology, photography, telegraphy, teaching, history, sociology, and religion.^{1,2}

John William Draper was born on 5 May 1811 in the parish of St. Helens, near Liverpool in Lancashire, England, the son of Wesleyan clergyman the Rev. John C. Draper and Sarah (Ripley) Draper. Draper senior had a moderate income but, because of his ministry, the family moved frequently from parish to parish throughout England. Until 1822 the young John was home-tutored, by his father, who had an interest in scientific subjects, and by private

tutors. Only at 11 years of age did he enter school – Woodhouse Grove in Leeds. This school had been founded by the Methodist Conference in 1812 to educate the sons of ministers, and John Wm. stayed there for four years until 1826, when he once again returned to home instruction. He showed an early interest and ability in science and in 1824 was selected to deliver the customary school address to the Wesleyan conference, which met in Leeds that year. In 1829 he entered the (then) recently opened University of London (it became University College in 1836) to major in chemistry under Dr. Edward Turner, author of the first English textbooks on organic chemistry. It was here that Draper gained an interest in the chemical effects caused by light, an interest which drove his subsequent career. In 1831, during his undergraduate education, he married Antonia (Ann) Gardner, the daughter of a court physician who served the Emperor of Brazil, Dom Pedro,² and who had been living with an aunt in London.¹ Later that same year John's father died unexpectedly and John Wm. never completed his London degree but was awarded a "certificate of honours" in chemistry instead.² His mother, his three sisters, and he and his new wife were persuaded to emigrate to the US in 1832 by relatives who had settled in Christiansville (now Chase City), Mecklenburg County, Virginia. Before the American Revolutionary War, several maternal relatives had migrated there and had founded a small Wesleyan colony where John Wm. hoped to gain a teaching post at the nearby Methodist College.

The family's arrival in the US proved to be too late for John Wm. to gain the prospective teaching post, so he established a laboratory in Christiansville and set to scientific experimentation on capillarity. He then published on this and a variety of other scientific subjects. He had had three papers published while in London and eight more came before he was able to further his education at the University of Pennsylvania. From 1835, he studied chemistry and physics under Dr. Robert Harris while taking the university course in medicine. He also had chemistry classes from John K. Mitchell, at that time Professor of Chemistry at the Franklin Institute in Philadelphia. His education was funded by his sister Dorothy Catherine. In London she had taught art and, once in Virginia, she and her sisters, Elizabeth and Sarah, opened the *Misses Draper Seminary for Girls*. Here she continued to teach drawing and painting and by 1835 had saved sufficient money to fund her brother's education.³ John Wm. Draper graduated in medicine in March 1836 and was soon employed teaching at Hampden Sydney College in Virginia.

This school, established to form good men and good citizens in an atmosphere of sound learning, had learned of Draper's abilities. However, his teachers motivated him to accept an appointment the following year at New York University, where he became Professor of Chemistry and Botany in 1838. By then he was the father of two boys. He was one of the founders of the New York University Medical School, becoming a professor in the school of medicine from 1840, and its president and professor of chemistry from 1850 until 1881. At the time he joined the Medical School there were few students, but with his enthusiasm and the help of his friend J. G. Bennett, editor and publisher of the *New York Herald*, the 1841-1842 session had some 240 students. He raised two further boys and two girls in New York.



Founders of the NYU Medical Faculty, 1846; John Draper lower right (from <http://www.westchesterarchives.com/HT/muni/hastings/jwDraperFull.html>) and reproduced courtesy of the Hastings Historical Society, Hastings on Hudson, NY

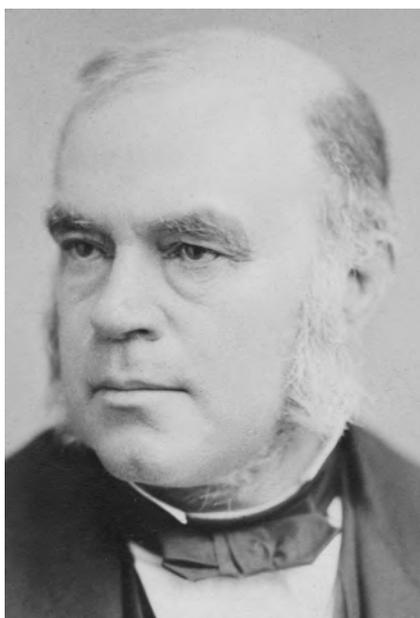
Leaving his historical writings aside (see below), John Draper's scientific work would span chemistry, physics, medicine, botany and scientific literature. From his undergraduate days in London there were papers on volcanoes and the formation of the Dead Sea, and one on electrical decompositions was published in 1833. However, it was from 1834 that his independent studies appeared. The first, a letter to the editor of the *American Journal of Science*,⁴ appeared in 1834 and was one of a series of studies on capillary action that led to definitive results on osmosis and on the circulation of sap in plants and blood in animals. The first paper concerning the action of light was the following year, when he reported the results of a study on whether light exerts a magnetic action. His first purely chemical paper was the "Chemical Analysis of the Native Chloride of Carbon, a singular mineral" published in the *Journal of the Franklin Institute* (of the State of Pennsyl-

vania) in 1834.⁵ The "native chloride of carbon" had been collected on the Isle of Sheppey (off the Kent coast and in the Thames estuary, England) in the summer of 1832 and, although most had been given to Prof. Turner at London University, he had taken some 12 grams (200 grains) of the sample to Christainsville. His studies concluded that the compound contained two atoms of carbon and one of chlorine and that the presence of hydrogen seemed unlikely. His concluding statement was: "The production of this substance, to judge by its scent at first, and the locality in which it was found, seems to be referable to a marine animal. But through what singular changes must a dead fish pass, before its remains would leave a chloride of carbon, nearly pure?" With the exception of well recognized marine products such as Tyrian purple,⁶ this, though incorrect, is one of the earliest chemical analyses of a marine species.

This paper was followed the following year by one on the analysis of coins and medals⁷ and, in 1836, a practical set of instructions and commentary for carrying out "microscopic chemistry".⁸ Draper's premise here was that much good chemistry could be carried out using semi-micro techniques (as we would now call them). It is particularly interesting to see him advocating the use of sand and water baths (admittedly in a domestic frying pan and domestic pan, respectively) for heating purposes, holding a hot tube by its neck with folded paper, and the use of apothecary phials for small scale distillation and sublimation. It needs to be remembered that in the 1830s organic chemistry was in its infancy, that only 55 elements were recognised (in 1835) and that measurement of chemical and physical properties was limited by the few instruments available. Many of the traditional early studies had been conducted using large retorts and big furnaces in expensive laboratories. Draper's premise was that chemistry should be available to and performed by anyone with an aptitude and skill for it, and his microscopic chemistry fitted well to this.

John Draper's career as a research scientist flowered from 1839 to 1856 as professor of chemistry at New York University, where he published some 45 papers and five textbooks, although his writing continued well into the 1870s. He published two chemistry books and others on physiology, natural philosophy and botany. His dominant contribution was on the constitution of "radiant energy" which led to some 28 publications. Some of his earliest investigations were directed to determining the various forms of energy that exist in solar light. In common with his contemporaries, he regarded heat and light as imponderable agents, entirely different from one another but co-existing in solar light. However, by the early 1870s, he had accepted the essential unity of radiant energy and subsequently was adept in discussing the chemical force in the spectrum.⁹

Draper approached radiant energy by studying the chemical action of light to determine the effect of the different kinds of light in photography, on chlorine gas, and on the growth of plants. Most studies of light from 1725 had involved its action on silver salts, leading to Scheele distinguishing radiant heat and light in 1777, and then the con-



John Draper mid-career

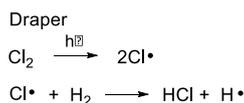
Dorothy Catherine Draper (from http://en.wikipedia.org/wiki/File:Dorothy_Draper.jpg).

cept of “chemical rays” from effects in the violet region of the spectrum by Ritter and Wollaston in the first years of the 19th century.² For many years, Draper had studied the various forms of energy that exist in solar light, with the chemical action of light being a particular fascination. He performed many experiments to distinguish the effects of the different forms of light on chemical change. He studied the effect of light in changing the colours of metallic salts and was quite accustomed to applying the photographic process in the solution of physical problems prior to Louis Daguerre’s 1839 discovery. This was a photographic process which became known as the daguerreotype and involved a direct positive being made in the camera on an iodine-treated silvered copper plate. Draper gained information of the process from Samuel Morse, at that time Professor of Fine Arts at the university and a close friend (see below) who had been in Paris. Draper improved the process by exposing the plates to bromine fumes, finding that the mixture of silver iodide and bromide was much more sensitive to light. This was to the extent that in the same year (1839), he took photographs

of the human face, being the first to use the daguerreotype in New York. He had the process so perfected¹⁰ by early 1840 that the image he took of his sister Dorothy Catherine is the oldest surviving human portrait photograph. It has often been misconstrued as the first human portrait.³ It is undoubtedly one of the earliest portraits and certainly the first of quality; it was taken with a 65 second exposure. That same year he presented the Lyceum of Natural History of New York with the first photograph of the moon’s surface and improved it over the ensuing years to show craters. The original came from a 20 minute exposure through a telescope giving an image about 2.5 cm in diameter. Draper perfected the process of portraiture enough¹⁰ to instruct in the art and, with Morse, opened the first ever portrait studio on the roof of his house on Fourth Street in New York in 1840.

The effect of light on chlorine gas provided what appears to have been the first documented example of a photochemical reaction in a laboratory.¹¹ In 1843, Draper announced to the British Association that chlorine underwent a significant change under the influence of sunlight. He described this as occurring by the absorption of “chemical rays” which changed the character of the gas to the extent that it would then unite with hydrogen gas, a property not seen from chlorine kept in the dark or with hydrogen. While we now find it easy to accept that the chlorine molecule absorbs a photon, dissociates into a pair of chlorine atoms and abstracts a hydrogen atom to produce HCl with the propagation of a chain reaction (Scheme 1), none of this was a part of 1840 thinking – the first persistent radical was the triphenylmethyl radical of Gomberg in 1900.

From this study Draper concluded that solar light consisted of a third and new imponderable: the agent that produced chemical change. He gave this the name “tithonicity” from Roman mythology. Tithonus was a beautiful youth with whom Aurora fell in love and married in heaven. Although he became immortal, he became feeble and decrepit – unlike his bride, lost all his strength and had to be rocked to sleep. Likewise, solar light was thought by Draper to be weakened from its interaction with matter. In addition to “tithonicity”, Draper extended his usage to include “tithonography”, “tithonic effect”, “tithonometer” and “tithonoscope” as “music in an English ear”.¹¹ That year he used this property (the decomposition of chlorine and formation of HCl) in the design of an actinometer to measure the force of the tithonic rays – his tithonometer.¹² The Draper actinometer was subsequently improved upon by Bunsen and Roscoe² who refined it to the extent that it allowed not only accurate comparative determinations, but reduced the chemical action of light to an absolute measurement.¹³



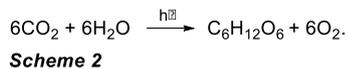
Scheme 1

As early as 1837, Draper had studied the impact of solar light on the decomposition of leaves, but his early study had involved plants under coloured glass and was inconclusive. Subsequently, he germinated the seeds under

glasses of different colour. Under red and violet glass the plants behaved as in the dark, while under yellow glass they promptly assumed a green colour and behaved normally. The experiment was repeated by germinating the seeds in the dark and then exposing the young plants to the differently filtered light to assess its impact; the plants under the yellow glass grew readily, but those under red and violet not so.¹⁴ He then assessed the decomposition of carbonic acid by grass under different light. Thus, water was degassed and saturated with the CO₂, and to it was added grass whose surfaces had been carefully freed of air. The sample was divided among seven tubes and the effect of the seven colours of the spectrum examined. The tubes onto which orange, green and yellow rays fell began to evolve gas within a few minutes and the volumes given off measured over a given time period as:

Yellow-Green: 43.00 volumes; Red-Orange: 24.75 volumes; Green-Blue: 4.10 volumes.

The other colours gave no gas evolution and were without effect – neither photosynthesis nor the generation of oxygen (Scheme 2). Draper read his paper giving these results to the centenary meeting of the American Philosophical Society, publishing it with the full details.¹⁵



Despite these early studies, it was his spectral investigations that led to Draper's understanding of radiant energy. Thus, in 1842 he proposed that only light rays that are absorbed can produce chemical change.¹⁶ This, now known as the Grotthuss-Draper law, is the first law of photochemistry as noted above. Draper's name is linked with that of Grotthuss who had reached the same conclusion some 25 years earlier, but had not been recognised for it. Furthermore, Draper subsequently concluded that "every part of the spectrum, visible and invisible, can produce chemical change and can modify the molecular arrangement of bodies", and that "the rays effective in producing chemical or molecular changes in any special substance are determined solely by the absorptive power of that substance".¹⁷ The studies prior to 1843 had used prismatic refraction, but that year he persuaded Joseph Saxton of the US Mint in Philadelphia to rule a diffraction grating for him. The results obtained were markedly improved when he silvered the surface with tin amalgam, providing a far more intense reflected spectrum than the former transmitted ones. Draper suggested that the best result would come from ruling the grating on steel or speculum metal (a mixture of *ca.* two-thirds copper and one-third tin that makes a white brittle alloy capable of being polished to a highly reflective surface). He also suggested that the regions of the spectrum should be denoted by their wavelengths, saying: "The measures of one author will compare with those of another and the different phenomena of chemical changes occurring through the agency of light become allied at once with a multitude of other optical results".¹⁸ By using the grating the first photograph of the solar spectrum was obtained. Draper used a daguerreotype plate sensitised by iodine and then bromine. This was exposed for 30 minutes giving maximum sensitivity at wavelength 0.00001538 Paris inch.¹⁹

In 1847 he published the observation that all solids glow red at about the same temperature (798 K), and this is now known as the Draper point,²⁰ the approximate temperature above which almost all solid materials visibly glow as a result of blackbody radiation. In addition, he concluded that as the temperature of an incandescent body is increased it emits rays of light of an increasing refrangibility. At that time the science of spectroscopy had evolved to the extent that all glowing solids were known to emit continuous spectra, unlike gases that emitted bands or lines. Draper went beyond defining what has become known as the Draper point to study the spectral composition of flames (the production of light by chemical action²¹) using a slit, a prism and a telescope. By examining a range of compounds (that included alcohol and its solutions with boric acid and strontium nitrate, oil, phosphorus, sulfur, carbonic oxide (CO), hydrogen, cyanogen (NC-CN) and H₂S) he concluded that, notwithstanding the diversity in colour, all the flames yield the same results. Every prismatic colour was found in them, even bright Fraunhofer lines of different colour, and even in those cases where the flame is very faint. The spectrum of cyanogen was, he said, "so beautiful that it is impossible to describe it in words or depict it in colours". Subsequently he came to the conclusion that "the occurrence of lines, whether bright or dark, is hence connected with the chemical nature of the substance producing the flame and that if we are ever able to acquire certain knowledge of the physical state of sun and other stars, it will be by an examination of the light they emit".²² In 1879 Draper built a spectrometer based upon the photometric method of Bouguer that he had used successfully in 1847. However, this instrument measured light intensity. He found that the colours of a gas flame and sunlight both disappeared in the reverse order of their refrangibility, red being the last to disappear. When the shutter admitting the daylight was slowly opened it was the extreme violet that disappeared first, red last; and on closing the shutter it was the red that appeared first. On reducing the extraneous light intensity all came into view at the same time.²³ These experiments proved that the apparent brightness of yellow, as seen by the eye, then accepted as the most intense in the spectrum, is a purely physiological phenomenon.



Draper in later life

Another area studied by Draper was phosphorescence.²⁴ His first report²⁵ included a general discussion of the

phenomenon starting from belief in the existence of the carbuncle, a stone supposed in the very infancy of chemistry to have the property of shining in the dark. He went on to define the phenomenon to include those bodies which shine in the dark after exposure to light or on being heated, and then described his experiments with John William on the fluorspar variety known as chlorophane. He selected this material because it could be obtained as both almost opaque and perfectly transparent, was easily cut and polished into almost any shape, and yields a superb emerald-green light. He found that when phosphorescence was triggered by an electric spark there was no perceptible change in volume or any molecular change detectable by polarized light. However, there was a small amount of heat generated. He concluded that the quantity of light emitted by a phosphorescent body was proportional to the intensity of the light to which it had been exposed. He went on to show that the rays which generate phosphorescence were the violet rays.

As early as 1834 Draper had studied the action of the galvanic battery and published design and construction improvements, and went on to describe the construction of a torsion galvanometer in 1839. However, it is his 1843 paper on the law of the conducting power of wires that deserves mention.²⁶ This was a study he performed to help Samuel Morse in perfecting his single wire telegraph, and showed that the diminution in strength of an electric current reduces rapidly with increasing wire length and that the conducting effect is represented by a logarithmic curve. Although Morse was not the first to perfect the telegraph, his code for word transmission – the Morse code – was universally adopted.

It is clear that John William Draper was a pioneer in photochemistry and a spectroscopist of exceptional ability and acumen. He had no doctorate in science, but was a 19th century physician gone astray. Yet he was popularly known for other things. He had many papers in the medicinal chemistry area and, in his later life, he gained fame as an author on account of his published books: *History of the intellectual development of Europe* (1862),²⁷ *Thoughts on the future civil policy of America* (1865),²⁸ and *A text-book on physiology* (1866).²⁹ His noted *History of the American Civil War* (for which he was given access to whatever records he needed by the then US Secretary of War) ran to three volumes, published³⁰ between 1867 and 1870, and his most well-known *History of the conflict between science and religion*³¹ was published in 1874. This last treatise went through more than twenty editions in its first ten years and was translated into most European languages. Because Draper was open and honest about the continuing conflict between science and religion his book was placed on the *Index Expurgatorius* of the Catholic Church.

There is one further role in Draper's life of which few in New Zealand are aware. He became inaugural President of the American Chemical Society.³² In 1874 a group of about 70 chemists had met in Northumberland, Pennsylvania on 1 August to celebrate the centenary of the death of Joseph Priestley and, while some subsequently joined the American Association for the Advancement of

Science, it became clear that the discipline of chemistry needed its own organisation. Charles F. Chandler, Professor of Chemistry in the School of Mines at Columbia University, was the main driving force for this, and on 6 April 1876 a group of 35 chemists met in the University of New York. Among those present was William Henry Nichols, a 24-year old chemical entrepreneur and former student of Draper who, speaking last, argued so forcefully for the establishment of the American Chemical Society that the passage of the vote was assured. The ACS came into existence that evening, a constitution was adopted and the New York participants selected officers. Chandler was an obvious choice as president because he was well known in New York, but he believed that the new organisation needed to be a national one that needed a president whose fame and reputation were known to the general public, who would attract members nationally, and who would have the society accepted by the organisations in Europe. In Chandler's mind there was only one person who met these criteria, and that was John Wm. Draper. At 65 years of age, Draper was invited and accepted the position on 11 April. He advised, however, that his health would prevent his active participation in the society, as he suffered from severe attacks of urinary stones, which prevented him from travelling.² Thus, Draper's name and reputation were used more than his active participation. He never chaired a monthly meeting and was unable to attend a dinner for foreign chemists attending the Philadelphia Centennial Exhibition in June that year. However, he did give his inaugural Presidential Address in November in New York City under the title *Science in America*.³³ Draper died at his New York home in Hastings on 4 January 1882.

Among the other awards accorded John Draper were membership of many learned societies in the US and Europe, the Rumford medals of the American Academy of Arts and Sciences (1875), the founding presidency of the American Union Academy of Literature, Science and Art (1869), Chairman of the American Photographic Association (1864) and an LLD from the college of New Jersey at Princeton. His house in Hastings-on-Hudson stands in Draper Park, now an historic nine acre property containing five nineteenth-century structures in a relatively intact landscape setting.³⁴ The entire site, buildings and park, was designated National Historic Landmark in 1975.

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Grants and awards

2014 Zonta Science award

The Zonta club of Wellington is calling for applications for the 2014 Zonta Science award. The award is for an emerging woman scientist (i.e., a recent Ph.D. graduate). Priority will be given to areas of science where funding is not readily available.

The fund aims to:

1. Encourage women to pursue a scientific career
2. Actively promote science as a career for women
3. Encourage others already in the scientific field
4. Acknowledge the valuable contribution of women scientists.

Applicants must be women who:

1. Have a Ph.D. (normally within 7 years of graduation)
2. Have excelled in the fields of pure and applied sciences (excludes clinical medicine)
3. Are New Zealand residents and reside in New Zealand
4. Are studying for further postdoctoral qualifications or are involved in research which has widespread benefits.

The award recipient receives \$15,000 cash to fund travel expenses and/or research material and equipment, return economy air travel to Europe or US to attend conference or place of further study and a commemorative medal.

Deadline: 10 February 2014

Contact Details:

The Convenor, 2014 Zonta Science Award, Zonta Club of Wellington, PO Box 10274, Wellington

Email: zontascience14@gmail.com

Charles Fleming Fund – Publishing Award

Up to \$8,000 is available annually to support the preparation of scientific books and relevant publications.

Applicants should describe the project for which the funding is being applied and explain how funding will assist in meeting its objectives (1000 words maximum). Include a budget with details of other funding received or applied for and a brief Curriculum Vitae (one-page) plus a list of any refereed publications for the previous five years; Include contact details.

Deadline: 31 March 2014

See: www.royalsociety.org.nz/programmes/funds/fleming/publishing/

Charles Fleming Fund – Senior Scientist Award

Up to \$10,000 is available annually to support the research of a senior scientist at a university or Crown Research Institute in New Zealand, and that of their research group.

The fund will give preference to requests for research expenses over and above those that a university or Crown Research Institute in New Zealand would normally be expected to cover.

Deadline: 31 March 2014

See: www.royalsociety.org.nz/programmes/funds/fleming/senior-scientist/

Talented Secondary School Students Travel Award

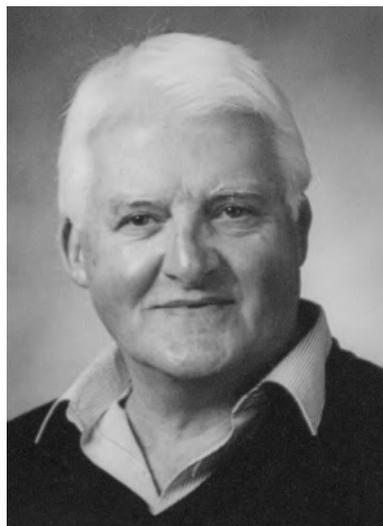
This has been established to support Year 9-13 school students, providing funds to help cover the direct travel costs to nationally recognised science and technology based events outside New Zealand.

The panel reviews applications approximately every 8-12 weeks for example: January; April; June; August and October.

See: www.royalsociety.org.nz/programmes/funds/secondary-school-travel/apply/

Obituary

Robert John (Robin) Ferrier (1932-2013)



Robin is honoured as the grandfather of carbohydrate chemistry in New Zealand. Three of his PhD student 'children', Regine Blattner, Peter Tyler and one of the authors (RHF) were founding members of the 35-strong world class applied carbohydrate chemistry group at Industrial Research Limited (now Callaghan

Innovation). Other 'children' have made significant contributions in industry, Crown Research Institutes and ministries in New Zealand and overseas.

Robin was born in Edinburgh and attended George Heriot's School. He described his discovery of organic chemistry as a 17-year-old schoolboy as a major piece of good fortune, and he immediately recognised it as the subject he wanted to pursue. He attended the University of Edinburgh and gained a Bachelor of Science with first-class honours in 1954 and a PhD in plant polysaccharides in 1957, under Professor Gerald Aspinall.

Appointed to a teaching position at Birkbeck College in the University of London, Robin's focus turned from polysaccharides to monosaccharides. New laboratory tools and methods enabled their reactions and mechanisms to be studied like normal organic compounds, rather than a separate field, and Robin pioneered this approach. In the early 1960s as a NATO Postdoctoral Fellow, he worked in Professor Melvin Calvin's group at the University of California, Berkeley. They were exciting times. While Robin was there, Calvin was awarded the Nobel Prize for Chemistry, and Robin met Carolyn, the pair marrying in Edinburgh in 1962.

Arriving in New Zealand in 1970 as New Zealand's first and Victoria's only Chair of Organic Chemistry, Robin continued to lead work on the monosaccharides, specialising in their use as starting materials for the synthesis of non-carbohydrate compounds of pharmaceutical interest. He had previously clarified the mechanism of the Fischer glycosidation and discovered an allylic rearrangement reaction of glycols, now known as the Ferrier rearrangement – the first of two reactions that bear his name. Many of Robin's best discoveries were made by following up unexpected chemical observations, which often led him into uncharted territory. His second 'name' reaction, the Ferrier carbocyclisation, was the result of this approach.

Robin had a small research group, high expectations of progress and a rigour that demanded all experimental re-

sults be fully validated before they could be believed. His firm approach was softened by a quick wit and mischievous sense of humour. In his 50-year career, Robin published 180 papers, reviews and books, and gave 10 invited plenary lectures at international symposia. His reviews were of particular benefit to the chemical community, but perhaps of most value was the book *Monosaccharide Chemistry*, written with Dr. Peter Collins in 1972, and extensively updated as *Monosaccharides: Their chemistry and their roles in natural products* in 1995. Robin was elected Fellow of the Royal Society of New Zealand (1977) and of the New Zealand Institute of Chemistry (1972), and was awarded a DSc (London, 1968).

Robin loved sport. He played for the school cricket team from age 14, was an East of Scotland doubles champion in tennis and sported a nose rearranged by rugby. He spent days burning to a crisp at the Basin Reserve watching New Zealand play test cricket, and later in life he took up golf, one of his few concessions to retirement. He also found opportunities where his chemistry could serve the nation. Notable were his service on the Toxic Substances Board in the 1980s and the leadership of the RSNZ report *Lead in the Environment* that confirmed the toxic effects of lead and began the phase-out of leaded petrol.

Robin and Carolyn were unfailingly hospitable to visiting chemists and loved to entertain people from all over the world. They were also loyal and regular members of the Presbyterian Church, St John's in the City; Robin became an Elder in 1974 and served as Session Clerk and on various committees throughout his life. He was also the Presbytery representative on the Board of Governors at Scot's College for 13 years.

After his retirement from Victoria University in 1998, Robin entered what he referred to as his 'supposed retirement', working with the carbohydrate chemists at Industrial Research. Here he continued to foster the next generation of carbohydrate chemists in New Zealand – his 'grandchildren', instilling his rigorous approach to chemistry with mentoring and assistance with the group's publications.

In August 2012, Robin celebrated his 80th birthday and retired a second time. Later that year, the Ferrier Trust was set up in his honour, to bring a superstar scientist to New Zealand each year, to engage with chemistry students and lecture. Peppi Prasit, a Ferrier PhD graduate and founder of Amira Pharmaceuticals and Inception Sciences in the US, was the trust's foundation donor. Despite Robin's failing health and memory, it was a delight to have him attend the inaugural Ferrier Lecture in March 2013.

Richard Furneaux
Sarah Wilcox

Are patents on genetic testing really a thing of the past?

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On 13 June 2013, the United States Supreme Court issued its landmark decision on the practice of gene patenting in *Association for Molecular Pathology et al. v Myriad Genetics, Inc. et al.* (“*AMP v Myriad*”).¹ The Court found that an isolated DNA sequence is not patentable. The decision has been hailed by some as a thrilling victory for patients. This, however, may overstate the significance of the decision.

Background

In the late 1980s, several groups were involved in the search for a genetic basis for breast and ovarian cancer. In 1990 a team of scientists from the University of California announced the precise location and sequence of the BRCA1 and BRCA2 (BRCA1/2) genes, mutations of which are associated with increased risk for breast and ovarian cancer. In 1994, another group of scientists from the University of Utah founded Myriad Genetics. Myriad, together with others, filed the first patent applications relating to the BRCA1 and BRCA2 genes in 1994 and 1995, respectively. Then, in 1996, Myriad launched their BRACAnalysis® product, which detects the mutations in BRCA1/2 genes responsible for putting women at high risk for breast and ovarian cancer. Since then, Myriad have obtained 24 granted United States patents relating to the BRCA1/2 genes, providing them with exclusive rights to the provision of BRCA1/2 diagnostic testing.

The Arguments

The BRCA1/2 genes represent only two of several hundred isolated DNA sequences for which patent protection has been granted in the United States. This practice of issuing so called “gene patents” has generated a great deal of controversy, as they provide their owners or licensees with exclusive rights to the DNA sequences concerned. Consequently, the Association for Molecular Pathology (“AMP”) has actively lobbied against the existence of, and exclusive licensing of, such patents.

In *AMP v Myriad*, AMP and others challenged nine composition claims in three of Myriad’s 24 patents on BRCA1/2, these claims relating to isolated DNA sequences (or genes) and complementary DNA (cDNA) sequences. Before the case reached the Supreme Court, other claims relating to methods of using the BRCA1/2 genes were also challenged. These claims were not considered by the Supreme Court.

AMP and others argued that the coverage provided by Myriad’s patents restricted research and therefore limited scientific progress. They also argued that Myriad’s monopoly made it impossible for a patient to obtain a second opinion on their diagnosis, and kept the cost of BRCA1/2 testing high by preventing competition. As well as these ‘moral’ arguments, AMP pointed out that United States

patent law excludes products of nature from patentability. They argued that isolated DNA is insufficiently different from DNA found in the body to be patentable. Myriad argued that isolated genes and their diagnostic tests were patentable on the basis that an isolated DNA sequence is no different from any other chemical compound. They also argued that an isolated DNA sequence itself is patentable, since isolation of the DNA sequence renders it different in character from that present in the human body.

Decision

The Supreme Court held that an isolated DNA sequence is not sufficiently different from the un-isolated product of nature and is therefore not patentable. Complementary DNA (cDNA), on the other hand, which differs mainly in respect of the lack of the non-coding introns, is patentable because it is not naturally occurring. Justice Thomas did provide one caveat to this; a very short strand of cDNA which is indistinguishable from natural DNA is also not patentable.

The Impact of the Myriad Decision

For many, the Supreme Court’s decision represented the end of Myriad’s monopoly on the BRCA1/2 genes and heralded the ability for patients to access alternate tests or to get a comprehensive second opinion about their results. Furthermore, given that a significant number of isolated genes have been patented in the United States, the decision represents a major shift in patent law. However, it is important to recognise what the decision does not do. Many of Myriad’s unchallenged claims relate to methods which apply knowledge about BRCA1/2 genes. As indicated above, the patentability of these claims were not considered by the Court. Nor did the Court have to consider the patentability of DNA in which the order of naturally occurring nucleotides has been artificially altered.

Consequently, there is an increasingly widespread belief that the decision will not have a dramatic impact on the life sciences industry, especially given the expense and technology required to develop competing tests. Indeed, following the decision Myriad was quick to point out that they still had “more than 500 valid and enforceable claims in 24 patents conferring strong patent protection for its BRACAnalysis® test”.²

Within hours of the Supreme Court issuing its decision, United States companies Ambry Genetics and Gene by Gene Limited separately announced their intention to begin offering fast, accurate and affordable genetic testing for the BRCA1/2 mutations to the public. Myriad and its partners promptly alleged that these competing tests infringe claims in ten different patents, including some claims challenged in the original lawsuit (but critically, not the claims that the Court rejected).

In its complaints against Ambry Genetics and Gene by Gene Limited, Myriad alleges that their patent claims covering various methods for detecting or screening BRCA1/2 mutations, synthetic primers, probes and arrays are infringed. Myriad are seeking monetary damages and have requested an injunction to prevent Ambry and Gene by Gene 'free-riding' off what Myriad say is the hundreds of millions of dollars invested in developing the science and market for clinical diagnostic testing for hereditary cancers.

On 15 August 2013, Gene by Gene Limited announced that it is teaming with Ambry Genetics to fight Myriad's infringement lawsuit on the basis that Myriad's patent claims are invalid and that Myriad is abusing its monopoly by enforcing the patents.

This latest round of litigation will test Myriad's assertions following the Supreme Court decision that they have other valid patent claims protecting their market position.

Conclusion

The Supreme Court decision in *AMP v Myriad* is narrow in that it only excludes isolated DNA gene sequences from patentability. The decision indicates that application

of the knowledge about gene function, for example, for genetic predisposition testing, is still patentable. Therefore, it cannot yet be said that controlled access to genetic testing is a thing of the past. Myriad continues to hold enforceable patent rights which may continue to prevent competitors entering into the market of BRCA1/2 gene testing, at least until Myriad's patent rights expire. Given the latest lawsuits filed by Myriad, litigation in this area is likely to continue for some time to come.

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

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2. Statement issued by Myriad Genetics on 13 June 2013. Source: <http://investor.myriad.com/releases.cfm>, viewed 20 August 2013, statement entitled "Supreme Court Upholds Myriad's cDNA Patent Claims".



Victoria Argyle and Tim Stirrup of Baldwins Intellectual Property in Auckland specialise in chemistry and biotechnology patents. Victoria obtained her PhD in supramolecular chemistry from the University of Otago in 2009. She is currently working towards registration as a patent attorney. Tim obtained his PhD in molecular biology from the University of Southampton in the UK in 2007. He qualified as a registered New Zealand and Australian patent attorney in 2011.



Dates of Note

Alfred Nobel was born on 21 October 1833, while the next day 75 years ago (1938) xerography was demonstrated for the first time by **Chester F. Carlson**. **Stephen Moulton Babcock**, the American agricultural chemist who is often called the father of scientific dairying because of his development of the 1890 Babcock test (a simple method of measuring the butterfat content of milk), was born on 22 October 1843. It is 210 years ago on 23 October since **John Dalton** presented his essay on the absorption of gases by water, at the conclusion of which he gave the atomic weights for 21 elements. The paper was read at a meeting of the Manchester Literary and Philosophical Society. The same day in 1873 saw the birth of **William Coolidge**. He was the American physicist, physical chemist and engineer whose improvement of tungsten filaments was essential in the development of the modern incandescent lamp and the X-ray tube. In 2003, 24 October saw the final scheduled flights of the British Airways *Concorde*. On 27 October in 1938, Du Pont announced that its new synthetic fibre yarn was to be called **nylon**. That date is also the 285th anniversary of **James Cook**'s birth (in 1728). **Isidor Traub**, the German physical chemist who founded capillary chemistry, died on 27 October

1943. **Carl Djerassi**, the Austrian-American chemist, novelist, and playwright, best known for his contribution to the development of oral contraceptive pills, has his 90th birthday on 29 October. Sir **Christopher Kelk Ingold**, the British chemist famed for developing mechanistic chemistry, was born on 28 October in 1893. **Marie Maynard Daly**, the first African-American woman to receive a PhD in Chemistry (1947) died 10 years ago on 28 October, as did **John Backus**, the American computer scientist who invented the FORTRAN computer programming language, 25 years ago. **George Eugene Uhlenbeck**, the Dutch-American physicist who with Goudsmit proposed the concept of electron spin in January 1925, died on 31 October 1988. That day 125 years ago (1888) saw pneumatic bicycle tyres patented by **John Boyd Dunlop**.

Severo Ochoa, the Spanish-American biochemist and molecular biologist who shared the 1959 Nobel Prize for Physiology or Medicine (with Arthur Kornberg) for their discovery of the mechanisms in the biological synthesis of ribonucleic acid and deoxyribonucleic acid, died on 1 November, 20 years ago. That day also marks the 165th anniversary of the opening of the Boston Female Medi-

cal School to 12 students; it was perhaps the first medical school in the world exclusively for women. **Georges Urbain**, the French chemist who first isolated the last of the stable rare earths – lutetium, died on 5 November, 75 years ago. Sir **Chandrasekhara Venkata Raman**, the recipient of the 1930 Nobel Prize for Physics for the 1928 discovery of Raman scattering, was born on 7 November 1888, 125 years ago; he died on 21 November in 1970. On 7 November in 1908 **Ernest Rutherford** announced in London that he had isolated a single atom of matter. **Ernst Otto Fischer**, the German theoretical chemist and co-recipient (with Wilkinson) of the 1973 Nobel Prize for Chemistry for his identification of the structure of ferrocene and sandwich compounds, was born on 10 November 1918. **Artturi Ilmari Virtanen**, the Finnish biochemist who improved the production and storage of protein-rich green fodder by the AIV method (named after him and vitally important to regions characterised by long, severe winters), which gave him the 1945 Nobel Prize for Chemistry, died on 11 November 1973. **Edward A. Doisy**, the American biochemist who shared the 1943 Nobel Prize (with Dam) for Physiology or Medicine for his isolation and synthesis of vitamin K, was born on 13 November 1893. **Leo Hendrik Baekeland**, the Belgian-American industrial chemist who invented Bakelite, the first thermo-setting plastic that did not soften when heated, was born on 14 November, 150 years ago, the day 75 years ago that **Hans Christian Joachim Gram**, the Danish pharmacologist and pathologist, who invented the Gram stain, died. **James W. Mitchell**, the American chemist best known for advancing the accuracy of trace element analyses by pioneering X-ray fluorescence methods for part per billion (ppb) trace element determinations, has his 70th birthday on 16 November. On 21 November 1783, **Jean Francois Pilatre de Rozier**, a professor of physics and chemistry, and the Marquis Francois Laurant d'Arlandes became the first men to fly by lifting their hot-air balloon off from La Muette, a royal palace in the Bois de Boulogne, Paris, and flying nearly nine kilometres in 25 minutes. On 1 December of that year, Professor **Jacques Alexander Cesar Charles** and **Marie-Noel Robert** rose to about 600 metres in their balloon, and landed 43 kilometres away after two hours in the air. **Wolfgang Ostwald**, the second child of 1909 Nobel Laureate Friedrich Wilhelm Ostwald and one of the founders of colloid chemistry, died on 22 November 1943, the day in 1903 that the American Leather Chemists Association was formed by nine founding members. **Karl Ziegler**, the German chemist who shared the 1963 Nobel Prize (with Natta) for discoveries in the field of the chemistry and technology of high polymers – the Zeigler-Natta catalyst – was born on 26 November 1898. **Lars Onsager**, the Norwegian-born American chemist whose development of a general theory of irreversible chemical processes gained him the 1968 Nobel Prize for Chemistry, was born on 27 November 1903. That day 50 years ago in 1963 the first flight of a space vehicle powered by a liquid hydrogen and liquid oxygen fuel combination (*Centaur II*) was made. Baronet Sir **Robert Abbott Hadfield**, the English metallurgist who developed manganese steel, was born on 28 November 1858. It is also the day 65 years ago that the Polaroid Land Camera first went on sale, and the day in 1828 that the Bakerian Lecture at the Royal Soci-

ety was presented by **William Hyde Wollaston**, wherein he described the method of powder metallurgy he had devised to produce platinum from its ore. **Christian Doppler**, the Austrian physicist of Doppler Effect fame was born on 29 November 1803. On the same day in 1813, 200 years ago, iodine was announced as a new substance at the French Institute by Nicolas Clément, in the name of its discoverer, **Bernard Courtois**.

Martin Heinrich Klaproth, the German chemist and a founder of analytical chemistry who discovered uranium, zirconium, cerium, was born on 1 December 1743. **Paul Crutzen**, the Dutch chemist who won the 1995 Nobel Prize for Chemistry for showing that chemical compounds of nitrogen oxide accelerate the destruction of stratospheric ozone, has his 80th birthday on 3 December. It is also the day that **Carl Zeiss**, the German industrialist and entrepreneur who gained a worldwide reputation as a manufacturer of fine optical instruments, died in 1888, 125 years ago. **Charles Martin Hall** was the US chemist who invented the inexpensive electrolytic method of extracting aluminium from its ore by using non-aqueous molten cryolite (sodium aluminium fluoride) as solvent. As a young chemist, he experimented in a woodshed, initially unsuccessful until he realised that a non-aqueous solvent for the aluminium oxide was needed during electrolysis. He was born 150 years ago on 6 December 1863. **Joseph Louis Gay-Lussac**, the French chemist best known for his work on gases, also was born that day, but in 1778. **Martin Rodbell**, the American biochemist who discovered the natural signal transducers G-proteins and gained the 1994 Nobel Prize for Physiology or Medicine, died 15 years ago on 7 December. **Fritz Haber**, the German physical chemist, winner of the Nobel Prize for Chemistry (1918) for his synthesis of ammonia from nitrogen and hydrogen, was born on 9 December 1868. **Claude Louis Berthollet**, the French chemist who was the first to note that the completion of chemical reactions depends in part upon the masses of the reacting substances, also was born that day, but in 1748. On 9 December 1968 the first demonstration of the use of a computer mouse was given at Stanford University.

Vincent du Vigneaud, the American biochemist who was awarded the Nobel Prize for Chemistry in 1955 for his biochemically important studies of sulfur compound's and especially the first synthesis of a polypeptide hormone, died on 11 December 1978 as did **Georges Friedel** (son of Charles Friedel), the French crystallographer who formulated basic laws concerning the external morphology and internal structure of crystals, in 1933. On 14 December 1933, **Ernest Rutherford** suggested the names *diplogen* for the newly discovered heavy hydrogen isotope and *dip-lon* for its nucleus; it was named *deuterium* by its original discoverer, **Henry Urey**. **Wolfgang Pauli** (of the Pauli Exclusion Principle fame) died on 15 December 1958, the day 235 years ago (1778) that **Sir Humphry Davy** was born. **Willard Frank Libby**, the American chemist who devised the technique for carbon-14 dating, was born on 17 December 1908. That day 15 years ago **Alfred Wolf**, the Brookhaven National Laboratory chemist who made pioneering contributions over almost 50 years in the field

of organic radiochemistry, died. **Thomas Andrews**, the Irish physical chemist who demonstrated the continuity of the gaseous and liquid states, was born on 19 December, 200 years ago. **Robert Andrews Millikan**, the American physicist awarded the 1923 Nobel Prize for Physics for his work on the elementary charge of electricity and on the photoelectric effect, died the same day in 1953. December 19 is also the day 150 years ago that **Frederick Walton** applied for a patent on his invention of linoleum in London.

William Hyde Wollaston, the English chemist and physicist who discovered palladium (1803) and rhodium (1804), died on 22 December 1828. **James Prescott Joule**, the English physicist who established that the various forms of energy were inter-related, was born on 23 December 1818. **Clemens Alexander Winkler**, the German chemist who discovered the element germanium, was born on 26 December, 175 years ago. On this same day in 1898, Polish-French scientist **Marie Sklodowska Curie** discovered the radioactive element radium while experimenting with pitchblende. **Carl Remigius Fresenius**, the German analytical chemist who devised a method for systematic identification and separation of individual metal and non-metal ions by selecting the most suitable reactions from the many that were known, was born on 28 December 1818, as was **William Draper Harkins**, the American nuclear chemist who was one of the first to investigate the structure and fusion reactions of the nucleus, in 1873. **Alexander Parkes**, an expert in electroplating and able to silver-plate such diverse objects as a spider web and flowers, was born on 29 December, 200 years ago. It is also the day 100 years ago that **William David Coolidge** patented a method for making ductile tungsten for use as filaments in electric lamps. December 31 marks the 200th anniversary of Westminster Bridge in London being illuminated with gas lights.

On 1 January 1989, the Montreal Protocol, an international agreement (adopted 16 September 1987) to reduce the use of ozone-depleting substances, came into force, while **Heinrich Hertz**, the German physicist who was the first to broadcast and receive radio waves, died that day in 1894. **Roger Adams**, the noted American chemist (Adam's catalyst) and teacher who joined the faculty at the University of Illinois at Urbana in 1916, was born on 2 January

1889. January 3 in 1919 was the day **Ernest Rutherford** succeeded in splitting the atom by bombarding nitrogen atoms with alpha particles. **Norman Heatley**, the English biochemist who solved problems in the extraction of penicillin from its mould, and paved the way for mass production, died on 5 January 2004, the day 125 years ago (1889) that the word *hamburger* first appeared in print. **Edmund Ruffin**, the father of soil chemistry in the US, was born on 5 January 1794. **Eilhardt Mitscherlich**, born on 7 January 1794, was the German chemist who promulgated the theory of isomorphism. January 7 also marks the 175th anniversary of **Louis Daguerre's** first announcement of his photographic system at the Académie des Sciences in Paris. The daguerreotype photo process needed only a few seconds, whereas earlier processes needed hours. The first samples of alizarin, synthetically prepared by **Carl Graebe** and **Carl Lieberman**, were presented at the Berlin Chemical Society on 11 January 1869.

Paul Hermann Müller, the Swiss chemist who received the Nobel Prize for Physiology or Medicine in 1948 for discovering the potent toxic effects on insects of DDT, was born on 12 January 1899. **Paul Ulrich Villard**, the French physicist and chemist who in 1900 identified a third kind of natural radiation, later called gamma rays, died on 13 January 1934, the day in 1404 during the reign of Henry IV that English alchemists were forbidden to use their knowledge to create precious metals. January 14 marks the centenary of **Henry Ford's** announcement of the advance in assembly line production of "modern" cars that reduced the assembly time of a car from over 12 hours to 93 minutes. On 19 January 1894, 120 years ago, Prof **James Dewar** exhibited several properties of liquid air and produced solid air, at the meeting of the Royal Institution in London. On 22 January 1939, the uranium atom was split for the first time using the cyclotron at Columbia University. **Richard August Carl Emil Erlenmeyer** (of flask fame), died on 22 January 1909. German-born **John Polanyi**, the German-Canadian chemist and educator who shared the 1986 Nobel Prize for Chemistry (with Herschbach and Lee) for contributions to the development of reaction dynamics as a new field of research, has his 85th birthday on 23 January.

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Author Index for Chemistry in New Zealand, Vol. 77, 2013

- Arabshahi, H.J.; Reynisson, J.: Qualitative testing of global QSAR models: The hERG K⁺ ion pump, 76-78
- Argyle, V.; Stirrup, T.: Are patents on genetic testing really a thing of the past? [Patent Proze], 143-144
- Avira, R.R.: *see* Schuster, G.B.; Chen, W.; Ma, Z.; Avirah, R.R.: Precise synthesis of conducting polymers by DNA-directed self-assembly, 69-75
- Boniface, S.: Report on the 45th International Chemistry Olympiad competition, 115
- Bowmaker, G.A.: *see* Zujovic, Z.D.; Gizdavic-Nikolaidis, M.; Bowmaker, G.A.: Solid-state NMR of polyanilines with different morphologies, 87-91
- Chen, W.: *see* Schuster, G.B.; Chen, W.; Ma, Z.; Avirah, R.R.: Precise synthesis of conducting polymers by DNA-directed self-assembly, 69-75
- Coles, M.P.: Fluorescent Minerals: a hobbyist's perspective (with a bit of chemistry...), 42-47
- Cooke, I.: Sands of time: Silica stardust in meteorites, 113-115
- Furneaux, R.; Wilcox, S.: Obituary – Robert John (Robin) Ferrier, 142
- Gizdavic-Nikolaidis, M.: *see* Zujovic, Z.D.; Gizdavic-Nikolaidis, M.; Bowmaker, G.A.: Solid-state NMR of polyanilines with different morphologies, 87-91
- Halton, B.: The 2012 Nobel Prize in Chemistry, 21-23
- Halton, B.: Some unremembered chemists
John Mercer FRS, FCS, MPhS – Part I. The formative years, 24-27
John Mercer FRS, FCS, MPhS – Part II. The industrialist, the chemist and the man, 52-55
Sir Edward Frankland KCB, FRS, FCS (1825-1899), 92-96
John William Draper (1811-1882), 136-141
- Halton, B.: Dates of note, 29-31, 57-58, 100-101, 144-146
- Haverkamp, R.G.: The Australian Synchrotron – A powerful tool for chemical research available to New Zealand scientists, 12-17
- Hebditch, K.: Change to data protection laws [Patent Proze], 56-57
- Hebditch, K.: *see* Stirrup, T.; Hebditch, K.: Accelerating examination of your patent application [Patent Proze], 27-29
- Hodder, P.: Primo Levi's periodic system, 48-51
- Ma, Z.: *see* Schuster, G.B.; Chen, W.; Ma, Z.; Avirah, R.R.: Precise synthesis of conducting polymers by DNA-directed self-assembly, 69-75
- Middag, R.: The importance of trace element chemistry in understanding ocean processes, 126-129
- Miller, I.: A Response to the "top ten" chemistry challenges [Letter to the Editor], 26-27
- Ralston, G.: HOTAIR: Can we make use of this anti-sense RNA?, 116-119
- Revell, L.: Linking anthropogenic climate change and stratospheric ozone depletion, 130-135
- Reynisson, J.: *see* Arabshahi, H.J.; Reynisson, J.: Qualitative testing of global QSAR models: The hERG K⁺ ion pump, 76-78
- Sarojini, V.: Peptides: From Emil Fischer to Psa, 79-86
- Schuster, G.B.; Chen, W.; Ma, Z.; Avirah, R.R.: Precise synthesis of conducting polymers by DNA-directed self-assembly, 69-75
- Sharif, S.: Helping scientists redefine the kilogram, 102
- Stirrup, T.: Indian patent decision highlights the bond between politics and patent law [Patent Proze], 96-99
- Stirrup, T.; Hebditch, K.: Accelerating examination of your patent application [Patent Proze], 27-29
- Wilcox, S.: *see* Furneaux, R.; Wilcox, S.: Obituary – Robert John (Robin) Ferrier, 142
- Wright, J.R.: A golden era in modern chemistry, 120-125
- Yorke, S.C.: The application of N-acetylmannosamine to the mammalian cell culture production of recombinant human glycoproteins, 18-20
- Zujovic, Z.D.; Gizdavic-Nikolaidis, M.; Bowmaker, G.A.: Solid-state NMR of polyanilines with different morphologies, 87-91

Subject Index for Chemistry in New Zealand, Vol. 77, 2013

Antarctic ozone hole	130-135	Nanofibres	87-91
Anti-cancer	120-125	Nitrous oxide	130-135
Antimicrobial peptides	79-86	Nobel Prize	21-23
Arthritis	120-125	Nucleosynthesis	113-115
Benchmarking	76-78	Obituary	
Calcite, fluorescence	42-47	Robin Ferrier	142
Cancer prognosis	116-119	Oxide-silicates	113-115
Carbon dioxide	130-135	Ozone	130-135
Chemical analysis	12-17	Patent Proze	27-29, 56-57, 96-99, 143-144
Chemistry challenges	26-27	Peptides	79-86
Chemistry Olympiad	115	Periodic table	48-51
Chemotherapeutics	120-125	Phosphate	126-129
Climate change	130-135	Phytoplankton	126-129
Computer aided drug design	76-78	Polyaniline	69-75, 79-86
Cross polarisation	87-91	Presolar grains	113-115
Dates of Note	29-31, 57-58, 100-101, 144-146	Primo Levi	48-51
DNA	69-75	Programmed synthesis	69-75
Draper, John William	136-141	Psa	79-86
Fire blight	79-86	Scheelite-powellite	42-47
Fischer, Emil	79-86	Sialylation	18-20
Fluorite, fluorescence	42-47	Solid phase peptide synthesis	79-86
Frankland, Edward	92-96	Solid state NMR	87-91
Glycoproteins	18-20	Surface analysis	12-17
Gold	120-125	Synchrotron	12-17
History	48-51	Templated polymer	69-75
Homogeneous catalysis	120-125	Therapeutic potential	79-86
Isotope signatures	113-115	Trace metals	126-129
Kilogram	102	Uranium-containing minerals	42-47
Known drug space	76-78	X-ray diffraction	12-17
Levi, Primo	48-51		
Long non-coding RNA	116-119		
Manganese	126-129		
Marketed drugs	76-78		
Mercer, John	24-27, 52-55		
Methane	130-135		
Minerals, fluorescent	42-47		
Modular functionality	116-119		
Montreal Protocol	130-135		