NZIC Chemistry IN NEW ZEALAND

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Articles and Features

Other Columns

NZIC President

Comment from the President

Welcome to the start of a new year and to the first issue of *Chemistry in New Zealand* for 2014. The journal now has a new editor, Catherine Nicholson and I would like to warmly welcome her to this role and to thank Peter Hodder for his past efforts with the journal. No doubt Catherine and the publishing team will continue to produce a quality product.

As the incoming President of the Institute, I would like to express my gratitude to outgoing President Michael Edmonds for his excellent work over the past year. I would also like to acknowledge two council members in particular who do a huge amount of work behind the scenes for the Institute, Honorary General Secretary Richard Rendle and Treasurer, Colin Freeman. Thank you both for your tremendous efforts to keep everything running well.

The 2013 conference in Wellington was a great success and I would like to thank Convenor Rob Keyzers (VUW), Conference Chair Richard Furneaux (Callaghan Innovation) and the other members of the organising committee; Matthias Lein (Treasurer) and Joanne Harvey (both from VUW), Tim Kemmitt and Ralf Schwoerer (Callaghan Innovation) and Wendy Popplewell (ESR) for their hard work in making the conference a memorable event.

We have many very talented chemists amongst our members and there were very strong fields of candidates for each of the 2013 prizes. This year the Easterfield Prize was awarded to Dr James Crowley from the Chemistry Department at the University of Otago and the Shimadzu Prize for Applied and Industrial Chemistry went to Dr Nigel Perry of Plant & Food Research, Otago. Both of these prizes were presented at the conference. The Maurice Wilkins Centre Prize for Chemical Research was awarded to Professor Robin Smith of the Chemistry Department, University of Otago and was presented at an Otago NZIC Branch meeting, while the ABA Books Denis Hogan Prize for Contribution to Chemical Education went to Duncan Smith of St Paul's Collegiate School, Hamilton and was presented at the school by Graeme Abbott of ABA Books. Congratulations to all of the prize recipients for 2013.

On an international scale, the 2013 Nobel prize in Chemistry was awarded to Martin Karplus, Michael Levitt and Arieh Warshel for the "development of multiscale models for complex chemical systems" or in other words, for computer modelling of chemical reactions. Their work and that of those that followed have enabled chemists to simulate reactions in an extremely realistic manner and gain real insight into chemical processes. Of course we also have Martin Karplus to thank for the Karplus equation, which describes the relationship between three bond coupling constants and dihedral angles in NMR spectroscopy and is well known to students of chemistry for its ability to predict stereochemistry in rigid systems!

Why is the NZIC relevant to chemists throughout New Zealand? There is an astounding degree of chemical ignorance amongst the general public, with television presenters telling us that the lead in pencils is made of lead and with many advertisers touting their "chemical free" products. As I vividly remember one of my lecturers, the late Gordon Rodley telling me, "Chemistry is everywhere". I feel that one of the roles of a professional body such as ours is to help educate the public of this fact and to ensure that Chemistry is seen as relevant and important, not the evil thing that taints all but our "chemical free" products!

I look forward to an exciting year as President of the Institute and to meeting many of you during my Branch visits throughout the year.

Michèle Prinsep
NZIC President

From the Editor

Happy New Year to you all! I hope you were able to enjoy some rest and relaxation time with friends and family over the festive season so that you are feeling refreshed and ready for what will no doubt be another busy year ahead.

This issue of *Chemistry in New Zealand* is my first as editor. Thanks are due to Peter Hodder for all of the hard work and dedication that he has brought to this role in the past. I am very pleased that Brian Halton has agreed to remain as consulting editor. Peter and Brian, along with Richard Rendle, our honorary general secretary, and Rebecca Hurrell, our publisher, have all been extremely helpful over the past few months as I have been learning the ropes. I very much look forward to working with everyone involved in producing each issue over the coming year.

Of course there would be no *Chemistry in New Zealand* without the contributions of NZIC members. Thank you to everyone who has submitted items for this issue. I would like to take this opportunity to genuinely encourage feedback from all members on any aspect of our publication that you feel is good, bad or indifferent. Is the current format working well? Are there any regular columns that could be added or improved? Unsolicited material including short articles, news, reviews and comment is always welcome. Please get in touch – your thoughts and suggestions are important for keeping content fresh and relevant to readers. It may not be possible or practical to implement all new ideas but they will certainly be considered and discussed.

Congratulations to everyone involved in organising the 2013 NZIC conference held in Wellington at the beginning of December. I attended the first day and was impressed by the quality and variety of the oral and poster presentations. Everything appeared to be running very smoothly which is no small task for this type of event. I enjoyed catching up with some old faces and meeting members from throughout the country. I hope to work with many more of you over the course of producing future issues.

Best wishes for 2014.

Catherine Nicholson

New Zealand Institute of Chemistry

supporting chemical sciences

January News

NZIC News

Dr *Gary* ***Evans*** of the Carbohydrate Group of Callaghan Innovation (The Ferrier Institute when this is in print) has been created a Member of the Order of New Zealand (MNZM) in the New Year Honours list.

The Royal Society of New Zealand has elected 1997 Nobel Prize Winner Professor Sir *John* ***Walker*** FRS to Honorary Fellowship. He is at the MRC Mitochondrial Biology Unit, Wellcome Trust, UK, and has used protein chemical methods to gain critical insights into the function of the key enzyme involved in cellular energy production, the adenosine triphosphate (ATP) synthase.

John Walker's interactions with New Zealanders began with hosting visiting New Zealanders at the MRC Laboratory of Molecular Biology in Cambridge. Then, in the 1980s a longstanding collaboration began with Dr *David* ***Palmer*** and Professor *Bob* ***Jolly*** from Massey University, on the protein in lysosome derived storage bodies from sheep with ceroid lipofuscinosis.

Since being appointed Director of the MRC Dunn Human Nutrition Unit (the MRC Mitochondrial Biology Unit since 2009), Walker has focused on how food energy is harvested and used, through expanded studies of mitochondria. The collaboration with Palmer has also occasioned three visits by Walker to New Zealand and through these a second major collaboration began with Prof *Greg* ***Cook*** (Microbiology and Immunology, Otago University), in which they have solved the first high-resolution (<3 Å) structures of the bacterial F1-catalytic domain, information used to initiate a structural analysis of the F1-ATPase from *Mycobacterium tuberculosis*, a validated drug target.

Former NZIC President and current co-Director of the Auckland Cancer Society Research Centre (ACSRC) at the University of Auckland, Distinguished Professor *Bill* ***Denny*** has been named as the recipient of the American Chemical Society's 2014 Medicinal Chemistry Award. This award is presented every second year and recognises a scientist or team of scientists from the U.S. or abroad whose research has made, either directly or indirectly, a significant contribution to the discipline of medicinal chemistry. Bill is the first recipient of this prestigious honour from outside the United States for more than 30 years.

In addition to being co-Director of the ACSRC, Bill is also a Principal Investigator of the Maurice Wilkins Centre for Molecular Biodiscovery, and was President of the NZIC in 1994 and Chair of the Auckland Branch in 1984-85. He was appointed an Officer of the New Zealand Order of Merit in 2003, and his many other awards include the NZIC ICI Prize (1986), Rutherford Medal of the Royal Society of New Zealand (1995), the Adrien Albert Medal of the UK Royal Society of Chemistry (2005), the Albert Lectureship of the Royal Australian Chemical Institute (2006), the NZBio Biotechnologist of the Year award (2007), and the University of Auckland Commercialisation Medal (2012).

The 2014 Medicinal Chemistry Award will be presented to Bill at the ACS National Medicinal Chemistry Symposium in Charleston, South Carolina, in May next year. The NZIC was involved in the nomination process for this Award, so it is especially pleasing to achieve a successful result.

AUCKLAND

School of Chemical Sciences, University of Auckland

Oktoberfest was held on the 9th of October with great beer, food and Germanic ambience. We thank Dr *Tilo* ***Söhnel*** and his team for a great performance. Danke schön!

Congratulations to our PhD student, *Wan-Ting* ***Chen***, who was awarded the best poster prize at the 7th Asia-Oceania Forum for Synchrotron Radiation Research held in Himeji, Japan. Wan-Ting's poster was entitled *CuO/TiO_2 – Low cost semiconductor photocatalysts for solar hydrogen production*. Also, Dr *Jon* ***Sperry*** was awarded a 2013 Rutherford Discovery Fellowship for the project *Inert C-H bonds: A gateway to molecular complexity.* Our student *Jane* ***Leung*** was awarded a Woolf Fisher PhD scholarship to study polymer science at Cambridge. *Tom* ***Wright*** who completed Honours in SCS last year, has also departed for Oxford University to start his PhD funded by a Rutherford Foundation scholarship. Associate Professor *Bob* ***Anderson*** was granted a full Marsden Fund award for developing the project *Improving radiotherapy outcomes: Chain release of drugs to kill refractory cells and inhibit metastatic spread* in collaboration with Dr *Jeff* ***Smaill***, Associate Professor *Adam* ***Patterson*** and Associate Professor *Brent* ***Copp***. Bob's laboratory, including the electron accelerator, has now been moved to the Grafton campus.

Associate Professor *Yacine* ***Hemar*** organised a successful three-day workshop on the *Rheology of bitumen* from 11th-13th December.

We have been fortunate to have had many recent visitors who have given brilliant presentations. Professor H. *Bernhard* ***Schlegel***, Department of Chemistry, Wayne State University, USA, gave a seminar titled *Exploring potential energy surfaces for chemical reactions*. We also hosted an NZIC lecture given by distinguished Professor *Peter* ***Schwerdtfeger***, Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University, Auckland, on the topic *Why is mercury a liquid at room temperature*? Professor *Lionel* ***Vayssieres*** from the International Research Centre for Renewable Energy, Xian

Jiaotong University, China, talked about *Oxied quantum structures and devices*. Professor *Gunnar* ***Westin***, Uppsala University, Sweden, gave a talk on *Complex materials by solution chemistry: from molecules to applications*. Finally *Paul S.* ***Weiss***, Director of California NanoSystems Institute, UCLA, gave a lecture on *Cooperative function in atomically precise nanoscale assemblies*.

The *Peter* ***Robertshaw*** retirement party was held at Old Government House. He gave an interesting account of all the archaic pieces of hardware and software we have in SCS that could become museum relics soon. Peter took good care of our IT needs for almost 20 years and we wish him all the best in his retirement.

Peter Robertshaw and his wife at his retirement function.

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

Congratulations to *John* ***Harrison*** who has been promoted to an Associate Professor. From the theoretical chemistry group: If you would like to know how theoretical chemistry can challenge diamond-anvil cell experiments, read our newest highlighted Angewandte Chemie paper *Melting at High Pressure: Can First-Principles Computational Chemistry Challenge Diamond-Anvil Cell Experiments?* in the December 2013 issue (DOI: 10.1002/anie.201308039).

The Auckland Cancer Society Research Centre (ACSRC)

2013 was a successful year for members of the ACSRC, especially *Bill* ***Denny***, who in addition to receiving the American Chemical Society Medicinal Chemistry Award mentioned earlier, was also successful in being awarded a five-year Health Research Council (HRC) Programme Grant to look at *Rational design of kinase inhibitors to target cancer*. Bill was also involved in the successful renewal of contracts with the Global Alliance for TB Drug Development, which employs five chemists under the leadership of *Brian* ***Palmer***, and with Genentech, which employs four chemists under the leadership of *Moana* ***Tercel***. An HRC project grant was also awarded to *Jeff* ***Smaill*** to develop *Novel small molecule therapeutics for treatment of smoking-related lung cancer*, while *Bob* ***Anderson***, *Kevin* ***Hicks*** and *Yongchuan* ***Gu*** were successful in receiving Marsden grants. ACSRC researchers are also involved in both of the joint New Zealand-Chinese Strategic Research Alliance research projects in the non-communicable disease category announced in November. One project, headed by chemist Jeff Smaill in collaboration with biologist *Adam* ***Patterson***, involves work with Professor *Ke* ***Ding*** at the Guangzhou Institutes of Biomedicine and Health and the Chinese Academy of Sciences. It will look at developing new drugs to target smoking-related lung cancer. The second project, led by Maurice Wilkins Centre Deputy Director *Peter* ***Shepherd***, involves collaboration with Professor *Ming-Wei* ***Wang*** at the National Centre for Drug Screening/ Shanghai Institute of Materia Medica, Chinese Academy of Sciences, in a project focused on developing new anti-cancer drugs against three new genetically defined targets.

The ACSRC-developed anti-cancer drug PR-610 continued in clinical trial for drug-resistant lung cancer in 2013, while the ACSRC-developed anti-tuberculosis drug TBA-354 begins clinical trial for resistant tuberculosis in early 2014. In other activities, a one-day Winter School in Anticancer Drug Development was held in July and in addition to several local speakers, external speakers included *Graeme* ***Stevenson*** from Griffith University in Queensland and *Richard* ***Furneaux*** from Callaghan Innovation in Wellington.

CANTERBURY

CPIT

CPIT ran its annual competition for Year 10 students in November, both in Christchurch and in Timaru. Across the two events, 26 teams from 14 schools participated. The Christchurch event was won by a team from Burnside High School with Rangiora High School the runner-up. The Timaru event was won by a team from Geraldine High School, with Timaru Girls' High School the runner-up.

The competition involved two chemistry practical activities plus a quiz covering all areas of science. Because calibration is an essential part of measurement quality in commercial laboratories, we included a thermometer calibration by ice point. The other practical activity involved identifying five compounds (NaCl, Na_2SO_4, $CaCO_3$, Na_2CO_3, $NaNO_3$) using simple test-tube reactions. The qualitative analysis tested both practical skills (following instructions; correct labeling) and problem solving (to use the test results to identify the compounds).

Along with CPIT's other competitions, this competition is an important way to encourage secondary school students in their studies and provides an opportunity for teachers to network.

University of Canterbury

Visitors

Professor *Richard* ***Keene*** visited the Department in September for three weeks. Richard recently retired from the School of Pharmacy and Molecular Sciences, James Cook University, Townsville (with Emeritus status), and is an Honorary Visiting Research Fellow, School of Chemistry and Physics, University of Adelaide. He is also an Adjunct Professor at UC, a former Erskine visitor and is Principle investigator for a Marsden programme in collaboration with

Peter ***Steel.*** Richard's interests are in various aspects of coordination chemistry and, more recently, in the interactions of metal complexes with biological systems.

Professor *Graham* ***Richards*** CBE visited the department between the 16th and 30th of November. Until 2008, Graham was the Head of the Chemistry Department at the University of Oxford, which is the biggest Chemistry Department in the Western world. His research is largely in the area of computer-aided drug design of which he was one of the pioneers, publishing more than 350 papers and authoring some 17 books. He was the scientific founder of Oxford Molecular Group Plc, which was grown from a £350,000 start-up, to a public company valued at its height at £450 million, before being sold for £70 million in two parts. He raised £64 million to build the new Chemistry Research Laboratory at Oxford University with the most innovative aspect being the deal he did with a City institution whereby half of the University's equity in spin-out companies from the Chemistry Department goes to the group in return for a substantial up-front payment. Out of that deal has grown IP Group Plc of which he is senior non-executive director. He also holds directorships in Oxeco Plc, Inhibox Ltd, TdeltaS Ltdand Crysalin Ltd, and chairs the African Institute of Mathematical Sciences. Among the awards he has received are the Ital Gas Prize, the American Chemical Society Award for Chemical and Pharmaceutical Research and the Mullard Award of The Royal Society. Graham gave a series of lecturers at the department focusing largely on entrepreneurship.

Awards and appointments

Professor *Bryce* ***Williamson*** received the University of Canterbury Students Association (UCSA) award for the "Most Extravagant Pogonotrophy* of the Year 2013". This writer has witnessed what one of Bryce's students aptly described as, "his wondrous Lorax-moustache". The award is well deserved.

(*) The act of cultivating, or growing and grooming, a moustache, beard, sideburns or other facial hair.

Professor *Ian* ***Shaw*** was awarded UCSA Science Lecturer of the Year at an awards evening on Friday 13th of September. Ian also received the award in 2009. Ian has also accepted an invitation to become Editor of the World Health Organisation Journal, *Water & Health*.

Doreen ***Bestmann*** has been appointed as Business Development Manager, College of Science. Doreen is a UC Maths graduate (1st class Hons) and has returned to Christchurch after gaining experience in the UK as a Commodity Analyst, and as a Service Delivery Manager for the company developing the UK's national computer network for research and education. More recently, Doreen has been a Senior Contracts Manager at Auckland UniServices, managing relationships, contracted projects and business development with existing clients in the education services area.

Chemistry Outreach

Paul ***Kruger*** and *Anthea* ***Lees*** participated in the 5th annual chemistry outreach activity with very enthusiastic Year 6 students at Queenspark School. "We conducted hands-on experiments with the students around the theme 'From Red Cabbage to Electrochemical Fruit'. It was fantastic to be amongst such enthusiastic children and to see their faces light-up as we all performed experiments using red cabbage juice as a striking acid/base indicator and testing it against various household items… these sessions continue to be a highlight in the teaching year and rank amongst our most memorable teaching experiences."

MANAWATU

The Manawatu Branch held their AGM in November, and have a range of upcoming activities planned for the year ahead, including the annual student event. *Paul* ***Plieger*** has taken over the role of Branch Chair from *Gareth* ***Rowlands***.

Congratulations again to *Ghislaine* ***Cousins***, *Justin* ***Bendall***, *David* ***Shillington***, *Mark* ***Waterland***, and *Paul* ***Plieger***, all of whom have been made Fellows of the NZIC in 2013

Ghislaine Cousins being awarded her certificate of fellowship by Manawatu Branch Chair Gareth Rowlands.

Massey University, Institute of Fundamental Sciences

Summer students working in the labs are *Rebecca* ***Severinson*** who is working on new planar chiral amino acids, *Joseph* ***Corrigan*** who is working with *Paul* ***Plieger*** on a Marsden project, *Tom* ***Hall*** who is doing work experience under the supervision of Paul Plieger and *Gareth* ***Rowlands*** on [2,2]paracyclophane magnets, and *Nina* ***Wan*** who is doing work experience on anion sensors.

Ashley ***Way*** has started her PhD under the supervision of *Mark* ***Waterland***, and *Matthew* ***Price*** has started his PhD under the supervision of Paul Plieger.

A group from IFS attended the NZIC conference in Wellington in December. Staff attending the conference included *Paul* ***Plieger***, *Mark* ***Waterland***, *Shane* ***Telfer***, *Gareth* ***Rowlands***, *Vyacheslav* ***Filichev***, and *Alex* ***Hamilton***. Students attending the conference included *David* ***Nixon***, *Sebastian* ***Blackwood***, *Ashley* ***Way***, *Ben* ***Munro***, *Luke* ***Liu***, and *Heather* ***Jameson***.

Chris ***Lepper*** attended a Physics of Biology conference in Geneva, Switzerland, a conference aiming to foster interactions between physicists and biologists active at the interface between the two disciplines. Young researchers, such as Chris, are provided with the opportunity to present their work in a short talk to the physics/biology community, or in poster sessions.

IFS hosted the 27th annual Massey – Victoria Symposium Day where students from both universities presented their research. A large contingent from Victoria helped make the event a great success.

Recent talks at Massey have included *Claudia* ***Vickers***, who spoke about isoprenoids. *Alan* ***Ferguson*** talked about the self-assembly of spin crossover molecular cages. *Karla* ***Dunn*** and *Josh* ***Blazek*** presented their BSc(Hons) research.

OTAGO

The Branch's 10th High School Chemistry Quiz was held on September 25th at the Otago Museum's Hutton Theatre, with 45 teams of Year 12 and 13 chemistry students from schools around Otago and Southland. As usual, pizza from Poppa's Pizzeria, along with drinks and chips were enjoyed before the serious quizzing began.

Sample Questions:

1. Where is the oldest university in New Zealand, and where is the oldest university in the world?

2. If 16 g of methane reacts completely with 16 g of oxygen gas, what mass of water is produced?

3. How many isotopes of phosphorus are there – 8, 15 or 23?

4. Name the superheroes associated with each of the following people: Alfred the Butler, Lois Lane, Gwen Stacy, David Banner, Thomas Logan, Amy Pond?

After five rounds of questions, and a tense tie-breaker round to decide the 2nd and 3rd place getters, the results were:

1st *Bond – Covalent Bond* (St Hilda's Collegiate School); Claudia Paterson, Ester Fogarty, Kate Holden, Harriet George

2nd *Only Taking Chem to make Meth* (Otago Girls High School); Thalia Wilkin, Kristy Pauling, Eleanor Hay

3rd *Team E* (St Hilda's Collegiate School); Ellen Buchanan, Kate Hesson, Anne-Sophie Page, Holly Campbell

The winning Chemical Haiku's were:

Helium, my friend
I watch you float above me
In a big balloon

CSC Stars

Dead Chemist, what now?
All my good ideas Ar-gon
Why don't we Bari-um?

In our element

Dr Phillips is cool
He draws nice dinosaurs
He is our idol

Only Taking Chem to make Meth

Tears, Time and Solvents -
Precipitates never form:
How I wish they would

Cinnamates

Blinding white lab coats
Mirror the brilliance of
True chemical form

John at the train station
(not a winning Haiku but definitely one of the best team names)

2013 Otago and Southland Interschool Chemistry Quiz winners

As always, our thanks to our sponsors, The University Bookshop, Poppas Pizzas, The Otago Branch of the NZIC and the University of Otago, as well as to the staff and students from the Chemistry Department who helped out on the night.

In November, 2012 NZIC Industrial and Applied Chemistry Prize winner *Steve* ***Moratti*** presented a seminar on *Supertough Gels: How and Why?* The seminar was followed by the Branch's Annual General Meeting.

University of Otago, Department of Chemistry

Three of the Department's staff received NZIC prizes for 2013. *Rob* ***Smith*** was awarded The Maurice Wilkins Centre Prize for Chemical Science, *Nigel* ***Perry*** was awarded the Prize for Industrial and Applied Chemistry, and *James* ***Crowley*** received the Easterfield Award.

The Royal Society of New Zealand's T.K. Sidey Medal for outstanding scientific research in the field of electromagnetic radiation was awarded to *Jim* ***McQuillan*** in November. The award recognises Jim's part in a research partnership that created the analytical technique surface-enhanced Raman scattering (SERS) and for developing infrared spectroscopy to examine wet metal oxide nanoparticles.

Mark ***Rizzacasa*** from the University of Melbourne visited the Department from the 24th of September to the 10th of October as a William Evans Fellow. During his time at Otago, Mark presented a research seminar and a 4th-year lecture course on advanced organic synthesis.

Jaydee ***Cabral*** of the Supramolecular and Polymer group gave an oral presentation at "Polymers in Medicine and Biology", an ACS conference held October 9-12, 2013 at the Hilton Sonoma Wine Country Hotel in Santa Rosa, California USA.

In July, *Sally* ***Brooker*** made her first ever trip to Belgium, presenting department seminars at both the Université Catholique de Louvain, Louvain la Neuve (hosted by Yann Garcia) and the Katholieke Universiteit Leuven, Leuven (hosted by her collaborator Liviu Chibotaru) - two quite separate places - before presenting an invited keynote lecture at the ACIN conference in Namur. In September she returned to Europe for a short sabbatical leave, based at Karlsruhe Institute of Technology as a Visiting Professor, hosted by Annie Powell. During this time she also visited a number of collaborators and presented department seminars at Southampton, Bielefeld, Göttingen, Mainz, Strasbourg, Montreal and Ottawa Universities. Her French PhD student *Sebastien* ***Dhers*** joined her in Strasbourg, visiting both the Chemistry Department (hosted by Mir Wais Hosseini) and ISIS (hosted by Luisa De Cola). He presented his research to the De Cola research group, and was interviewed by Jean-Marie Lehn that weekend, before he travelled to Karlsruhe for the European Conference on Molecular Magnetism (ECMM), at which he presented a flash lecture and award winning poster (see photo). Sally gave the opening plenary lecture at the ECMM.

The ECMM conference, Karlsruhe, October 2013. Sally Brooker giving the opening plenary lecture (top), and Sebastien Dhers, third from right, won a poster prize (bottom).

Sally and her team (including local Associate Investigator's *Carla* ***Meledandri*** and *Guy* ***Jameson***, and postdoc *Humphrey* ***Feltham***) recently received the good news that they have been awarded a Marsden grant for *Designer Spin Crossover*. In December, *Humphrey* ***Feltham***, currently a MacDiarmid funded postdoc in Sally's group, presented an invited lecture on his newly developed SCO active tailed complexes and the successful transfer of them to a solid support, at the NZIC conference in Wellington. In addition, Sally was an invited keynote lecturer at the IC'13 conference in Brisbane. *Michael* ***Bennington***, an Honours student in Brookers Bunch in 2012, has recently returned to do a one year research MSc, and a new PhD student, from the University of Barcelona, *Santiago* ***Rodriguez***, joined Brookers Bunch early in 2014. On successfully completing her PhD in the Brooker Bunch, *Rajni* ***Wilson*** went on to complete a three-month publishing bursary, then worked for a few months in Carla Meledandri's research group before accepting a research position in the Dental School. In June, *Matthew* ***Cowan***, a PhD graduate of Brookers Bunch, received a North American Membrane Society (NAMS) Travel Award for early career researchers. Subsequently, he presented a poster regarding his postdoctoral work on ionic liquid/polymer membranes, as well as 'filling in' to give the invited lecture of his supervisor Prof. Richard Noble, at the NAMS meeting in Boise, Idaho. *Nick* ***White***, ex-Honours in Brooker Bunch, recently graduated in person with his DPhil from Oxford University. He started a Killam Postdoctoral Fellow in Mark MacLachlan's research group at UBC, Vancouver earlier this year (*www.youtube.com/watch?v=phu_2shegB4*).

Winner of the 2013 Panckhurst Memorial Award for Excellence in Chemistry Teaching was *Jenny* ***Howden*** from Waitaki Girls High School. Jenny was the also the recipient of the RSNZ Endeavour Teaching Fellowship from January to July last year and spent her time working with the Plant & Food Research Plant Extracts Research Unit on how she could use the chemistry of food to engage her pupils' interest. This included developing an application of the colorimetric total phenolics test to use in the classroom.

Lyall Hanton presents Jenny Howden with the Panckhurst Memorial Award for Excellence in Chemistry Teaching

Owen ***McDougal,*** an Associate Professor of Chemistry at Boise State University, Boise, Idaho is spending his sabbatical year working on the chemotaxonomy of Sophora (aka kowhai) while in the laboratory of *Nigel* ***Perry***. This is a collaborative project with Peter Heenan of Landcare Lincoln, updating the knowledge of the chemistry of this iconic New Zealand plant.

University of Otago, School of Pharmacy

The School of Pharmacy welcomes a new lecturer, *Andrea* ***Vernall***. In 2006 Andrea graduated with a PhD in organic chemistry from the Department of Chemistry, University of Canterbury, and then moved to The Institute of Molecular Bioscience in Brisbane. Here she was involved in peptidomimetic and peptide-focused research with *Paul* ***Alewood***. She then moved to the School of Pharmacy, University of Nottingham in the UK to work with *Barrie* ***Kellam*** and *Stephen* ***Hill*** on the development of fluorescent tools to study G protein-coupled receptors (GPCRs). In October 2013 Andrea took up a Lecturer position in medicinal chemistry at the School of Pharmacy. Her research at Otago focuses on developing small molecules to target GPCRs, including fluorescent ligands, allosteric and bivalent/bitopic ligands, peptidomimetics, and fragment-based drug design.

WAIKATO

University of Waikato

Michael ***Mucalo*** recently attended and presented at two conferences conveniently occurring in the same suburb of Melbourne and at almost the same time. He attended the Australian Synchrotron User Group Meeting 21-22 November at the NCSS at the Australian Synchrotron and the 19th ISE Satellite Electrochemistry Conference held at the CSIRO Clayton Campus over 25-26 November. He presented the results of a research project in IR spectroelectrochemistry where EXAFS/XANES have been applied (through awarding of beamtime at the Australian Synchrotron from the NZSG) to study the products of anodic polarisation at a nickel electrode in the presence of pseudohalide ions. He was particularly impressed with the scope and level of quality research being carried out at the Synchrotron Users Groups meeting due to the phenomena that are now able to be studied using the various imaging and spectroscopic techniques made possible by use of the beamlines available from this excellent facility. *Michèle* ***Prinsep*** attended the *10th International Marine Biotechnology Conference* in Brisbane, in mid-November and gave a keynote lecture on trends in marine natural products research. She was also a panelist at the *Australia, New Zealand and China Collaboration Forum on Marine Biotechnology* which took place during the conference.

Haiming Tang has just started a PhD on gold chemistry with *Bill* ***Henderson*** and *Charlotte* ***Bradley*** is starting her MSc with Bill on hydroxymethylphosphorus chemistry.

Chemquest 2013

In the annual ChemQuest competition, held recently by the Department of Chemistry, Hamilton schools took out the top five prizes. First place went to Hamilton Boys' High School to match their win in the Analytical Chemistry competition earlier in the year. This was also the first time in the history of the contest that Hamilton Boys' High School has won the competition. Around 150 students from the greater Waikato region,

Dr Michèle Prinsep, bursting a hydrogen balloon during the quiz.

Hamilton Boys' High school winning team for 2012 with quizmaster Michèle Prinsep, Waikato Branch chairperson, Michael Mucalo and Martin Brock (Hill Laboratories). From left to right: Michèle Prinsep, Michael Mucalo, Jordan Sahlie, Codi Merito, Nicolaas Portegys and Martin Brock.

the Bay of Plenty and Taupo participated. As usual, this was a fun-filled evening for students studying NCEA level 2 Chemistry.

Prizes were awarded as follows:

1st Place: Hamilton Boys' High School: (Codi Merito, Nicolaas Portegys, Jordan Sahlie)

2nd Place: St Pauls Collegiate: (Kendal Buchanan, Sahil Patil, Sukhjit Sarai)

3rd Place: St Pauls Collegiate: (Callum Connell, Jordan Ogilvy, Emma Walker)

4th Place: Hamilton Boys' High School: (Adam Cameron, Daniel Carson, Patrick Webb)

5th Place: Hamilton Girls' High School: (Cecelia Lockley, Ashleigh Miles, Anna O'Hara)

The quiz was generously sponsored by the Waikato Branch of the New Zealand Institute of Chemistry, the University of Waikato's Faculty of Science and Engineering, Hill Laboratories and James & Wells Intellectual Property. Question master was *Michèle* ***Prinsep*** with *Jo* ***Lane*** the chief judge, ably assisted by numerous other staff and students from the Department.

We congratulate recently retired Associate Professor *Alan* ***Langdon*** who was awarded the title of Honorary Fellow by the University of Waikato as recognition of his leadership in development of science and technology programmes and in forging links between academic research and local and regional industry.

WELLINGTON

The Branch has re-established the 1949 inaugurated ***Mellor Lecture***, given in honour of the extraordinary but little known New Zealand educated scientist, teacher and author *Joseph William* ***Mellor***; it lapsed some 10 years ago. Such was his impact on 20th century inorganic and ceramics materials science that most chemistry libraries on the planet still host a collection of Joe Mellor's works, notably his monumental 16-volume *Comprehensive Treatise on Theoretical and Inorganic Chemistry* which was published from 1921 to 1937. He was, without a doubt, one of the most prolific and influential textbook authors of his time as well as the author of well over 100 papers in British Ceramic Transactions alone. As described below, this event formed the October meeting. Furthermore, the Branch has instituted the ***Halton*** and ***Curtis Lectures***, which will run in a three-yearly cycle with the Mellor Lecture. These named lectureships acknowledge the active and continuous research of Emeritus Professors Brian Halton and Neil Curtis in their respective fields of organic and inorganic/organometallic chemistry, and their significant and on-going contributions to science in New Zealand and to the NZIC. The ***Inaugural Halton Lecture*** will be held in 2014 and the ***Inaugural Curtis Lecture*** in 2015.

The announcement of the 2013 ***Wellies*** saw Dr *Richard* ***Furneaux*** named the Wellington Scientist of 2013 – congratulations Richard.

Branch Secretary, Dr *Nicola* ***Gaston***, delivered the September Branch lecture and entitled it: *What makes a metal? The unusual properties of gallium, and other stories*. She reminded us that metals make up ~80% of the periodic table, yet our understanding of what makes one metal different from another, e.g. the way that the chemistry of carbon and nitrogen are different, is surprisingly simplistic. The limits of our current understanding was discussed and then the chemistry of one of the most unusual metals, gallium, given attention. The unusual structure of the metal and the reason for its low melting point were discussed in the context of just how good at answering these kinds of questions we can be, armed with nothing but Newton's laws of motion, Schrödinger's quantum mechanics, and modern supercomputing capacity. Nicola has been a regular contributor on *Nights with Bryan Crump* on Radio NZ.

NZIC 2nd Vice-President Dr *Ian* ***Brown*** (Callaghan Innovation), whose group researches at the forefront of the field of Advanced Materials eloquently described the life and contributions of Joseph Mellor, relating them to the current state-of-play in ceramic materials for the 2013 Mellor Lecture in October. His lecture was entitled: *Modern ceramic chemistry – a journey from clay science to 3D printing*. Ian surveyed Mellor's contribution to inorganic and ceramic chemistry from 1900 to his death in 1938 and examined how ceramic chemistry transformed from the bare bones 'cups, saucers and bricks' technology of that time to the development of high performance, high functionality materials that we now recognise in modern cutting tools, fuel cells, superconductors and space shuttle tiles. Today's ceramics research is very much shaped by application of research tools we now take for granted: electron microscopy, solid state NMR, thermal analysis – tools that Mellor could never have imagined. The presentation showed how these and other tools have transformed ceramic and materials science in New Zealand and internationally through enabling understanding and use of the key relationships between 'ceramic chemistry ↔ microstructure ↔ physical properties'. Many examples encompassing classical clay science, non-oxide ceramics, membrane ceramics and state-of-art 3D printing were used to illustrate how this ever-advancing field is transforming great chemical science into new technologies. Ian illustrated 3D printing with the titanium underwater knife used in the America's Cup and an elegant bottle opener. This lecture was one of the best in the Branch for several years and any repetition of it during Ian's 1915 Presidential year should attract large audiences.

November 6 saw a lecture from Prof *Christine* ***Winterbourn*** **(**Centre for Free Radical Research, Otago Medical School of Pathology, Christchurch) that was preceded by the Branch AGM. Christine has received numerous awards and was the first woman recipient of the RSNZ Rutherford Medal; she is a Companion of the NZ Order of Merit. Her topic was: *Chlorine Chemistry: Its role in Antimicrobial Defence and Inflammation*. She reminded us that chlorine bleach (hypochlorous acid) is best known as an effective water purifying agent and disinfectant which, if not used wisely, can be dangerous and toxic. She pointed out that its

presence in the body is not simply from low level ingestion but also by generation and the lecture focused on this and the dissipation of HOCl. It is the white blood cells that provide the body with its front line defence against infection through their ability to kill invading micro-organisms. To do this they also use HOCl that they produce via the action of the enzyme myeloperoxidase. While removal of pathogens is clearly beneficial, hypochlorous acid production can have its downside in chronic inflammatory conditions where there is persistent myeloperoxidase activity. HOCl is a strong oxidant that can modify numerous biological molecules, often with deleterious effects on structure and function. She discussed in some detail these aspects of chlorine chemistry in humans.

The AGM saw long-serving Treasurer *Suzanne* ***Boniface*** move to the Chairmanship and the Secretary Nicola Gaston hand over to one of the Callaghan Innovation folk to provide the elected Branch Officers for 2014 as per:

Chairperson (VUW)	Dr *Suzanne* ***Boniface***
Secretary (VUW)	Ms *Leah* ***Graham***
Treasurer (Callaghan Innovation)	Dr *Ralf* ***Schwoerer***

Callaghan Innovation

Neil ***Milestone*** attended the 35th NZ Geothermal Workshop in Rotorua in November and presented a paper entitled *The role of silica in geothermal well cementing*. The cements group is working with Mighty River Power and Contact Energy to develop new carbonation resistant cements for our geothermal wells. Corrosion trials are due to commence early this year. There is renewed interest from Japanese researchers in acid resistant cements as they reactivate their geothermal interests due to loss of electricity generation from nuclear power plants.

ESR

Dr *Wendy* ***Popplewell*** gave birth to a baby girl in August 2013. She is on maternity leave until August next.

The past months have been busy for staff at ESR. *Samantha* ***Coward*** attended the 20th International Council on Alcohol, Drugs and Traffic Safety Conference in August 25 to 28 in Brisbane, Australia while *Matthew* ***Hosking*** gave a presentation on testing hair for the presence of drugs to the Family Law Society Annual Conference in Auckland on 22 November last. Dr *Hilary* ***Hamnett*** (Forensic Toxicologist) who has also worked in science books and journals for the last five years has given three seminars on hints and tips for science publishing to graduate students at VUW. She also spoke at the Wellington Early Career Researchers' Meeting in mid-November and the MacDiarmid Institute's Student Symposium on Science Communication at the end of that month. She will be running a one-day course *Getting Published in Science* in the VUW Professional & Executive Development, three times in 2014.

Dr *Helen* ***Poulsen***, *Alison* ***Colgate*** and *Eleanor* ***Smith*** attended the Forensic and Clinical Toxicology Association conference (FACTA) in Sydney in early December. They had three presentations *Drug use by impaired drivers in NZ*; *False identification of phentermine* and *Roadside oral fluid testing following ingestion of hemp seed and poppy seed products*. At about the same time ESR held a science conference at Lincoln University that was attended by 128 staff across its various sectors. The aim was to foster collaboration and make new connections between the different groups. Dr Hilary Hamnett, *Rosy* ***Moar*** and *Michelle* ***Birch*** represented Kenepuru Science Centre's *Specialised Analytical Services*.

Victoria University – SCPS

In September Prof *Ken* ***MacKenzie***'s PhD student *Michael* ***Welter*** successfully defended his PhD thesis entitled *Fibre-reinforced geopolymer composites* undertaken with a MacDiarmid Institute PhD Fellowship. That month Ken attended the International Conference on Traditional and Advanced Ceramics (ICTA2013) in Bangkok, and presented an invited paper on the work of MacDiarmid PhD Fellowship student *Mahroo* ***Falahpoor***, entitled *New composites of inorganic polymers (geopolymers) with Cu_2O nanoparticles for photodegradation of organic pollutants*. Also presented at the same conference was a paper by Ms *Naprarath* **Waijarean**, a PhD student from King Mongut's University in Bangkok, who spent much of the last academic year working with Ken's group in Wellington. Her presentation was entitled: *The effect of the Si/Al ratio on the properties of water treatment residue (WTR)-based geopolymers* and was based on the work she carried out while in Wellington.

Joanne ***Harvey*** left for a six-month sabbatical in December. She is spending three months in Prof. Karl-Heinz Altmann's lab at ETH, Zurich and then a month with Prof Richard Taylor at the University of York. In mid-January she attended the 27th International Carbohydrate Conference at the Indian Institute of Sciences in Bangalore and presented an invited lecture entitled *Reactions of glycal-derived* gem-*dihalocyclopropanes: Applications to the synthesis of modified carbohydrates and TAN-2483B*. However, a month before her departure her former PhD student *Russell J.* ***Hewitt*** (Institute of Chemical and Engineering Sciences, A*STAR, Singapore) visited and gave a lecture on his work there. It was entitled *From discovery to manufacturability: improved synthesis of antifouling amides.* Russell outlined the work taking the previously synthesised piperidinyl amides to optimization as a "green" commercial reality that has involved an entirely new synthesis.

Article

A Cursory Study of the Bulk and Glaze Composition plus Metal Leaching Properties of a Selection of Antique, Vintage and Present Day Food and Drink Ceramic Wares using XRF, FTIR, ^{27}Al, ^{29}Si, ^{31}P MAS NMR and ICP-MS for Providing a Characterisation of the Types of Domestic Ceramic Ware used in New Zealand Currently

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Introduction

The ceramic utensils used for eating and drinking such as plates, cups, bowls and other items have been a fundamental part of many societies since ancient times. The word "ceramics" is itself derived from the Greek word **κεραμικός** ("Keramikos")[1] meaning "of or for pottery". The art of making ceramics dates back thousands of years with evidence of pottery from 20,000 years ago[2] being reported recently from Xianrendong Cave in China. Ceramics manufacture depends on a source of various materials, namely clay, e.g. kaolinite, silica and feldspar.[3] When these clay and mineral materials are mixed and soaked in water with removal of the excess water, a wet clay is produced which can then be fashioned into the desired shapes using moulds. Water is then removed via drying and the articles fired at temperatures up to 1170 °C during which complex chemical transformations occur in the clay with physical changes in the added silica and feldspar. Kaolinite ($Al_2Si_2O_5(OH)_4$) is converted via a series of precursor compounds to mullite ($Al_6Si_2O_{13}$) and cristobalite (SiO_2). The feldspar acts as a flux with the alkali metal ion content (Na_2O, K_2O and CaO) causing a lowering of the melting point of the silica early on in the firing process. This melt effectively forms a glass which then draws the individual particles of the fired mixture together and additionally reacts with them so giving the ceramic body strength (when it cools) and reducing porosity.

The most distinctive and aesthetic features of ceramic articles are the glazes applied to them. Glazes are comprised of glassy substances or glass and crystals that are able to be formulated to produce certain colours and textures when applied to the clay body. It is oxides like silica and boric oxide that will form glasses when heated to melting point. However, stoichiometric proportions of the sodium, potassium, calcium, aluminium and lead oxides need to be included for tailoring properties. Colouring agents can also be added if needed. Lead silicate was often a favoured glaze in the past due to the brightness of colours it produced and the ease with which transition metal oxides (which are responsible for some of the beautiful colours possible) could dissolve in it. Certain elements are associated with particular colours, e.g. blues in glazes are due to Co^{2+} ions in a tetrahedral coordination environment.[3] Unfortunately due to the risk of lead (and other potentially toxic metals) leaching out of glazes when in contact with liquids or food, many industrialised nations such as those comprising the EU[4,5] have long since introduced directives to curtail or regulate the leaching of potentially harmful substances from glazed ceramics.

The history of food and drink ceramics in New Zealand is restricted to a narrow time-frame of about 170 years since European colonisation occurred, which is brief when compared to the global history of such materials which stretch back millennia. The first chinaware to come to New Zealand would have been predominantly British in origin. As an illustration of this historical fact, the Christchurch earthquake, which brought down many old buildings in the central business district, proved a boon for archaeologists as clearing and excavation of land under these old buildings revealed many old domestic artefacts and broken china.[6] It is obvious from what has been found that English sourced crockery from Staffordshire (which possessed a china industry buoyed by the Industrial Revolution[7]) was a very common sight in those times.

The next part of ceramics history in New Zealand was played by a local West Auckland-based company known from 1948 as "Crown Lynn".[8] The precursor of this company began manufacturing the first household ware for the New Zealand market in the late 1930s. However, production stepped up from 1940 onwards when World War II temporarily stymied imports of crockery from Britain. Under the direction of the company's charismatic owner Sir Tom Clark (1916-2005), the company reached its heyday in the 1970s where it was reputed, according to Valerie Ringer Monk's book,[8] to be turning out about 15 million pieces of china every year. Hence ceramic ware from Crown Lynn was prevalent in New Zealand homes alongside the usual British, European and Japanese/Asian ceramics which were also being imported at the same time. In the mid 1980s, the process of removal of these import controls was accelerated under "Rogernomics" so opening up trade and allowing even more extensive flooding of the New Zealand domestic market with a wide variety of inexpensive chinaware, mostly from Asia. This provided a great deal of choice for the local consumer. Crown Lynn eventually closed its doors in 1989.

Nowadays, a stroll through the premises of various New Zealand retailers who sell imported china and other goods from abroad reveals how completely dominant the takeover of mostly Chinese-manufactured domestic ceramics has been. Earlier New Zealand-made or British domestic

ceramics now tend to be found in secondhand, antique and collectable shops, charity shops, specialist modern craft shop outlets and on online auction sites like Trademe and eBay.

The variety of glaze colouring of this current era of overseas-manufactured china in New Zealand is as vast as it was for past ceramic ware. The quality of imported ceramic ware that dominates our domestic market is also widely varying, and in the case of Chinese ware is made by a range of largely anonymous or hard-to-trace manufacturers. A search through a global trade website like *www.alibaba.com*[9] reveals the diversity of products produced and the large number of Chinese manufacturers and suppliers who provide these wares for sale. To date there has been no dedicated academic study of this current batch of china in New Zealand nor any attempt made to chemically characterise the glazes. From an environmental health perspective, it is also of interest to establish the leaching behaviour of such ceramics in various media. Such tests form a crucial part of assessing the safety of use of these items when placed in contact with food and drink. In particular, Pb used in glazes is a significant health concern[10] as levels in blood from 10-150 μg/dL are associated with health problems ranging from preterm/reduced birthweight in unborn children and decreases in IQ and growth in young children through to brain and kidney damage at high doses in adults. Barium (Ba), which is often used in ceramic glazes, can cause gastrointestinal disturbances and muscular weakness when poisoning due to its ingestion is acute. It also has a chronic long term effect of causing hypertension when consumed above a maximum consumable level of 2 ppm.[11] There are also other commonly used elements in ceramic glazes which are of concern such as Cd, Co, Sn and Zn.

The main aims of the study presented here are thus to sample some selected ceramic ware which is presently available on the market in New Zealand and to characterise the glaze/bulk composition of such modern day ceramics using standard solid state and spectroscopic techniques. As it is of interest to compare such findings with what was available historically, some examples of ceramic materials from Britain (Staffordshire) from the Victorian era, mid-20th century British wares and examples from the extensive New Zealand-made Crown Lynn range of china that exists (and is used) still to this present day, were also studied. The study does not pretend to be truly representative of all ceramic types imported into New Zealand over the ages but serves to give a cursory indication of how these materials have changed in terms of glaze characteristics over the decades and whether, on the basis of these cursory leaching tests, they are of concern from an environmental health perspective.

Experimental

The food and drink ceramics used in the investigations

Ceramic food wares including bowls, plates, tea mugs, saucers and dinner or bread plates made by various manufacturers from New Zealand and overseas and from different eras (1890 to present day) were obtained from various sources (see Table 1). Most of the present day Chinese ceramic wares and one Indian bone china tea mug analysed were purchased from well-known retailers. The selection of the modern items were also based on the various glaze colours of the items. The traditional New Zealand made Crown Lynn and English made ceramic wares were either purchased from antique and charity shops or borrowed from personal collections. Since some intact pieces of English Victorian bone china would be too valuable to be subjected to some of the destructive analytical techniques used in this study, samples of these for characterisation and experimentation were instead sourced from broken eBay or Trademe online purchases. Hence the choice of Victorian/Edwardian era (1892-1911) or mid-20th century British-made ceramic samples investigated in this study is entirely fortuitous.

Type 1 water (distilled deionised) (G =18 ± 2 μs) from a Barnstead water purification system was used for all experiments. All ceramic samples were cleaned thoroughly and dried prior to analysis. Scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis (Hitachi S-4700), Fourier transform infrared spectroscopy (FT-IR) (Perkin Elmer Spectrum 100), solid state NMR spectroscopy (Bruker Avance 300 MHz spectrometer with a 4 mm bore magic angle spinning (MAS) solids probe), X-ray fluorescence (XRF) (Spectro X- Lab 200) and inductively coupled plasma mass spectrometry (ICP-MS) (for elemental analyses of leachate solutions) were used in the study. The major and minor aims of the instrumental characterisation of the ceramic wares were respectively to i) provide an elemental analysis of the ceramic ware particularly of the glazes applied so that a list of elements to analyse by ICP-MS of leaching solution could be determined, and, ii) to provide some structural characterisation of the bulk ceramic item. SEM/EDX techniques were found to be unreliable for providing an idea of elemental composition because EDX analysis sometimes failed to detect elements known to be in the ceramics glaze, e.g. Pb. EDX can suffer from reduced accuracy due to overlapping of peaks[12] as well as from sample inhomogeneity which may prevent escape of X-rays from the sample for analysis. Instead, XRF was found to be very useful for providing a list of elements to analyse for by ICP-MS. Samples analysed by XRF were examined as pressed pellets. Blanks for the XRF measurement were pressed pellets of analytical grade aluminium oxide. XRF calibration standards were Geostandard BX-N (Bauxite) containing major and trace elements similar to elements present in the ceramic samples. FT-IR spectral analysis of the ground ceramic powders was performed using KBr disks with spectra acquired in the range 4000 – 400 cm^{-1} at 4 cm^{-1} resolution. ^{29}Si, ^{27}Al and ^{31}P NMR magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of the various ceramic wares were obtained using direct polarisation scanning techniques with packing of the ground ceramic powders into zirconia rotors with KEL-F caps. These were spun at the magic angle of 54.74° in a solids probe. Specific parameters used in the spectra for each nuclei are detailed in Table 2**.** NMR spectra chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid sodium salt (^{29}Si), yttrium aluminium oxide (garnet) (^{27}Al) and ammonium dihydrogen orthophosphate (^{31}P).

Table 1. List of samples with sample code, picture and manufacturer's details

Sample type	Sample Code	Sample picture	Manufacturers' details and Colour
Bowl	A1		Made in: China Source: The Warehouse Colour: Black
Bowl	A2		Made in: China Source: The Warehouse Colour: Blue
Tea mug	A3		Made in: China Source: The Warehouse Colour: Red Brand: Nova
Sauce Dish	A4		Made in: China Source: The Warehouse Colour: White Brand: Harrison & Lane
Bowl	A5		Made in: China Source: The Warehouse Colours: Yellow, red, black and blue
Plate	A6		Made in: China Source: The Warehouse Colour: Red Brand : Harrison & Lane

Tea Mug	A7		Made in: India Source: The Warehouse Colour: White Brand : Home Concepts
Bowl	A8		Made in: China Source: The Warehouse Colours: Blue and white
Tea Mug	A9		Made in: China Source: The Warehouse Colour: Blue Brand : Nova
Tea mug	A10		Made in: China Source: Farmers Colours: Green, white and yellow Brand : Haven
Tea Mug	A11		Made in: Thailand Source: The Warehouse Colours: Bluish green and yellow (outer), white (internal)
Bowl	B1		Made in: England (1893-1905) Source: Broken online purchase from eBay, UK Colours: White, blue, green, gold and brown (inner surface mostly white) Brand: David Chapman and Sons Ltd, Stafford-shire

Plate	B2		Made in: England (1892-1911) Source: Broken online purchase from Trade me Colours: Blue and white (inner and outer surface) Brand: Wileman & Co, Longton, Staffordshire (precursor to Shelley Potteries)
Small Plate	B3		Made in: England (1892-1911) Source: Broken online purchase from eBay, UK Colours: Red and white Brand: Wileman & Co, Longton, Staffordshire.
Bowl	B5	 	Made: England (post World War 2, mid-20th Century) Source: Antique shop, Hamilton Colours: Blue and White, high gloss glaze Brand : Bleu De Roi Alfred Meakin, England
Tea mug	B6		Made in: England (mid 20th century) N.B. tested cup exhibits heavy crazing Source: Personal collection of M. Mucalo Colours: Cream, pink and green with transfers on the outer surface Brand : Alfred Meakin England
Tea Mug	U1		Made in: Unknown, possibly British made Source: Antique and collectables shop, Hamilton Colour: Grey Brand : None recorded
Tea Mug	C2		Made in: New Zealand Source: Antique and collectables shop, Hamilton Colour: Blue Brand : Crown Lynn
Saucer	C3		Made in: New Zealand Source: Antique and collectables shop, Hamilton Colour: Pink Brand : Crown Lynn

Small Plate	C4		Made in: New Zealand Source: Antique and collectables shop, Hamilton Colour: Brown and Green Brand : Crown Lynn
Plate	C5		Made in: New Zealand Source: Antique and collectables shop, Hamilton Colour: Purple, green, brown red and white Brand : Crown Lynn
Small plate	C6		Made in: New Zealand Source: Salvation Army Shop, Hamilton Colour: Dark brown with yellow-orange colouration Brand : Crown Lynn
Plate	C7		Made in: New Zealand Source: Salvation Army Shop, Hamilton Colour: Yellow Brand : Kelston ceramics (Crown Lynn)
Coffee Mug	C8		Made in: New Zealand Source: Salvation Army Shop, Hamilton Colour: Honey brown colour Brand : Crown Lynn

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ICP-MS instrument used for measuring elemental concentrations of various metals in the ceramics leaching studies was a Perkin Elmer ICP-MS spectrometer ELAN DRC 11. The materials and methods involved in preparing the leaching solutions for analysis were as follows:

Materials in which extract/leaching samples were prepared

Polypropylene beakers and volumetric flasks were used in experiments involving the exposure of the ceramic ware to various leaching solutions as well as various single user filters, pipette tips and Falcon tubes. Calibrated auto pipettes were used for pipetting out sample solutions.

Solutions used for leaching experiments on ceramics

4% acetic acid solution prepared from 60.5% glacial acetic acid (Ajax Finechem Pty Ltd) was used as a standard leaching solution[13] (see below). Other leaching solutions were cold doubly distilled water, domestic beverages such as Coca-Cola, and Lipton Tea (black tea and lemon tea).

Elements analysed by ICP-MS and the standards to calibrate the analysis.

For ICP-MS analysis carried out on leachate solutions, the elements chosen for analysis (see later for discussions on how these were selected) were as follows: ^{10}B, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{51}V, ^{53}Cr, ^{54}Fe, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{85}Rb, ^{109}Ag, ^{111}Cd, ^{118}Sn, ^{137}Ba, ^{205}Ti, ^{207}Pb,

Table 2. Solid state NMR spectrometer acquisition parameters for the ceramic materials investigated in this study.

Isotope	Relaxation delay (sec)	Pulse length (μ sec)	Power level dB	Acquisition (AQ) time (sec)	Frequency used (MHz)	Number of scans	Spinning Frequency (kHz)
^{29}Si	8	3.5	2.0	0.043	59.69	5000	5
^{27}Al	1	1.0	0.50	0.0346	78.2	2000	10
^{31}P	2	4.0	3.0	0.021	121.5	1000	10

^{238}U. A number of calibration, quality control and certified reference material (CRM) standards were used in the ICP-MS analysis for check and balances. The main calibration standards used were an Inorganic Ventures multielement calibration standard IV-ICP-MS 71A which consisted of most elements tested at a concentration of 50 ppb in 3% (v/v) nitric acid as well as 2 further standards from Merck, one of which contained similar elements to the Inorganic Ventures standard plus Na, K, Ca and Fe. An additional standard was used for Sn and Zr analysis (Plasma CAL from SCP Science). The performance of the ICP-MS was checked against a CRM called SLRS-5 or "Ottawa River Water". Interferences were overcome using drift corrections through recalibrating the instruments every 24 samples by running a flush blank followed by quality control standards and calibration standards. It should be noted that although results obtained were carefully checked against standards, the University of Waikato is not an accredited analytical laboratory hence all results presented and discussed should be taken as indicative. Samples were generally analysed in duplicate.

Leaching test solutions used

The 4% acetic acid leaching test followed an American Society for Testing and Materials (ASTM) C738-94 protocol[13] for determination of the leaching of heavy metals extracted into the 4% acetic acid from glazed ceramic surfaces. Ceramic samples for testing were cleaned, dried and then pre-weighed prior to filling with the testing solution, i.e 4 % acetic acid, up to the rim until overflowing. Ceramic wares tested were covered with para-film and then with aluminium foil to prevent evaporation and any light induced processes. No contact between the Al foil and testing solution occurred. Samples stood undisturbed for 24 hours at room temperature (22 ^{o}C – 24 ^{o}C) with 5 mL aliquots of the testing solution being withdrawn into 15 mL Falcon tubes, stirred and then diluted with 5 mL Type1 water followed by mixing. For leaching in cold water, Type 1 water at about 2^{o} C was added to the clean drinking mugs (with codes A3, A7, A9, A10, A11, B6, U1, C2, C8, see Table 1). After 10 minutes, the weight of each was recorded and a 10 mL aliquot of test solution was pipetted from each into a 15 mL Falcon tube. Blanks for this test were the unexposed cold Type 1 water. For tests involving exposure to tea samples, 2 L of Type 1 water was boiled in a conical flask containing 8 tea bags (approximately 2 g each) and left to soak for several minutes until the tea extracts in the bags were infused into the boiling water. 0.5 L of milk was then stirred in and the drinking mugs/cups were filled to the rim, the weights were recorded and the mugs/cups were sealed in a similar manner to the 4% acetic acid samples and allowed to stand for 10 minutes. The blank was the unexposed tea solution. A hot water blank test was also done to check for any contamination from the glass conical flask used to contain the tea. Samples were filtered through a 0.45 μm filter and diluted to 10 mL (v/v) with Type 1 water. Lemon tea was also used and sampled following an identical procedure for tea but *without* milk being added. pH was measured of both the tea with milk and lemon tea solutions used for leaching. For samples exposed to Coca-Cola solutions, the ceramic drinking mugs/cups tested were filled with Coca-Cola and sealed in a similar manner to items tested with 4% acetic acid and tea. The blank was unexposed (to ceramic ware) Coca-Cola solution. Sampling followed similar procedures to other leaching solutions. A 1 mL aliquot was taken from each sample tested then mixed with 9 mL (v/v) of Type 1 water prior to analysis.

Results and Discussion

Molecular spectroscopic characterisation of ceramic wares used in this investigation

FTIR spectroscopy and solid state MAS NMR were performed on the ceramic wares to gain some insights into what ceramic molecular species existed in the bulk of the materials being tested. This, however, did not provide any information on glaze components which was important for guiding ICP-MS studies into leaching from the ceramics. For this purpose, XRF was used to obtain information on the bulk elemental and glaze components in the ceramic ware. It should be noted that the ground up ceramic material contained mostly bulk and some glaze hence the (trace) levels reported will represent only indicative values of glaze components due to the unknown dilution factor due to mixing of the glaze and bulk components. The actual levels in the glaze would be higher than these numbers suggest.

IR and solid state NMR characterisation of the ceramic wares studied in this investigation

IR spectra

The FTIR spectra obtained from all ceramic ware sampled in this study typically either showed mullite/silica type features or showed evidence of the presence of added tricalcium phosphate as in bone china ware. Fig. 1(a)/(b) illustrate the two IR spectra types. The IR spectra representing bone china specimens were exhibited by samples B1, B2, B5 and A7. Sample B2 produced the spectrum shown in Fig. 1(a) and shows peaks at 1043 cm^{-1} and 602, 558 and 462 cm^{-1} which are due to the fundamental stretching and bending vibrations of the -PO_4 functional group[14] from the added tricalcium phosphate. Bone china is known to be a mixture of tricalcium phosphate, silica glass and anorthite.[15] Anorthite has the formula

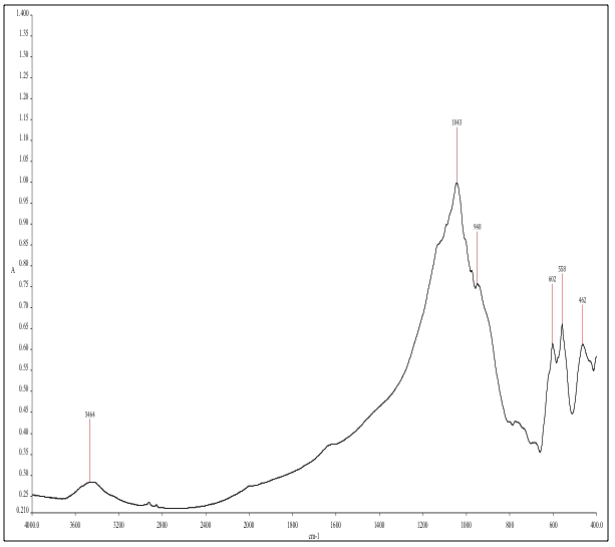

Fig. 1(a). FTIR spectrum of Wileman bone china (B2) of the Victorian era.

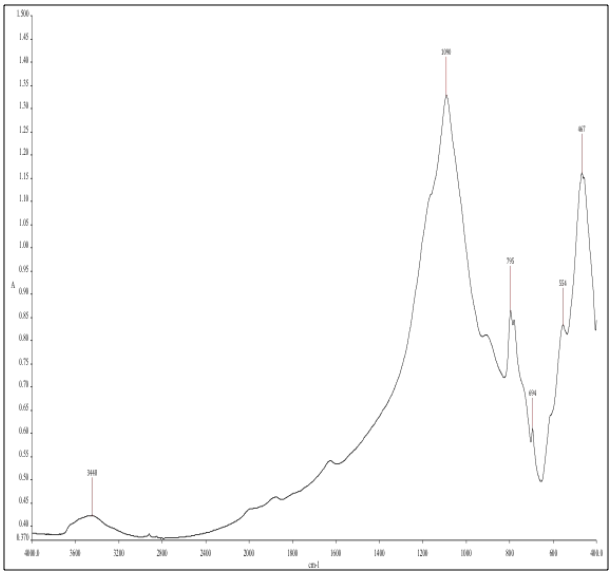

Fig. 1(b). FTIR spectrum of sample C5, a Crown Lynn manufactured item.

$CaAl_2Si_2O_8$ hence Si-O- or Al-O-associated vibrations in this phase are probably responsible for the broad underlying band structure for the intense peak centred at 1043 cm^{-1} and other features as shown in Fig. 1(a). As for the other ceramic wares studied in this investigation, all gave practically identical IR spectral patterns (with peaks at 1083, 796, 778, 693, 555 and 455 cm^{-1}) corresponding to the mullite and cristobalite phases present in these wares.

Solid state NMR spectra

Table 3 provides a summary of features observed in the ^{29}Si, ^{27}Al and ^{31}P MAS NMR spectra acquired from most of the ceramics samples. Fig 2(a)–(e) represent typical ^{27}Al, ^{29}Si and ^{31}P spectra of some selected domestic ceramics items. All samples of ceramics examined by ^{29}Si and ^{27}Al MAS NMR produced peaks as would be expected from materials containing mullite and cristobalite phases. The following tentative interpretations follow for spectra observed. Ideally these solid state NMR spectra should have been accompanied by an extensive XRD analysis. However, this was not done because the main

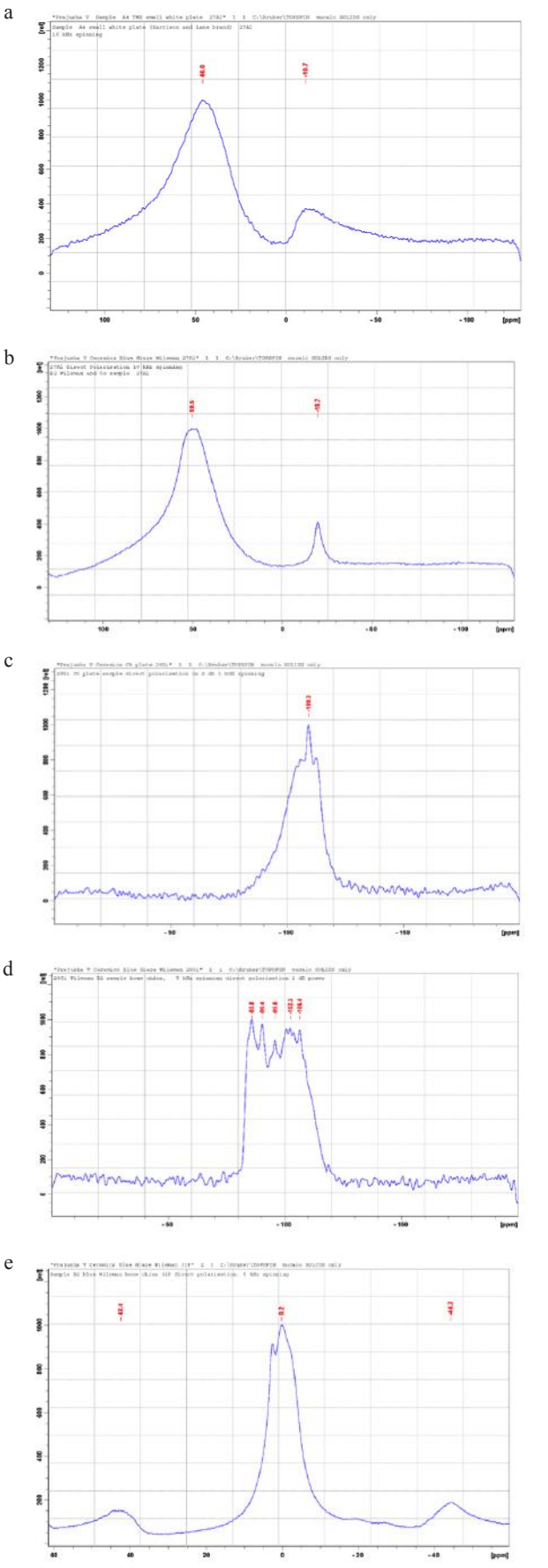

Fig. 2. Solid state NMR spectra of ground domestic ceramic ware: (a) ^{27}Al MAS NMR of a Chinese made white ceramic (A4) sample, (b) ^{27}Al MAS NMR of sample B2, Wileman and Co bone china manufactured in Britain in Victorian/Edwardian times (1892-1911), (c), ^{29}Si MAS NMR of a Crown Lynn "Fleurette" patterned breadplate, (d) ^{29}Si MAS NMR of the B2 sample and (e): ^{31}P MAS NMR of the B2 sample.

aim of this study was to study leaching which involved learning more about glaze elemental composition rather than the bulk ceramic body itself.

The modern era Chinese-made ceramics (all "A" coded ceramic samples except for A7) and the New Zealand made Crown Lynn ware ("C" coded samples) gave mostly similar ^{27}Al MAS NMR spectra. In general, an asymmetric and generally strong ^{27}Al peak was observed from 45-52 ppm with a weak/broad (sometimes barely discernible peak) at 0.6 to -15.6 ppm. These ceramics contain[16] mullite or "$Al_6Si_2O_{13}$" which has a structure consisting of columns of octahedral AlO_6 units cross linked by SiO_4 and AlO_4 tetrahedra. ^{27}Al peaks at -0.9 to 3.5 ppm represent octahedral "AlO_6" species in mullite[17] while peaks in the same compound occurring over the range 57-63 ppm correspond to "normal AlO_4", i.e. tetrahedrally coordinated aluminium species, with a distorted tetrahedral "tricluster" environment in regard to the Al centre (and called the "Al*" unit) producing peaks at 42-48 ppm. The Al* designation represents environments in mullite phases which involve three distorted tetrahedral Al-O groups where charge imbalance in structure (caused by cross-linking SiO_4 and AlO_4 tetrahedra) is compensated for by formation of characteristic oxygen vacancies in conjunction with three distorted tetrahedral Al-O groups.[17] In ^{27}Al spectra of the ceramics shown in Table 3, the peaks referring to the *tetrahedral* Al species in mullite, i.e. over 45-52 ppm, are considerably broad and hence may contain a range of tetrahedral aluminium species extending into the chemical shift ranges discussed for mullite above, i.e. above 50 ppm. It is also important to note that ground ceramics specimens contain not only the bulk ceramic material but also the glaze which will contain various metal ions for colourant or opacifier purposes such as zirconia/zirconium silicate or tin oxides which may have unknown effects on the width and chemical shift of the ^{27}Al peaks observed. Sample A2 (the blue glazed Chinese made bowl) differed from the other samples in that the ^{27}Al spectrum of this sample exhibited a relatively more intense peak at 0.7 ppm and a *less* intense peak at 37.7 ppm, which means that octahedrally coordinated Al species in this ceramic were more prevalent than tetrahedrally coordinated Al species prevalent in other samples of ceramics.

^{29}Si MAS NMR spectra of the modern Chinese made and Crown Lynn ceramics featured peaks varying from -103 ppm to -109.4 ppm [see Fig. 2(c)]. The peaks were partially symmetrical in shape but broadened considerably in the case of bone china specimens [see Fig. 2(d) and later discussion]. In general, according to McKenzie and Smith,[17] mullite gives ^{29}Si shifts at -86, -90 and -94 ppm. It has been shown by ^{29}Si MAS NMR[18] that as kaolinite-containing clays are fired, dehydration occurs and metakaolinite forms with a "sudden" appearance of free silica in the mix (at 970 °C), which is then followed by the formation of the mullite above 1100 °C. The ^{29}Si MAS NMR spectrum of the finally developed mullite phase indicated by McKenzie *et al*[18] in their study is practically identical to the spectrum exhibited by the Chinese made

Table 3. Chemical shifts observed in the ^{29}Si, ^{27}Al and ^{31}P solid state MAS NMR spectra of selected ground ceramic wares studied

Sample Code	^{29}Si shift/ ppm	^{27}Al shift /ppm	^{31}P shift /ppm
A1 Black Chinese-made bowl	-102.1	51.6 (strong) 2.9 (broad,weak)	No peaks detected
A2 Blue Glazed Chinese-made bowl	-103.7	46.2 (medium) , 0.6 (strong)	No peaks detected
A3 Red NOVA brand Chinese-made mug	-107.3	45.4 (major) -15.6 (weak,broad)	No peaks detected
A4 White Harrison and Lane Chinese made bowl	-107.6 (major), -88.4 (weak shoulder)	46.0 (strong), -11.0 (weak, broad)	No peaks detected
A7 White Bone China Indian made Home Concepts brand Mug	-86.9, -90.4, -95.7, -101.4 and -106.1 (one broadened peak with splittings)	51.3 (broad, major), -20.3 (narrower, minor)	0.5 (with spinning side bands)
A10 Green/Yellow Mug, Haven Brand with printed transfer of Fruit on outside. Chinese made	-106.2	46.2 (strong, broad), -11.5 (medium)	No peaks detected
B2 (Wileman and Co, Staffordshire)	-84.3, -85.8, -90.1, -95.4, -100.3, -101.9, -105.9 (peak positions of one broadened peak with multiple splittings)	47.9 (major, broad)), -19.8 (medium, narrower)	0.5 (strong), 2.8 (sh) (with spinning side bands)
B5 (Alfred Meakin, Bleu du Roi bowl, Staffordshire)	-90.2, -96.6, 101.59 (peak positions of one broadened peak with multiple splittings)	50.5 (strong) and -20.6 (medium)	1.1 (with spinning side bands)
C4 Crown Lynn Breadplate, New Zealand made with Tartanesque design, Roydon Tam O Shanter brand.	-106.9	46.6 (strong), -9.8 (weak, broad)	No peak detected
C5 Crown Lynn Breadplate New Zealand made with floral design under glaze "Fleurette Brereton Ware" pattern.	-109.3 (sharp peak superimposed on broader base)	45.0 (strong), -12 (weak,broad)	No peak detected
C7 Crown Lynn (Kelston Ceramics brand) New Zealand made breadplate	-109.4 (sharp peak superimposed on broader base)	46.1 (strong), -10.3 (weak)	No peak detected

plain white dish sample (A4) which in composition (see later for XRF studies and Table 4) contains mostly Si and Al and possibly some Zn oxide as an opacifier/to prevent crazing. Hence this ceramic would contain mullite and silica, i.e. cristobalite, which gives a ^{29}Si chemical shift at -109 ppm[17], in its composition. Though not directly comparable to the A4 sample, a library-referenced XRD analysis of a sample of ground A5 (striped multi-coloured Chinese made bowl) indicated that cristobalite and mullite phases were principally responsible for the XRD peaks detected. The Chinese-made samples A1 and A2 exhibited ^{29}Si shifts of -102.1 and -103.7 ppm, respectively, which differs from shifts given by the A4 sample suggesting a different mineral mix alongside mullite phases. Without extensive XRD analysis, it is difficult to confirm. In these particular specimens which are highly coloured (black and blue respectively), the influence of the glaze colourants and other additives (XRF indicates the presence of Cr, Zr, Zn, Ba and Sn in these ceramic wares) should also be considered. The ^{29}Si MAS NMR spectra of the C5 and C7 Crown Lynn samples featured a sharp peak at -109.3 to -109.4 ppm superimposed on a broader peak indicating cristobalite to be present in these specimens.

The bone china containing ceramic items (A7, B2, B5) examined by MAS solid state NMR spectroscopy were the only samples to give ^{31}P MAS NMR spectra due to the use of tricalcium phosphate in these items. Hence samples B1, B2 (Victorian bone china), B5 (mid-20th century British bone china) and sample A7 (modern Indian made bone china mug) gave intense peaks centred at 0.5 to 1.1 ppm in ^{31}P MAS NMR spectra. The positioning of the peak was in the region expected for the orthophosphate (-PO_4) functional group[14]. The ^{29}Si signals for the bone china specimens were different to those given by the other ceramics samples as they gave characteristically broad signals centred at *ca.* -95 to -100 ppm and consisting of several superimposed peaks on top ranging from -86 ppm to -106 ppm. In the case of the Wileman (B2) British Victorian Era ceramic, a library referenced XRD analysis of the sample indicated among other phases the presence of anorthite ($CaAl_2Si_2O_8$) as expected. Anorthite, a plagioclase feldspar is known[17] to exhibit ^{29}Si chemical shifts from -83 ppm to -105 ppm. The ^{27}Al MAS NMR spectra of the bone china specimens (A7, B2 and B5) invariably featured two peaks, an intense peak at ~50 ppm corresponding to tetrahedrally coordinated Al as in mullite and a weaker and sharper peak at -20 ppm ±1 ppm which could be due to an $AlPO_4$ phase in the material.[17]

XRF studies of the food and drink ceramics

In general, XRF detected a total of 48 trace elements (levels reported as ppm levels) and 10 major elements (reported as oxides presented in percentage (%) values) in the analysed ceramic wares. Table 4 presents a complete summary of the results for all samples investigated. Some interesting comparisons can be shown between the different types of china studied. Some surprises have also been thrown up by the results especially with regard to New Zealand made ceramics but can be well understood in terms of the age and history of the pieces and normal practices used for glazing in the relevant eras of production of the domestic ceramics.

Bulk compositions of the ceramics studied

General comments on the bulk composition (shown as % units in Table 4) of ceramic items investigated by XRF can be made as follows. The modern non-bone china Chinese-made ceramics (A1-A5, A9, A10 and A11) gave a % Si signal from 27.26 to 33.8 %. The % Al was 9.42 to 13.27. Mullite and cristobalite phases would comprise the bulk composition of these ceramic wares. The New Zealand-made Crown Lynn ceramic ware and unknown origin (British made) grey cup exhibited similar % values as the Chinese-made ceramics with respect to Si and Al, i.e. for C2-C8, and U1(British) % Al was 9.89 to 14.28 and % Si was 32.14 to 34.63. As for the Victorian and mid-20th century British bone china bulk compositions, the presence of calcium phosphate from bone in the bulk composition affected the % Al and % Si values. % Al varied from 7.43 to 8.66 while % Si varied from 16.8 to 21.53. The Wileman (B2) bone china cup had the lowest % Si value. In addition to the Al and Si signals, the % P varied from 5.54 to 6.38 in specimens and the % Ca varied from 14.45 to 15.08. The modern A7 (Indian made) bone china cup, exhibited % Si and % Al values of 20.93 and 7.43 respectively while % Ca and % P were 15.08 and 6.38 respectively.

Glaze components of the ceramics studied

XRF analysis of the ceramic wares in this study provided indicative levels of the specific glaze components. These informed ICP-MS analyses of solutions exposed to various leachate solutions and helped in understanding the colours and finish of the ceramics in question. In addition, the XRF analyses threw up some surprises with respect to glaze compositions of locally made ceramics. These could, however, be well understood in terms of the age of the pieces. Current trends in glazing practices can also be understood from the XRF results obtained for the modern Chinese-made and Indian or Thai-made ceramic pieces.

It is important to understand the basic function of glazes and what some specific compounds formulated in glazes are for. In general, a glaze can have the dual function of acting as a pottery or ceramic sealant as well as providing a way of decorating the piece. Colomban *et al*.[19] discuss glaze attributes in relation to old French porcelain ware made in Sèvres. It should be noted that many types of glaze exist with varying chemical composition. Factors like the Al/Si ratio and the fluxing agent used in the glaze can vary widely between glaze types. This area is complex both in practice and in study. When decorating ceramic ware, common colourants are oxides of metals such as iron, cobalt, copper, chromium, manganese, antimony and titanium. These metals give a characteristic range of colour tones though these will depend on factors like the glaze composition (which acts to enhance the colouration), the firing temperature, the atmosphere in the kiln, the degree of grinding of the glaze components, etc. The actual colour arises from various outcomes[19] such as the dissolution of the colourant in the glaze mixture, precipitation of new phase in the glass matrix or dispersion of a preformed phase in the glaze. It is also possible to have underglaze colours as an alternative to externally applied colourants which consist of a pigmentary oxide or a

mix of oxides with flux used to bind the colourant to the surface of the ceramic to be decorated. Sometimes pigments used can also be sulfides such as cadmium sulfide for instance though glaze colourants are mainly oxides. Other functions added to the glaze mixture are components known as opacifiers which are compounds which disperse the incident light on the ceramics, making it look "opaque". Typical opacifiers are zirconium(IV) silicate[20] and tin(IV) oxide. Zirconium silicate is also recognised as being highly resistant to corrosion by alkali materials which would be of relevance when cleaning these items using caustic cleaning agents in a dishwasher. Other additives are very useful in preserving the functional integrity of the glaze when subjected to the usual wear and tear of domestic use. Zinc oxide[21] has a high heat capacity, thermal conductivity and high temperature stability. It also has a low coefficient of expansion which is a desirable attribute to possess when used in ceramics production. When added to the glaze, it can hence affect the melting point and optical properties. Due to its low expansion properties, it can be beneficial to the elasticity of glazes by inhibiting viscosity changes as a function of temperature. This attribute hence prevents crazing and shivering in food and drink ceramic items. Thermal conductivity is increased and heat capacity decreased if ZnO substitutes BaO and PbO in a glaze. Zinc oxide is also useful for providing a glossy and attractive look to ceramic surfaces.

The colours present in glazes are mostly due to metal oxides included in the glaze composition known as colourants. Specific elements are associated with specific colours. Black and grey colours can be created via use of Co, Mn, Ni, Cu, and Cr-based colourants.[19] Blue is most often provided, at least historically, by the use of Co, although Zr-V-based pigments are nowadays used for this purpose. Greens are provided by Cu, Ti, Fe and Cr(III) oxide colourants, while yellows can be created by the use of colours like "Naples Yellow" which utilises chromium titanate mixed with titania. "Naples Yellow Hue" uses synthetic iron mixed with titania to create the colour. The original but now defunct Naples Yellow colour had been created by Pb(II) antimonite, $Pb(SbO_3)_2/Pb_3(Sb_3O_4)_2$ which was toxic.[22] Other compounds used in the past to achieve yellow colouration were CdS[23] and lead chromate. Brown and tan pigments for ceramics can be created via the use of Zn/Fe/Cr spinels or use of Cr, Fe or Sn-based compounds in a zinc oxide glaze.[19]

(a) XRF analysis of British-made Victorian and mid 20th century ceramics (Samples B1, B2, B5)

Examination of Table 4 indicates that the B1 sample contained, apart from the usual bulk Si, Al, Ca and P components, 12,010 ppm of Pb together with 266-268 ppm of Rb and Sr most likely emanating from the bulk ceramic composition. This clearly indicates that this item of bone china contained lead oxide in the glaze. The item was mostly glossy white in appearance with a sparse amount of decoration and gold gilt. B2 exhibited a similar trend composition-wise to the B1 sample with Pb (8179 ppm) being a prominent feature (in the ppm concentration range). The mid-20th century-manufactured Alfred Meakin bone china (B5) contained the highest amount of Pb (27,420 ppm) of all the ceramics samples investigated. The only other British-manufactured item subjected to XRF analysis was the grey teacup sample U1. XRF indicated 3974 ppm of lead in U1 and a variety of other components (S: 997 ppm, Co: 500 ppm, Zr: 795 ppm, Sn: 2082 ppm), which could have been used as colourants, opacifiers and fluxes.

(b) New Zealand-made Crown Lynn ceramics

XRF analyses of samples C2-C8 are as detailed in Table 4. The Crown Lynn wares gave variable results in terms of glaze components which depended on the colouring of the glaze present in the ceramic wares. The most interesting aspect of the analysis was the fact that high Pb content was indicated by XRF ranging from 4000 to > 18,000 ppm. The honey-glaze brown Crown Lynn breadplate (C7) had the highest level of Pb in its glaze of the Crown Lynn items. These results were an initial surprise but could be understood in terms of the usual practice in the 1960s and 70s of using lead-based glazes on domestic crockery. The presence of a large amount of Pb oxide in a glaze should not be automatically regarded with alarm because lead oxide has been used successfully and safely for many years but glazes containing it must be properly formulated if leaching is to be avoided.[10] This is normally accomplished by fritting, where the lead oxide is combined with high amounts of silica in a frit (premelted and preground glassy materials that are composed of measured percentages of glaze oxides). In these, Pb is bound tightly in the silicate matrix making it less leachable. Items manufactured earlier like some items of British bone china as in samples B1 and B2 (see later in ICP-MS leaching studies section) did appear to suffer from greater relative leachability of the Pb from glazes under stress. Later technological developments led to glaze formulations involving Pb oxides becoming more food safe.

Other components indicated by the XRF analyses in the Crown Lynn ceramic items can be understood in terms of their roles as opacifiers or fluxes and their colour. The C2 sample, a dark blue teacup, contained a relatively high amount of Zn (3586 ppm), Zr (3586 ppm), Sn (448 ppm), and Ba (5478 ppm). The glaze on this particular Crown Lynn item was more matte than shiny and could perhaps be understood in terms of the high Zn content which is reputed to have a complex effect on glaze colourings when present at high concentrations.[21] Compared to all other Crown Lynn samples investigated for Cd, this was the only item to show a value for this element (88 ppm) suggesting it could possibly be contributing to the glaze colouring. The XRF analyses for the C3, C4, C5, C6 and C7 specimens were not especially remarkable and apart from their prominent lead content contained varying amounts of Ba, Zr, Sr and other minor elements. However, zinc oxide as a glaze component is noticeably absent in the Crown Lynn wares, apart from sample C2 (cf XRF analyses of Chinese, Indian and Thai-made ceramic wares later) and might explain why some of these older Crown Lynn items are subject to more crazing in their later life.

Table 4. Summary of XRF results of ceramic ware studied. Not all ceramic ware illustrated in Table 1 was subjected to XRF analysis.

Element	Measured as	A1	A2	A3	A4	A5	A7	A9	A10	A11	B1	B2
Na	%	3.075	0.735	1.16	1.06	0.685	1.18	1.115	1.06	1.35	1.4	0.655
Mg	%	0.15	0.13	0.42	0.32	1	0.38	0.468	0.53	0.08	0.26	0.23
Al	%	10.345	13.27	10.48	10.84	12.275	7.43	11.97	11.52	9.42	7.98	7.515
Si	%	30.465	27.26	30.04	33	28.005	20.93	33.8	32.19	30.74	21.53	16.8
P	%	0.05	0.03	0.05	0.01	0.05	6.38	0.050	0.03	0.04	5.54	5.705
S	ppm	84.5	93	169	85	142.5	57	162.8	1034	95.00	< 19	< 14
Cl	ppm	113	116	53	< 1.2	114	77.7	< 1.3	187	119.00	< 3.6	63.45
K	%	1.08	2.77	1.8	1.92	1.25	1.51	1.949	2.97	1.75	1.63	1.5
Ca	%	0.8	0.615	0.54	0.15	1.1	15.08	0.409	0.16	0.63	14.05	14.5
Ti	%	0.14	0.415	0.05	0.03	0.345	0.06	0.065	0.04	0.05	0.01	0.01
V	ppm	<4.0	117	4	13.7	112	< 5.3	< 3.6	26	<4.1	< 2.2	< 2.4
Cr	ppm	880	99.5	106	9.3	110.5	36	473.2	59	23.50	87	26
Mn	%	0.04	0	0.03	0.03	0.01	0.00	0.029	0.06	0.03	0	0
Fe	%	0.97	0.47	0.41	0.28	0.44	0.20	0.413	0.42	<4.2	0.23	0.20
Co	ppm	320	209	23	16.5	51	15.8	261.6	104	12.70	23	36
Ni	ppm	40	22	29	17.1	25.5	< 1.9	16.4	24	2.55	5	5.55
Cu	ppm	18.7	7.4	4.2	11.1	12.4	13.4	7.8	29	4.50	33	26.5
Zn	ppm	822.5	282.5	1210	42	550	100	568.1	269	3243.50	314	129.5
Ga	ppm	26.5	28.5	33	34	25.5	12.3	36	15.2	31.50	17.3	23.5
Ge	ppm	2.35	3.05	2.2	0.9	2.1	< 0.7	2.9	3.1	4.30	< 0.9	<0.8
As	ppm	13.85	3.75	< 0.9	< 0.6	1.8	126	1.2	< 5.3	29.50	19	11.9
Se	ppm	1.3	2.15	55	0.3	5.7	< 0.5	0.7	< 0.6	0.90	< 1.1	<0.9
Br	ppm	0.8	1	0.4	0.2	1.9	< 0.5	0.5	1.4	<4.5	< 0.6	2.3
Rb	ppm	127.5	111	243	346	83.5	78	259.6	695	421.00	268	255.5
Sr	ppm	38	291.5	291	28	124	386	381	31	115.50	266	279.5
Y	ppm	30	30.5	66	152	23.5	9.4	99.2	16.7	43.50	< 0.5	<0.5
Zr	ppm	453.5	413	3397	99	774.5	127	1287	114	738.00	43	38
Nb	ppm	19.45	23	35	36	19.1	10.2	33.9	23	42.00	27	22.5
Mo	ppm	2.45	4.05	7.3	2.7	4.25	1.5	5.7	0.8	2.90	0.7	0.4
Ag	ppm	<0.4	<0.4	1.1	< 0.4	<0.4	< 0.4	< 0.4	10.6	< 0.4	0.8	0.8
Cd	ppm	<0.5	0.55	191	< 0.5	17.4	2.9	< 0.5	< 0.5	1.20	< 0.5	<0.5
In	ppm	<0.7	<0.7	< 0.7	< 0.7	<0.7	< 0.7	< 0.7	< 0.7	<0.7	< 0.7	<0.7
Sn	ppm	29.5	7.4	1413	15.3	7.9	18	20.7	262	44.50	10.6	39
Sb	ppm	2.55	<0.9	0.8	< 0.9	<0.9	8.4	< 0.9	294	<4.6	4.2	0.4
Te	ppm	4.8	1.55	2.8	< 1.2	1.6	< 1.2	3.8	< 1.2	6.50	< 1.2	<1.2
Cs	ppm	40.5	19.4	16.5	13	20.25	3.8	35.8	45	87.00	9.6	9.75
Ba	ppm	3345	1906	2534	120	1122	1393	2784	98	4203	218	376
La	ppm	61	61	47	61	48	< 4.9	94.9	18.4	44.50	< 4.9	<4.9
Ce	ppm	110.5	114	71	77	93.5	8.2	127.6	38	69.00	11.8	<5.8
Nd	ppm	29	42.5	42	68	43	< 10	64.6	19.4	44.00	< 10	<10
Hf	ppm	16.3	14.35	77	12	20.05	< 3.7	33.1	7	2.80	11.8	9.3
Ta	ppm	10.15	6.95	14.9	16.4	7.7	< 5.9	12.9	9	110.00	< 4.0	<3.5
W	ppm	15.25	6.65	4.1	13.6	3.7	2.9	4.3	22	7.80	20	22.5
Hg	ppm	1.1	0.55	1.7	< 0.4	0.7	< 1.0	0.9	< 0.9	23.00	< 1.5	<1.2
Tl	ppm	3	2.45	2.1	1.7	1.65	< 1.6	2	< 2.1	14.90	< 4.2	<3.4
Pb	ppm	49.5	29	132	71	56	288	154	3907	111	12010	8179
Bi	ppm	6	2.7	6.1	< 0.4	1.75	< 1.6	5.2	< 1.9	7.8	< 4.6	<3.5
Th	ppm	28.5	32.5	50	35	29	13.5	48.4	2.6	23	< 1.5	<1.5
U	ppm	15.6	12.1	7.5	13.5	10.4	2.1	< 1.5	10.5	14.5	13.7	7.6

Element	B5	U1	C2	C3	C4	C5	C6	C7	C8	Blank 1 Al_2O_3	Blank 2 Al_2O_3
										Directly sampled	Ground for analysis
Na	1.116	1.33	1.51	1.21	1.43	0.93	1.31	1.03	1.27	0.36	0.43
Mg	0.262	0.34	0.29	0.28	0.14	0.27	0.36	0.38	0.10	< 0.0067	< 0.0068
Al	8.655	10.53	12.54	12.07	9.89	12.64	12.58	14.28	12.96	49.71	50.41
Si	20.76	32.14	33.6	31.69	33.19	34.3	33.95	36	34.63	0.10	0.35
P	5.815	0.08	0.05	0.06	0.02	0.03	0.09	0.04	0.08	< 0.0030	< 0.0030
S	< 27	997	240	185	1047	240.7	259	443	227.5	132.8	153.1
Cl	< 4.3	82	30	33	77	< 2.9	< 3.8	< 3.6	< 2.7	< 10	< 10
K	2.016	1.1	1.21	1.26	1.15	1.06	0.96	1.24	1.38	0.00	0.01
Ca	14.45	0.55	1.74	1.69	0.32	0.35	0.34	0.24	0.38	0.04	0.05
Ti	0.011	0.41	0.3	0.31	0.34	0.42	0.47	0.58	0.50	0.00	0.00
V	< 2.1	58	49	61	63	71	50	85	72	3.4	4.6
Cr	10.2	31	116	41	54	44.5	28	43.3	9.8	< 0.3	14.7
Mn	0.005	0	0.01	0	0	0	0.03	0	0.30	0.00	0.00
Fe	0.20	0.37	0.45	0.45	0.46	0.46	0.59	0.47	0.60	0.01	0.01
Co	92	500	58	15	53	58	86	74	61	< 0.5	< 0.6
Ni	31.6	24	38	11.4	11.5	9.9	11.2	9.6	12.3	3.9	3.4
Cu	33.1	4.4	6.6	4.9	4.1	7.2	6.1	10.6	24	< 0.3	< 0.3
Zn	69.7	80	1360	43	47	64	38	47	35	6.8	6.2
Ga	< 6.2	11.1	19.3	9.9	11.1	< 2.9	< 4.0	< 4.1	< 2.8	59	58
Ge	< 1.5	< 0.5	< 0.6	1.5	< 0.5	< 0.7	< 1.0	< 1.0	< 0.7	< 0.2	< 0.2
As	< 22	< 5.2	< 6.6	< 6.2	< 5.2	< 9.6	< 14	< 15	< 9.4	< 0.2	< 0.2
Se	< 2.1	< 0.5	< 0.7	< 0.6	< 0.5	< 0.9	< 1.4	< 1.5	< 0.9	0.6	0.5
Br	9.1	0.9	0.9	0.9	0.6	1.7	2.9	3	1.1	0.2	< 0.1
Rb	402.4	62	64	64	67	61	80	72	117	0.6	1.2
Sr	163.2	41	78	89	49	305	71	382	64	1.7	1.5
Y	< 0.5	26	36	40	32	5.1	< 0.5	< 0.5	6.1	1	0.9
Zr	55.7	795	3586	1309	215	286	235	330	297	18.6	18.8
Nb	29.8	28	23	21	19	22	29	31	24	0.9	1
Mo	< 1.0	4.3	8.7	4.5	2.3	2.8	2.1	3.1	4.7	0.8	0.6
Ag	< 0.5	2.1	1	0.5	< 0.4		1	1.3	< 0.4		
Cd	< 0.7	< 0.5	88	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.1	< 0.5	< 0.5
In	137.8	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7
Sn	13.3	2082	448	290	9.7	14.2	12	9.6	8.8	< 0.7	0.7
Sb	< 1.2	2.5	6.9	1.4	1.5	25	3	0.4	1.2	0.9	0.7
Te	< 1.5	< 1.2	1	< 1.2	2.3	< 1.2	0.7	< 1.2	< 1.2	2	1.3
Cs	10.2	6.1	11.1	7	24	5.7	3.4	3.4	8.1	10.2	8.7
Ba	121.1	367	777	121	590	242	139	311	231	10.7	14.1
La	< 4.9	11.2	19.3	14.5	49	10.9	10.7	10.2	23	18.6	23
Ce	< 5.8	27	208	34	75	28.9	33	29	52	24	22
Nd	< 10	10.5	13.5	< 10	54	< 10	10.9	< 10	< 10	29	47
Hf	8.9	22	78	31	9.8	14.5	13.2	10	13.1	3.3	3.3
Ta	< 5.1	< 2.0	< 2.7	< 2.1	< 1.9	< 2.5	< 2.9	< 3.1	< 3.0	3.5	2.6
W	< 3.5	12.9	< 4.7	15.1	10.3	11.4	13.1	12	9.8	3.5	2.7
Hg	< 2.6	< 0.8	< 0.9	< 0.9	< 0.8	< 1.3	< 1.8	< 1.8	< 1.2	1.3	1.1
Tl	16.6	< 2.0	< 2.6	< 2.5	< 2.0	< 3.6	< 5.3	< 5.5	< 3.5	1.7	1.4
Pb	27420	3974	5478	5229	4087	9992	17180	18010	9756	2.1	3.5
Bi	< 8.8	< 2.0	< 2.7	< 2.4	< 2.1	< 3.8	< 5.6	< 5.1	< 3.3	1.1	0.8
Th	< 1.5	17.7	48	16.3	9.1	26.3	< 1.5	< 1.5	6.1	2.3	2.4
U	5.4	9.4	9	8	9.7	8.1	8.3	5.6	4.8	4.4	4.1

(c) Modern ceramic wares (made in China, India and Thailand)

The XRF analyses of the modern ceramic wares (see A1-A11 entries in Table 4) gave variable glaze content depending on the colours of the items tested. However, some commonality of trends can be observed between the samples. The first observation is that apart from sample A10 (Haven brand screen printed coffee mug made in China), Pb content of these items was either low or insignificant compared to the British-made or New Zealand-made ceramic wares. This is a consequence of modern manufacturing practices in ceramics industries which have leant towards non-Pb oxide based glazes in domestic food and drink items. The replacement for Pb oxide in the glazes of the modern ceramic items appears (at least as to what can be implied from these current XRF analyses) to be Ba-based glazes as compared to the older ceramic items studied. Ba features strongly in all the analyses of the modern ceramic items apart from A4 and A10 (which are either colourless ceramic items or only contain transfer printing as in the case of A10 where this printed pattern contained Pb in the colouring/glaze). Even the bone china cup made in India that, had it been an older British made item would have been glazed using a Pb oxide glaze, contained significant Ba and only a moderate amount of lead (288 ppm). Hence Ba-containing compounds are important for developing strong colours in the glazes. Most of the modern ceramic wares apart from a white glazed dish (A4) and white bone china mug (A7) contained significant levels of Zn with the highly coloured Thai-made mug (A11) containing a very large amount of Zn (3243.5 ppm). Zr, presumably present as zirconium silicate, is also common in the modern wares where it functions as an opacifier. Samples A4, A7 and A10 do not have such high levels compared to the rest of the samples. Other common components were Sn, likely present as tin (IV) oxide and used in a similar manner to zirconium silicate as an opacifier.

Some individual samples exhibited unique components. The A1 sample (black glazed bowl) featured a significant Cr content (880 ppm) which is likely correlated to its use as a colouring agent, along with 320 ppm Co, in the glaze. Sample A3 (red coffee mug) was the only item of the *modern* ceramic items analysed by XRF to give a significant (above baseline) level for Cd which is likely correlated to its red colouration. S content was similar at 169 ppm, so a CdS colourant might have been used (Table 4). The cup had a matte finish to its glaze and this might be correlated to the relatively high Sn content (1413 ppm) if the tin functioned in its role as an opacifier. Blue coloured items A2 and A9 would have had Co-containing compounds in their glaze (analysed at 209 and 261.6 ppm respectively). As stated earlier, ceramic item A10 contained an unusually high level of Pb in its glaze which can probably be attributed to the printed pattern on its outer surface. The S level in the XRF analysis for this item was correspondingly high at 1034 ppm implying that PbS or galena may have been used as the source of the lead glaze, though without further analyses this is speculative. As mentioned above, lead was detected in all the modern ceramic samples but at comparatively modest levels compared to the Crown Lynn and British ceramics. The detection of lead in the modern ceramic item A10 shows that Pb can still be used in some items which may be of concern if it is not food safe.

Inductively Coupled Plasma Mass Spectrometry Results

As stated earlier, the following elements were analysed in the ICP-MS investigations: ^{10}B, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{51}V, ^{53}Cr, ^{54}Fe, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{85}Rb, ^{109}Ag, ^{111}Cd, ^{118}Sn, ^{137}Ba, ^{205}Ti, ^{207}Pb and ^{238}U. Some of these elements were chosen based on their presence in the XRF analyses while others were chosen out of general interest, e.g. As, and because they had standards associated with them.

The 4% acetic acid test was used because metals such as Pb may have a higher tendency to leach from glazes when exposed to acid conditions.[10] Table 5 summarises the ICP-MS detection limits for some of the metals of interest that may leach from ceramics. All ICP-MS results should be taken as indicative.

Table 5. Instrument detection limit (for the Perkin Elmer instrument used in this study) in ppb for analysis of selected metals by ICP-MS

Cr 53	Co 59	Cd 111	Ba 137	Pb 207
0.10	0.00	0.01	0.04	0.02

4% acetic acid leaching results

(i) British Victorian era and mid 20th-Century bone china ceramic wares

The results for the British Victorian era and mid-20th century bone china ceramic wares after leaching with 4% acetic acid in the dark (covered with Al foil) at ambient temperatures are shown in Table 6. Included is the sample labelled "U1" which is also British made (mid 20th-century).

Table 6. Leaching results from the first leaching test for selected elements in 4% acetic acid leachate solution from British Victorian era and mid 20th-century ceramic samples after a contact period of 24 hours. Values shown as means and errors (where given) are 95% confidence errors.

Elements (ppb)	**B1**	**B2**	**B5**	**B6**	**U1**
Pb	4695 ± 94	16628 ± 146	61 ± 8	10 ± 0.0	2893
Cd	<DL [a]	1 ± 0.1	<DL	<DL	<DL
Ba	4 ± 0.1	522 ± 3.9	13 ± 1.1	0.83	27
Cr	<DL	35 ± 4.8	<DL	<DL	3
Co	3 ± 0.1	94 ± 1.1	5 ± 0.4	0.01	102

[a] < DL indicates below detection limit.

The results clearly indicate that the bone china items from earlier eras (B1 and B2, Victorian era) leached a significantly larger amount of lead into the acetic acid relative to later Pb-glazed bone china items from Britain manufactured in the mid-20th century (B5, B6). However, the grey cup (U1) leached lead levels which were high for a supposedly more modern item. According to Lehmann's article,[10] lead glazed ware subjected to the acetic acid test should release less than 500-2000 ppb of lead if it is con-

sidered to be safe for use with food. Samples B5 and B6 easily pass the test, however B1, B2 and U1 clearly fail the test. It may be important to note however that due to the fact that samples of B1 and B2 were received as broken chinaware that this necessitated the soaking of *broken* pieces in the 4% acetic acid solution which might have enhanced extraction of Pb via acid action on the fracture edges of broken chinaware. Although the U1 sample is clearly an exception, the apparent differences in lead release noted reflect different glazing practices with the Victorian bone china wares being less well fritted compared to the more modern British bone china pieces from the 1950s where lead glaze fritting technology would have been more developed to prevent lead release. This is especially the case with the B5 sample as this contained the highest level of Pb detected amongst all ceramic specimens tested based on its XRF analysis and yet this item showed a very low release of Pb in the 4% acetic acid test. As a test of reproducibility of behaviour some of the Victorian era bone china test pieces were subjected to a second 4% acetic acid leaching test and the behaviour exhibited was largely reproduced.

(ii) New Zealand-made Crown Lynn ceramic wares

The Crown Lynn samples (C2-C8) were shown to have appreciable levels of Pb in their glazes by XRF analyses (see Table 4). Crown Lynn samples analysed included a mix of plates and tea mugs and some account must be taken of release when occurring from different shaped ceramic ware, for instance bowls vs. plates. The results obtained from the 4% acetic acid leaching test with regard to the amount of Pb, Cd, Cr, Co and Ba leached from the Crown Lynn wares are given in Table 7.

Table 7. Heavy metal concentration in 4% acetic acid leachate solution from Crown Lynn samples after a contact period of 24 hours. Values are shown as mean values.

Elements (ppb)	C2	C3	C4	C5	C6	C7	C8
Pb	75	215	16	33	353	688	4880
Cd	<DL[a]	<DL	<DL	<DL	<DL	<DL	1
Ba	10	9	32	41	11	54	95
Cr	<DL	4	7	<DL	<DL	14	5
Co	2	1	4	15	11	12	69

[a] < DL indicates below the detection limit of the instrument.

The results of the Pb release are interesting as despite having high levels of Pb in their glazes as indicated by the XRF analyses, most of the Crown Lynn pieces leached relatively low – and from a safety viewpoint, acceptably safe – levels of Pb into the 4% acetic acid solution (with the exception of the C7 and C8, a honey glaze coloured mug). This indicates the Pb glazes on most of the Crown Lynn specimens were well fritted to immobilise Pb. However, unusually C8, which represented a honey glaze coloured mug (see Table 1 for illustration) leached a relatively large amount of Pb into the solution (4880 ppb). It is not obvious from the XRF analysis as to why this mug should release an exceptionally greater level of Pb although of the Crown Lynn items analysed by XRF, the C7 mug exhibited the highest level of Pb present (18,010 ppm). As stated earlier, values of Pb released into 4% acetic acid should be below a range of 500 to 2000 ppb[10] and in line with this definition, most pieces apart from C8 and arguably C7 broadly passed this test though, it should be borne in mind, that this conclusion was based on the concentration of Pb detected by ICP-MS and does not take into account the ceramic items' shapes.

As for other elements leached, the amount of barium leached out was in the range 9 ppb to 95 ppb while the values for Cd, Co and Cr leached in all the dishes were perceived as benign.

(iii) Modern ceramic wares (China, India and Thailand)

Leaching results for the modern ceramic wares (A1-A9) in 4% acetic acid are shown in Table 8. The modern ceramic wares were usually tested 2-3 times with the acetic acid solution to assess reproducibility of trends. Those which contained mostly colourless glazes were not tested twice.

The amount of lead leached from the modern ceramic wares during the first leaching test was extremely low and not above 40 ppb, well within the lower safety limit of 500 ppb. The leaching potential of Ba is of far greater relevance in these ceramic wares due to its greater prevalence in the glazes, especially of highly coloured items as shown by XRF. In general, the amounts leached were variable but generally judged to be low and below 50 ppb except for sample A6, a Chinese-made red glazed plate for which, unfortunately, an XRF analysis was not done, nor was a second leaching test done. This leached Ba at a concentration of 815 ppb, which we regard to be somewhat high and hence a measurement to be regarded with some suspicion. Other elements analysed showed that little had leached out of the modern ceramics into the 4% acetic acid. Although health hazards related to the acute ingestion of barium are known, especially barium carbonate or barium chloride, no standard limit for leaching of barium from ceramic wares has been set. As per the US Environmental Protection Agency (EPA)'s "Ba fact sheet" the "maximum contaminant level goal (MCLG) and "maximum contaminant level" for Ba in drinking water is 2 ppm for each (MCL and MCLG).[11] The levels shown in Table 8 for samples A1-A9, with the possible exception of A6, are well below this level

Summary of leaching tests involving black and lemon tea, cold water, and Coca-Cola

In general these tests were not carried out as per a designated standard procedure like the 4% acetic acid test which is a globally recognised test but were designed specifically by the authors as part of this study. As such the results from these will be summarised as bar graph figures where interesting trends arise to show the relative leaching behaviours of items tested. Furthermore, testing was generally restricted to items which could reasonably contain the testing solutions so ceramic items tested were generally teacups or mugs. Flatware ceramic dishes and broken bone china, e.g. samples B1 and B2, were not able to be tested conveniently in this manner.

Table 8. Heavy metal concentration in 4% acetic acid leachate solution in ppb from modern ceramic samples after a contact period of 24 hours. Tests were repeated 2-3 times for most coloured ceramic items studied. Mean values of replicates are reported for each leaching test with fresh 4% acetic acid used to conduct each test. (a) samples A1-A3, (b) samples A5-A9, (c) samples A10-A11.

(a)

Tests / Elements	A1			A2			A3		A4
	1st [a]	2nd	3rd	1st	2nd	3rd	1st	2nd	1st
Pb	8	16	3	15	14	<DL	18	20	<DL
Cd	<DL[b]	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ba	33	34	5	7	7	31	7	7	1
Cr	1	2	1	20	5	2	4	<DL	4
Co	10	62	3	7	6	21	<DL	1	<DL

(b)

Tests / Elements	A5			A6	A7	A8		A9
	1st	2nd	3rd	1st	1st	1st	2nd	1st
Pb	5	3	<DL	6	<DL	<DL	<DL	1
Cd	<DL	<DL	<DL	15	<DL	<DL	<DL	<DL
Ba	12	11	8	815*	6	46	18	34
Cr	<DL	<DL	<DL	8	5	5	2	<DL
Co	1	1	<DL	<DL	<DL	13	6	<DL

* unusually high level of Ba which is considered suspect and is subject to confirmation.

(c)

Tests / Elements	A10			A11	
	1st	2nd	3rd	1st	2nd
Pb	37	<DL	2	3	<DL
Cd	<DL	<DL	2	<DL	<DL
Ba	<DL	<DL	<DL	15	6
Cr	6	<DL	<DL	<DL	<DL
Co	1	<DL	<DL	<DL	<DL

[a] 1st, 2nd, 3rd refers to the first, second and third samplings respectively. [b] < DL indicates below the detection limit of the instrument.

Figs. 3-4 are bar graphs showing the comparative leaching behaviour of the selected ceramic ware in the various liquids or beverages that had been placed in them. A quick comparison of the bar graphs reveals that heat and low pH on average produced more leaching in the items than with cold water which is to be expected. In general, the pH of the lemon tea was measured to be 3.2 and the temperature 85-90 °C. Coca-Cola beverages are known[24] to have a pH as low as 2.5, hence are reasonably acidic. Black tea (Tetleys brand) has been reported[25] to have a pH at approximately 4.9 and is stated as being less of a problem in terms of acidity to teeth compared to more acidic carbonated drinks like Coca-Cola.[24] Adding milk to black tea, however, increases the pH of the beverage and in fact this was measured in the current study to be 6.73 for the leaching solution consisting of the black tea with milk added. Other components are present as well in black tea which may have chelating abilities for metal ions such as the salks of oxalic and citric acid[25] which will have chelating abilities depending on the pH of the medium. Cold water exposed to CO_2 will generally[26] have a pH approximately equal to 5.5. In general, lemon tea and Coca-Cola can all be regarded as being relatively more acidic solutions relative to black tea with milk added and cold water. With this information in mind, the results for these leaching tests involving various beverages can now be compared.

It is clear from looking at Fig. 3, which summarises leaching data for ceramic items exposed to hot lemon tea, that the acidic nature of this beverage has influenced results. There may also be an influence of chelating ions like citrate or oxalate which could form complexes with metal ions leached from the glaze, e.g. Pb^{2+} though this may be highly dependent on pH and solubility issues in the case of oxalate.[27] Samples U1 and C2 gave the most significant concentrations of leached elements in the samples tested. The largest numbers in the set relate mostly to Pb and to a much lesser extent Ba leaching occurring with the Crown Lynn cup C2 with the dark blue outer surface and light blue inner surface. Pb leaching would be the most prominent due to its level in the glaze (see XRF data in Table 4) whereas Ba content in the glazes for U1 and C2 were moderate to low. The higher release of Pb may be understood in terms of its physical state as there were scratches due to former use on the inner surfaces of the cup and this could be a point of release of metals when under stress (hot, acidic liquids like lemon tea). These were also older items. The other more modern ceramic items from China or India either returned no significant readings (below detection limit for the elements concerned) or else returned very low readings for any elements tested suggesting more leach proof glazes under the conditions tested.

The results for hot black tea with milk added (pH = 6.73) showed apparently low numbers below 20 ppb for all elements tested, indicating that this beverage causes low leaching, especially for items U1 and C2 which normally gave higher values (especially for Pb) in the other tests (see Figs. 3 and 4). The same was observed when the items were exposed to cold water.

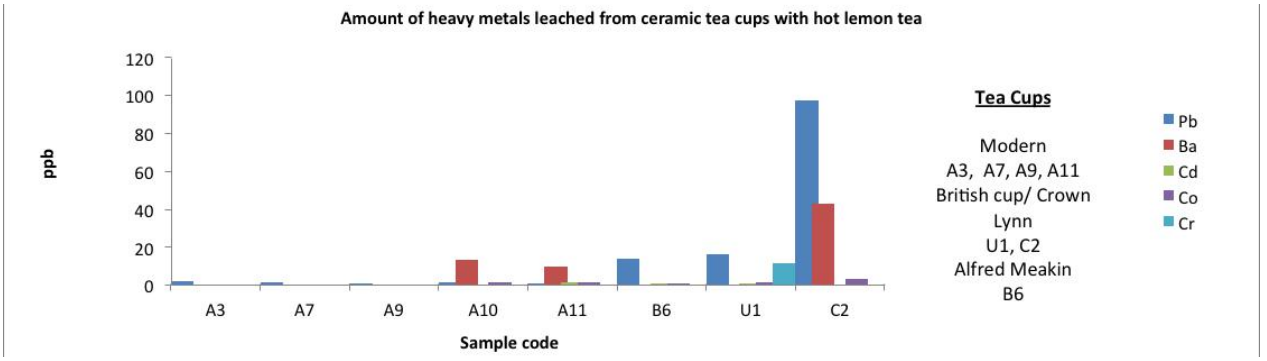

Fig. 3. Leaching results for ceramic mugs/teacups exposed to hot lemon tea

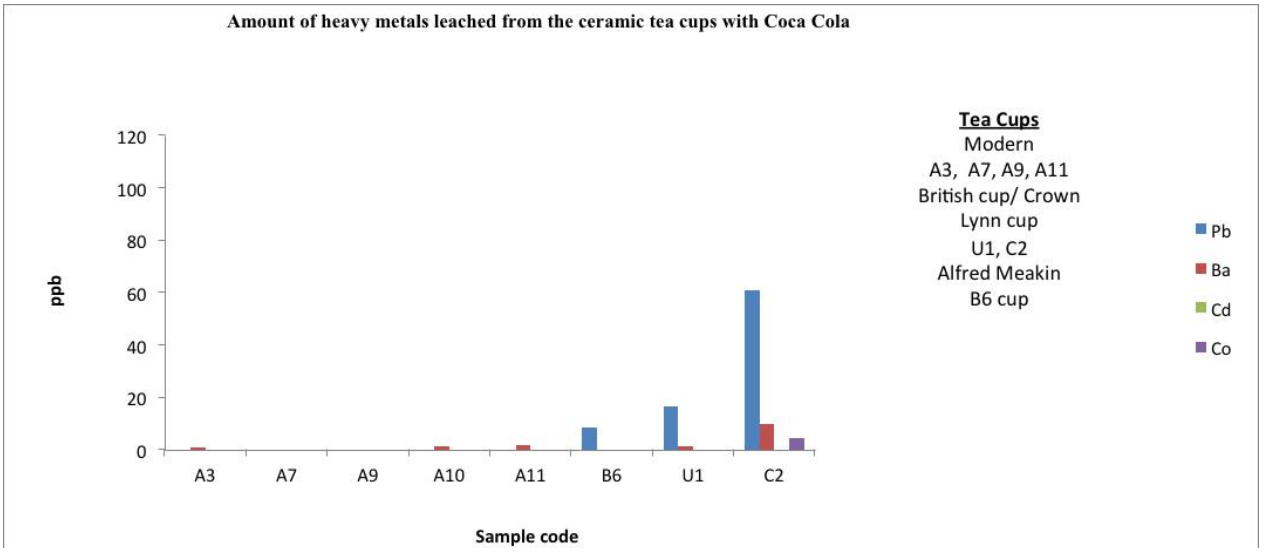

Fig. 4. Leaching results for ceramic mugs/teacups exposed to Coca-Cola.

Conclusions

Overall the FTIR, XRF, solid state NMR and ICP-MS analyses have indicated some interesting trends in the glaze components of New Zealand domestic food and drink ceramics. It is obvious that past ceramic ware was predominantly glazed with Pb-containing compounds, even New Zealand-made wares manufactured in the recent past during the 1960s and 70s. The contemporary Chinese, Indian and Thai-made ceramics sampled show that Ba has replaced Pb in glazes where colours are involved in the glaze patterning. In addition, other components such as Sn or Zn oxides and zirconium silicate are detected in the modern ceramic wares which probably function as opacifiers in the glazes. Leaching testing on older wares shows some concerns with Pb leaching on selected items in 4% acetic acid, especially the British Victorian bone china specimens. In contrast, more recent (1950s) British manufactured bone china containing Pb in the glazes are better fritted in comparison given the lower leaching of Pb observed in these specimens by ICP-MS. In general, with the shift to Ba-based glazes, this element and its leaching potential should be placed under greater scrutiny in leaching studies of modern ceramic items. Additional work in this area would be of great interest.

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A Vaccine Against Malaria?

Anthea Lees

The World Health Organisation (WHO) published figures which indicated that in 2010 malaria was responsible for approximately 660,000 deaths from *c.a*. 219 million reported cases of the illness. People living in the poorest countries in the world are susceptible to catching malaria and account for about half the world's population (3.3 billion people).

Malaria is caused by *Plasmodium* parasites (the most deadly being *Plasmodium falciparum*) which are spread to people through the bites of mosquitoes. An effective vaccination could be the key to the eradication of this disease together with the current use of bed nets, insect repellents and malarial drugs which are all used in the fight against malaria.

The UK government has pledged £1bn in funding to be used over the next 3 years in the fight against malaria, TB and AIDS as part of the Global Health Initiative. Global Health Fund initiatives are humanitarian initiatives that fund-raise and distribute monies to strengthen health systems in developing countries.

The British drug maker GlaxoSmithKline (GSK) together with the Path Malaria Vaccine initiative (PMV), supported by the Bill and Melinda Gates foundation, are developing a vaccine known as RTS,S. The vaccine is currently in Phase III trials and is the most advanced vaccine candidate.

The large scale phase III African trail of RTS,S showed that the vaccine continued to protect children for up to 18 months after it had been administered. RTS,S also showed a 46% reduction in the cases of clinical malaria in children aged between 5 and 17 months compared with children who were immunised with a control vaccine. It also showed a 27% decrease in cases of malaria in babies aged between 6-12 weeks. This was Africa's largest-ever clinical malarial trial and involved around 15,500 children and covered seven countries. GSK ultimately aims to submit a regulatory application to the European medicine's agency (the European Union agency for the evaluation of medicinal products) in 2014.

The CEO of GSK, Sir Andrew Witty said "We're very encouraged by these latest results, which show that RTS,S continued to provide meaningful protection over 18 months to babies and young children across different regions of Africa. While we have seen some decline in vaccine efficacy over time, the sheer number of children affected by malaria means that the number of cases of the disease the vaccine can help prevent is impressive. These data support our decision to submit a regulatory application for the vaccine candidate which, if successful, would bring us a step closer to having an additional tool to fight this deadly disease. We are grateful to the scientists across Africa and GSK and to our partners who have worked tirelessly for almost 30 years to bring us to this point."

Halidou Tinto the Principal Investigator from the Nanoro, Burkina Faso trial site and chair of the Clinical Trials Partnership Committee (CTPC), which oversees the RTS,S Phase III programme stated: "In Africa we experience nearly 600,000 deaths annually from malaria, mainly children under five years of age. Many millions of malaria cases fill the wards of our hospitals. Progress is being made with bed nets and other measures, but we need more tools to battle this terrible disease."

To find out more about malaria visit the Malaria Atlas Project (*http://www.map.ox.ac.uk/*) which has free and downloadable information on all aspects of malaria.

Biochars and Carbonised Biomass: A New Zealand Perspective with a Focus on Chemistry

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Key words: *char, carbonisation, pyrolysis, biochar, charcoal.*

This article covers some important chemistry related to the solid carbon-rich materials produced from the pyrolysis of biological precursors such as plant biomass. A brief history of the study and applications of these materials in New Zealand, along with a brief overview of recent interest in using charring and carbonisation of biomass to sequester carbon, follows.

Terminology

The term "biochar" is said to have been coined by Peter Read of the Centre of Energy Research at Massey University, Palmerston North.[1] Peter Read has been trying to replace the commonly (mis)used term "charcoal" with "biochar" for the carbonaceous materials made from recent biomass, probably to avoid confusion with coals. In some circles the term "biochar" is only used for biomass-derived carbonaceous materials that are applied to soil and/or used to sequester carbon, specifically excluding those biomass-derived chars used for fuel or metallurgy, and a story goes that the term "agrichar" was going to be commonly used until it was found to have been trademarked.[1] An interesting debate concerning both the terminology and potential widespread application of biochars can be found on the website of The Guardian newspaper involving letters from Peter Read, James Lovelock, Jim Hanson, Pushker Kharecha, and Chris Goodall in response to a very critical article by the columnist George Monbiot in 2009.[2-5]

Researchers, especially in Russia and the Americas, often also use the term "biocarbon", usually when well-carbonised biomass is investigated for applications such as electrodes.[6-9] According to IUPAC definitions, all these materials are technically called "chars" and fall in the category of "non-graphitisable carbons".[10] Non-graphitisable chars can also be produced from other precursors such as some synthetic resins, often those rich in oxygen or chlorine.[11]

What are Biochars and Carbonised Biomass?

Biochars and carbonised biomass are black solid materials produced through heating of biomass (wood, leaves, and a range of mostly plant materials) usually in a low oxygen or anoxic environment. This heating removes most of the mass and preferentially removes hydrogen and oxygen content as various liquid and gaseous pyrolysis products. After initial charring and production temperatures exceed about 350 °C, the solid products are greatly enriched in carbon and most of this carbon is part of large conjugated and aromatic structures, thus the black colour. These chars can then carbonise during prolonged exposure to higher temperatures, typically between 500 and 1000 °C. This higher temperature carbonisation process usually removes the remaining aliphatic material, removes most of the other functional groups, and organises the aromatic carbon into larger more condensed polycyclic aromatic structures and/or a tangle of graphene-like layers.[7,12]

An important point worth repeating is that a black charred material produced around 400 °C is generally chemically and nanostructurally very different to a well-carbonised black charred material produced at temperatures approaching 1000 °C.[13,14] The structural changes which occur over this carbonisation temperature range greatly alter a variety of important and interesting properties.[7,12,14]

When compared to chars produced around 400 °C, chars carbonised to between 800-1000 °C often have:

- 10,000 to 100,000 times higher electrical conductivity.[15]
- 10 to 100 times higher surface area as measured by N_2 adsorption (often using B.E.T. methods).[12,14]
- 6 to 10 times higher values of some mechanical properties such as hardness and stiffness.[15,16]

The answer to the question "what is it?" for the case of charred materials depends greatly on how well-cooked or how well the material was carbonised. The maximum temperatures employed and the amount of time spent at elevated temperatures during production using conventional heating methods can determine the structure and properties of the resulting carbonaceous material. Most of the biochars researched recently for applications in soil, often with the goal of sequestering carbon in a long lasting solid form, have been produced at a range of production temperatures between 300-700 °C and the suitability of a given char for a given application is likely to be greatly influenced by how well-carbonised that char is. The well-known changes which occur as these materials are prepared at increasing temperatures are represented in Fig. 1.

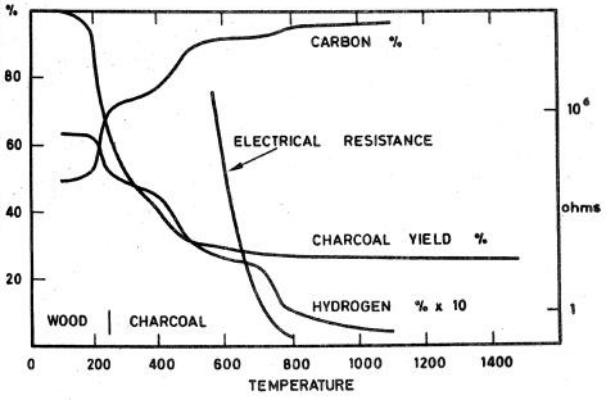

Fig. 1. Progress of carbonisation with temperature. Reproduced with permission from Callaghan Innovation.[17] Temperature in °C.

At the micrometre scale, the structure of chars often resembles the biological architecture of the biomass precursor. This can be seen in the selection of scanning electron microscope (SEM) images in Fig. 2, with the cellular structures of the pine wood still visible along with smaller fragments of the cell walls caused by the grinding of this particular sample. The charred and carbonised material has what is called a pseudo-glassy appearance and undergoes brittle fracture. The smoothing or fusing of some finer features often distinguishes carbonised biomass from un-carbonised lignocellulosic biomass.

Before the more famous X-ray diffraction studies on the structure of DNA in the early 1950s, Rosalind Franklin discovered that carbonaceous materials can be graphitisable or non-graphitisable and produced the first reliable model of the structure of chars at the nanometre-scale. The non-graphitising behaviour, fine porosity, hardness, and isotropic nature of chars was attributed to strong cross-linking which holds the stacks of nanometre-sized graphite-like layers (graphene sheets as they would likely be called today) at a random orientation with respect to neighbouring stacks. The cross-linking and random orientation of these stacks of graphene-like layers in chars acts to limit their growth which in turn hinders long-range ordering into large flat graphene sheets and true graphite crystals even after annealing at temperatures as high as 3000 °C.[11,12,18,19]

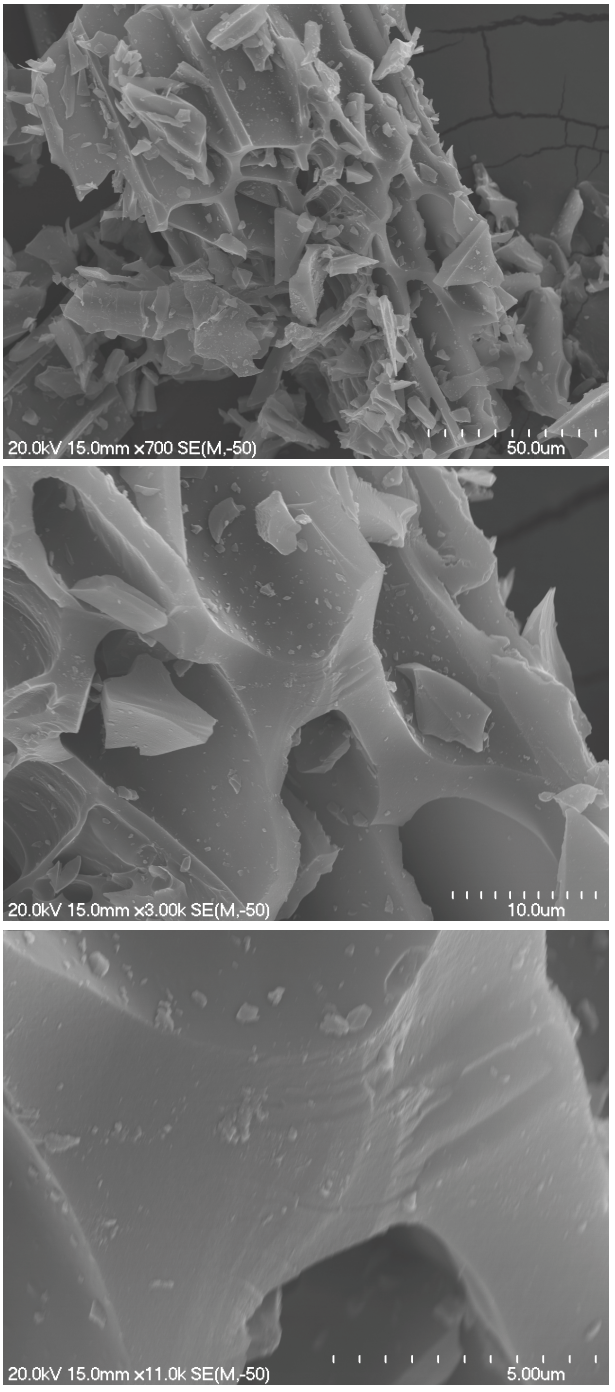

Fig. 2. Scanning electron microscope images of radiata pine wood char prepared at a temperature close to 600 °C and then ground to a fine powder. The three images represent the same area viewed under different magnifications.

Techniques for the Analysis and Characterisation of Chars

Higher production temperatures generally lead to the formation of larger and more condensed polyaromatic networks. Such large condensed polyaromatic structures are considered more resistant to biotic and abiotic conversion back to CO_2 when compared to the smaller aromatic and aliphatic structures more common in chars produced at lower temperatures.[20,21] Determining the extent of carbonisation in a given char sample often requires an estimate of the size and degree of condensation of the polyaromatic structures. Determining the H/C atom ratio by combustion-based methods are often employed, and lower H/C ratios are becoming established as the indication of well-carbonised chars. Solid state Nuclear Magnetic Resonance (NMR) methods are also employed and researchers at Massey University have been correlating H/C_{org} ratios to NMR measurements of the carbon aromaticity in order to assess degree of thermal modification and predict long-term stability.[21]

Raman spectroscopy can be used to study the growth in the condensed polycyclic aromatic layers and the material's development at a nanostructural level. With Raman spectroscopy being especially sensitive to carbon nanostructure, it can quickly distinguish the hydrogen-rich amorphous structures common to chars prepared at lower temperatures from the more graphene-like structures with nanometre-scale disorder common to the well-carbonised chars prepared at higher temperatures.[13] Both Raman and X-ray diffraction results have been used to estimate the size of the graphene-like domains which usually form disordered stacks, although caution must be used when interpreting these results or when calling the stacks "crystallites" as they usually lack true graphitic interlayer order.[11,19,22]

Solid state NMR spectra (such as those shown in Fig. 3) can show the removal of non-aromatic signals and oxygen functional groups such as the O-alkyl signals common to cellulose with increasingly severe heat treatments and a corresponding increase in a broad aromatic carbon signal near 128 ppm which will eventually account for almost all the carbon signal as the carbonisation progresses towards 700 °C.[23,24] Once the vast majority of carbon is contributing to the 128 ppm signal then the typical NMR methods which detect the char's ^{13}C atoms become less useful and an alternative method involving the measurement of the

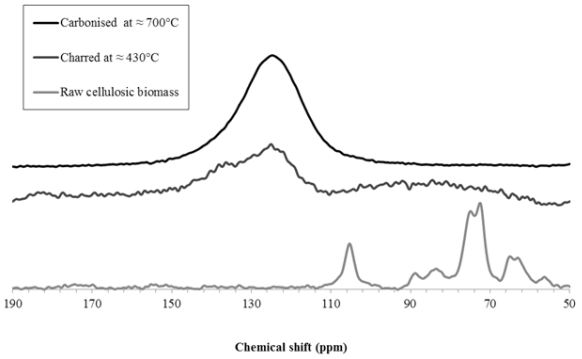

Fig. 3. Representative ^{13}C solid state NMR spectra between 190 and 50 ppm demonstrating the conversion of an O-alkyl rich cellulose-based biomass into chars rich in aromatic carbon. Biomass precursor was in this case *Phormium tenax* leaf fibres.

chemical shift change of adsorbed ^{13}C-labelled benzene can be used to estimate of the size of condensed polyaromatic structures in chars involving calculations of ring current effects.[25,26]

Chars, especially those produced at lower temperatures, often contain volatile and solvent-extractable molecules which can be analysed with gas-chromatography mass-spectrometry methods.[27]

Most biomass contains inorganic elements and these are often referred to as ash content in carbonised biomass. When certain precursors such as manures are used to make biochars, the inorganic component can be over 50% of the mass of the resultant material. The chemical form of the inorganic elements can vary based on a number factors and is particularly important for the availability of elements such as phosphorus for the use of biochars as a fertiliser.[21]

Potential for Carbon Sequestration

Most of the recent interest in biomass charring and carbonisation has involved it being an option for sequestering carbon removed from the atmosphere by photosynthesis through conversion into a more recalcitrant solid form. Over the longer-term timescales of decades and centuries it is considered better to convert biomass to a biochar, rather than letting it rot or burn in fires which would quickly return more of the carbon back to the atmosphere as indicated in Fig. 4. There is still plenty of uncertainty concerning how long biochars can be expected to resist biotic and abiotic oxidation in a given environment. Chars can contain different types of carbon-based components (volatiles and solvent-extractable molecules, oxygen and hydrogen-rich amorphous carbon, and condensed aromatic/graphene-like carbon) and each component will likely have different rates of decay. The half-lives estimated for the more labile components are around a few days to ten years, moderately stable components are around a few hundred years, and half-lives estimated for the most recalcitrant components have been estimated to be between 1000 and 50,000 years.[21,30] The chemical and ecological conditions under which a char is stored are also likely to have a great influence on the rates of decay.

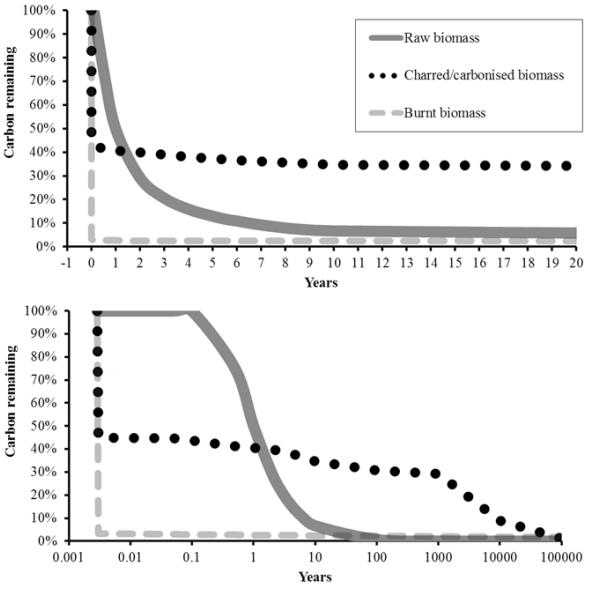

Fig. 4. Schematics illustrating the broad concepts behind using biomass charring and carbonisation to sequester carbon fixed through photosynthesis. The figure is largely based on similar plots produced by Joseph Lehmann and updated with estimated half-lives and a rough three component decay model based on two recent theses from Massey University.[21,28,29] Decay curves are to illustrate the concept; in reality the longevity/recalcitrance of all these types of solids will likely be highly dependent both on their specific structure/chemistry and the environment (chemistry/ecology/geology) where they are stored.

A Brief History of Research, Interest and Applications in New Zealand

The recent interest in adding biochars to soils to improve various properties such as drainage and nutrient retention appears to be largely inspired by the study of dark earths found in the Amazon Basin in Brazil and reported to have been created by human activity over 800 years ago and known as "*terra preta de indio*".[28,31] Other examples of soils modified by char addition by historic human activity exist around the world.[30] In 1923, scientists at the Chemistry Laboratory of the Cawthron Institute published an investigation concerning large areas of former garden soil in Nelson, deliberately modified by char addition during Maori settlement and cultivation of this land.[32]

The presence of large quantities of char in sites associated with early human habitation in New Zealand has also been documented by a few keen observers such as Leo Fowler who had an article on the subject published in 1957.[33]

"One of the things which has interested me during the excavation of ancient pa sites and habitation sites is the ubiquity of charcoal deposits. One naturally would expect to find charcoal in pit sites, but in actual practice it is likely to appear wherever one digs in the vicinity of pa and habitation sites, sometimes quite distantly removed from what one would assume to be centres of population. It would appear that charcoal as charcoal, that is a deliberate and not an accidental product, was known and used by the prehistoric Maori, and that it possessed properties which make for its preservation under conditions where wood and bone tend to perish almost to vanishing point."

Fowler goes on to detail the accounts of his older Maori friends in many districts. With this oral history and the support of archaeological evidence, he concludes that there was considerable manufacture of charcoal as an industrial practice by Maori, with chars often valued as a fuel which burned cleaner and longer than wood.[33]

Along with a few operations which have mainly provided barbeque charcoal to supply the NZ domestic market, there are reports of the use of charcoal as a vehicle fuel during the world wars.[33]

In 1961, a Department of Scientific and Industrial Research (DSIR) technical report was produced and distributed which indicates that some serious thought was given to re-establishing biomass carbonisation at industrial scales in New Zealand. This report provides an interesting literature review and feasibility study about creating a wood carbonisation industry primarily to provide the Bluff aluminium smelter with electrode carbon and potentially create a New Zealand chemical industry around many of the pyrolysis by-products.[17] Presumably, any plans to implement this idea were abandoned due to increased availability of cheap oil, coal, and natural gas in subsequent decades. Following this DSIR report there appears to be about a 40 year gap in New Zealand research in this area (the author would be interested to hear of any sources of information relating to this time period).

At the University of Hawaii, researchers have investigated the production of chars using a flash carbonisation process and the creation of carbonised biomass doped with boron and phosphorus; these chars were characterised at the universities of Hawaii and Waikato.[24,34]

Massey University in Palmerston North created the New Zealand Biochar Research Centre (NZBRC) after earlier research through the MAF sustainable farming fund. NZBRC researchers have investigated using biochars for carbon sequestration and as a soil amendment.[21,29]

Research associated with Massey University has also covered the use of biochar as a hydroponics growing media, turning a mix of wood chips and sewage solids or manures into biochars for fertilisers, and the use of biochars to treat wastewaters and contaminated soils.[21,35,36] Researchers at Landcare in collaboration with the University of Waikato have investigated the use of biochars in soils to adsorb steroid hormones and veterinary antibiotics.[37]

Investigations into the engineering of pyrolysis equipment, modelling the pyrolysis and charring reactions, and the use of radiata pine as a feedstock have been carried out by researchers at Massey University, Callaghan Innovation, and the University of Waikato.[38-40]

Scion has been researching the reactions which occur during the torrefaction of radiata wood by heating it to between 200 °C and 300 °C. The torrefied wood is more roasted than charred, and is considered more energy dense, more hydrophobic, and easier to grind when compared to the original wood, with these properties having advantages for solid fuels.[41]

Researchers at Lincoln University have investigated ammonia absorption on biochars in soil and its subsequent bioavailability.[42] This research featured biochars provided by the Blenheim-based start-up company Carbonscape™ which has attracted plenty of media coverage concerning their proprietary microwave carbonisation process.[1] A number of other hobby and start-up small-scale producers and users of biochars for soil applications exist across New Zealand and they have formed an interest group with a website (*www.soilcarbon.org.nz*).

A Brief Summary of Applications in Japan

Japan has had a long history of char production and application. The charring of rice husks and their use in productive soils is reported to have been a common practice for thousands of years. With its large coverage of forests, Japan practiced large-scale charcoal production until presumably cheap fossil fuels became more commonly used. Japan still produces large quantities of biomass-derived char which are utilised in a very diverse range of applications. These include chars used for air and water purification, humidity control materials in buildings, addition to fertilizer products, soils and composts often to promote the growth of beneficial microorganisms, and for promoting the growth of symbiotic mycorrhizal fungi with tree seedlings. Japan is also a major producer of activated carbons and other carbonised products with coconut shells being a major precursor and applications including electrode materials for lithium ion batteries and supercapacitors.[30,43]

Conclusions

Although sparse over many decades, there has been a considerable amount of investigation and application of charred and carbonised biomass in New Zealand. The recent interest in using biochars as an additive to improve cultivated soils appears to echo some of the earliest applications of chars in New Zealand. The basic concept behind using biomass carbonisation to sequester carbon definitely has potential, despite some uncertainty about predicting the long-term stability of these materials. The production of carbonised biomass in New Zealand for other applications such electrode carbon has been considered in the past although was unfortunately not developed into a major industry. Another island nation with extensive forests, Japan, has been able to become a major industrial producer of carbonised biomass for both newer products such as electrodes and activated carbons, as well as more traditional applications such as an additive for soils, composts, and fertiliser mixes.

Acknowledgements

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Article

Tales of the Periodic Table (The Ytterby Odyssey)

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Introduction

My impression of students' first reaction to the Periodic Table is that it is akin to the very large manual that used to come with new computer software – pretty much unintelligible until you had used the software for a couple months. To counter this I try to add interest with such stories as helium being detected in the sun before being found on earth, rubidium and caesium are named after predominant lines in their spectra, the flurry of discovery of new elements by Humphry Davy once he got his hands on an electrochemical cell. As we go through the course the numbers in the element boxes and shape of the Periodic Table begin to make more sense. At some stage in my teaching career I read about Ytterby and its importance to the Periodic Table and it is a story I regularly include in my teaching. Over the years the story has had the potential to grow as the historical context of the Ytterby mine has become clearer. There are two strands to this article that meet up at the end.

The Historical Strand

The early civilisations of China had a well developed chemical technology. Best known are their development of fireworks and pottery.

Archeological excavations in China indicate that the use of pottery goes back as far as 18,000 years. China has an abundance of clays that are suitable for firing and because the country straddles two tectonic plates the types of clays are different in different regions. Two of the best known pottery types are terracotta and porcelain (china – as in dinner sets, cups and saucers etc)

Terracotta (from Italian for 'baked earth') is generally made from reddish clays. The red colour is due to iron compounds which act as a flux (melting agent) and allow the clay to be fired at a relatively low temperature of around 1000°C. The most famous of historical examples is the terracotta army found in China in 1974 and have been dated as being created in about 210 BC. Common garden pots are often terracotta which is porous when unglazed. For that reason it is unsuitable for vessels required to hold liquids but good when excess water is needed to drain away, as in garden pots.

Porcelain has been known in China since around 200 AD and production techniques were developed and the quality improved by succeeding dynasties. Porcelain has a pure white translucent appearance. The name is attributed to Marco Polo who in the 13th Century, after visiting China, likened the appearance of porcelain to that of cowrie (or cowry) shells (which were called *porcellana* in Italian meaning 'little pigs' due to the curved shaped back of the shells).

The key to making porcelain was the discovery of 'china stone' or *petuntse*, a mineral containing quartz (silica, SiO_2) and forms of feldspar (sericite and mica). This mineral is unique to China. Feldspars are a group of aluminosilicate rocks containing potassium, sodium and calcium [$KAlSi_3O_8$ – $NaAl\ Si_3O_8$ – $CaAl_2(Si_3O_8)_2$]. They make up about 60% of the earth's crust and on weathering and subject to terrestrial forces (heat and pressure) undergo changes in composition. The mica acted as the flux or vitrifying agent (turning to glass) but china stone alone proved difficult to fire as it would only vitrify properly over a narrow range of temperatures. Mixing the china stone with kaolin, another feldspar derivative, proved much more successful. Kaolin is named from the Chinese mountain *kao-ling* and contains the mineral kaolinite, $Al_2Si_2O_5(OH)_4$.

Cowrie shells

Chinese kaolin is high in alumina, which gives the clay its white colour, makes the clay more plastic, and helps to control vitrification. When the Chinese potters mixed kaolin with china stone and fired it at 1450 °C, the feldspar in the china stone partially vitrified and infused into the pores of the kaolin, reforming as microscopically fine crystals known as mullite needles. These mullite needles are unique to porcelain and give it its strength, translucence, and resonance. The quality of the porcelain improved as the percentage of kaolinite was increased until a 50:50 ratio proved to be the optimal. When produced this way porcelain is non-porous but is frequently glazed to protect any decorating and to enable the surface to be easily cleaned. Glazing is achieved by dusting with a powder or dipping the article in a liquid prior to firing. This surface coating vitrifies at the temperature of the kiln forming a protective layer. Chinese glazes were made by adding crushed limestone $CaCO_3$ to the same mix as used to make the porcelain. Modern glazes are composed of silica (SiO_2) with compounds of Group 1 or Group 2 metals added as a flux to lower the melting point.

The Chinese developed the technique of underglazing where a coloured pattern was applied to the porcelain surface before the glaze. Because of the high temperatures required in the firing process the choice of coloured pigments was limited as many decomposed at these temperatures.

The most common pigment used was cobalt oxide which gives the intense blue characteristic of many decorated porcelain items. Copper(I) oxide was also used which gave a red colour.

Overglazing (applying the pattern after glazing) is also used. After applying the pigments the article was again fired but at a much lower temperature which allowed a greater range of pigments to be used.

Chinese porcelain was brought to Europe by traders in the 1100s. It was greatly admired, but it was so rare and expensive that only wealthy people could afford it. As trade with the Orient grew during the 1600s, porcelain became popular with the general public. The custom of drinking hot tea, coffee, and chocolate became widespread and created a huge demand for porcelain cups and saucers. Drinking tea from pewter beer mugs didn't quite cut it and the drink cooled rapidly.

Bone China was developed in England as potters there tried to emulate the porcelain from China. It was made by adding bone ash to clays and produced a strong translucent porcelain-like product. It is thought the use of bone ash may have been inspired by a returning Jesuit missionary who misinterpreted the recipe. In China the different ingredients were referred to as 'the bones' and 'the flesh' of the pottery and English potters took the bones reference literally. However, the recipe was successful and bone china is now made world-wide. Despite this initial transfer of information it is believed that china (porcelain) was finally developed independently in Europe in 1708.

The two names associated with the European discovery of porcelain in Europe in the early 1700s are the Germans Johann Friedrich Böttger and Erhnfried Walter von Tschirnhaus. Böttger was an alchemist spending his time trying to find out how to convert base metals into gold. In this context he came under the control of the monarch of Saxony, Augustus the Strong. Not surprisingly Böttger was unable to please the king who diverted him to help von Tschirnhaus with his other status project – making porcelain. It appears Böttger was reluctant to work with von Tschirnhaus, but acquiesced when the alternatives were outlined.

von Tschirnhaus had initiated a systematic testing of various combinations of clays and was finally successful in making porcelain. The proposal to establish a porcelain factory with von Tschirnhaus as director stalled when he died suddenly and it was left to Böttger to announce that porcelain had been successfully made. He was given credit for discovering the process but subsequent information indicated that the credit should go to von Tschirnhaus. The porcelain was initially made by fusing with kaolin and alabaster (gypsum, $CaSO_4.2H_2O$). The final composition also included feldspar.

And this finally is where Ytterby enters the story. Ytterby is a small village in the Stockholm archipelago (the name means 'outer village') and since the 1500s there had been a mine producing quartz for the iron industry. From the 1700s it also produced feldspar for the porcelain and glass industries. If that was all it did the name Ytterby would have very little historical importance.

In the 1700s Stockholm was protected from sea-borne attack by a fortress on an island close to the town of Vaxholm, now considered the gateway to the archipelago and about an hour by ferry from Stockholm city. In the fortress in the late 1700s was a garrison that included an amateur geologist Lt. Carl Arrhenius. He found time to explore and, in the tailings from the Ytterby mine, he found a dense black rock that attracted his attention (chance favours the prepared mind). Through his contacts the rock finally came into the hands of Johan Gadolin, a chemist. Through his and others' work the rock yielded seven new elements. Four of these are named after the tiny village of Ytterby (yttrium, atomic number 39, symbol Y; terbium, atomic number 65, symbol Tb; erbium, atomic number 68, symbol Er and ytterbium, atomic number 70, symbol Yb). Element 64 was named after Gadolin, gadolinium (Gd), element 67 was named after Stockholm, holmium (Ho) and element 69 was named after an old name for Scandanavia (Thule), thulium (Tm).

The Seismic Strand

Council of the NZIC had a meeting at the University of Canterbury Ilam Staff Club rooms on 22 February 2011. We had just broken for lunch when Christchurch was hit by the devastating earthquake. We gathered after evacuation, the meeting obviously abandoned and the local members went home to check their properties. Some out of town delegates went to Christchurch relatives which left three; Brian Halton, Julian Eaton-Rye and Gordon Rewcastle. I suggested they come to our place not knowing what state it would be in. As it turned out it was pretty much unscathed and even had power on so we watched the dramas unfold. An hour or so later I went into the hallway to find three total strangers standing there. Noela, my wife, who works in the city, had been searching for our grand daughter who was at school in the CBD. She was subsequently found safe, but in the meantime Noela came across three distressed back-packers totally confused by Civil Defence officials urging everyone to go to Hagley Park. Having arrived in Christchurch the night before they had no idea where Hagley Park was. Noela encouraged them to forget Hagley Park and go with her. They flagged a bus down which was timetabled to run an entirely different route but the driver realised that was not an option and agreed to take them to Burnside along with a few other passengers. They later told us that agreeing to go with Noela was a difficult decision because in planning their OE they had been to meetings where it was regularly stressed "Do not go anywhere with strangers". But these were exceptional times.

Earthquake refugees from left to right: Theresia Francissen (Germany), Hannah Frisk (Sweden), Richard Rendle, Gordon Rewcastle (NZIC Auckland), Julian Eaton-Rye (NZIC Otago), Brian Halton (NZIC Wellington), Noela Rendle, Linda Åkesson (Sweden)

The night of 22 February 2011 amid continuing after shocks we had eight people sleeping (or attempting to) at our place. During the next few days all managed to get flights (NZIC delegates to get home) and the girls (Hannah and Linda from Sweden) to continue their travels. Theresia, from Germany, left a few days later on a coach tour. Our overseas guests left with the plea that we had to visit them.

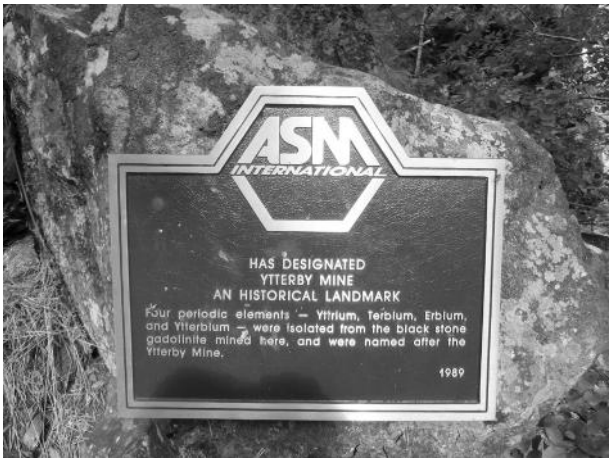
Over the next year or so we realised that through various circumstances a number of people from other countries had stayed with us and become friends and had invited us to visit. So the plans for a major overseas trip developed. These plans came to fruition in September/October 2013 with a visit over 38 days to 12 destinations in North America, Europe, UK and Scandinavia.

With Stockholm on the itinerary, we decided a pilgrimage to Ytterby was an absolute must. It took a number of hours surfing the web over several evenings to find out where the village actually was and how to get there. The Swedes are proud of ABBA, Volvo, Nobel and *The Girl with the Dragon Tattoo*, but not so interested in mine sites of historical chemical importance. The original plaque at the mine site was installed by the American Society for Metals (now ASM International) not the Swedes. In the meantime I had emailed the Vaxholm Tourist Information Centre and got a reply that pretty much confirmed what I'd gleaned from web sites. They also referred me to the custodian of the Museum on Fortress Island that had an exhibition about the Ytterby mine. I emailed Erik and the first part of his reply was:

What fun that you teach your students about Ytterby in Christchurch in New Zealand!

Our visit happened to be after the museum had closed for the summer season and if Erik had been in Vaxholm he would have opened it for us and even offered to drive us out to the mine. As it turned out he was away so we didn't see the museum and were left to find our own way to the mine.

The new steps to the mine site



The ASM plaque

The Final Assault

We arrived in Stockholm at around 10pm in the evening. Next morning we set out confidently – two blocks to the bus stop, bus 40 to Universitetet södra, Bus 670 to Engarn, followed by bus 628 to Ytterby using the directions provided by Google maps. It all went to plan and in a little over an hour we were walking down Ytterbyvägen. A check with a local confirmed we were on the right road and a walk of 20 minutes brought us to the two rocks that mark the entrance to the path that led to the mine site – just as I'd seen them on Google street view.

The few web sites that describe the site mention a difficult scramble up a scree slope to get to the mine. But we were in luck. Right beside the shingle "path" was a set of steps, so newly constructed that the bags of off-cut timber were still nearby.

Standing at the ASM plaque was a bit strange. Firstly when telling students about Ytterby, I never in my wildest dreams thought I'd ever be there. Secondly, in one sense it was a non-event; it could have been at any depression in the rocks on the Port Hills, but thirdly there was the poignancy that this was a site of immense historical importance to chemistry and the Periodic Table, where the first rare earths were found.

The notice at the path leading to the mine reads:

YTTERBY MINE

History

It was here that quartz was quarried in the 1500's for ironworks in north Uppland. The quarrying of feldspar for the porcelain and glass industry started at the beginning of the 1700's and continued until 1933 when the mine was shut down. In the beginning the feldspar was mined by the old-time baking method (make a fire and then chill with water). Later a method of blasting within the shaft was applied. The entrance to the mine, which nowadays is blocked off with rock waste for safety's sake, lies 100 m higher on the crest and the vertical mine shaft is approx. 170 m deep. The broken ore was transported to Ytterby jetty whence it was shipped by barge to the Rörstand and Bustavsberg Porce-

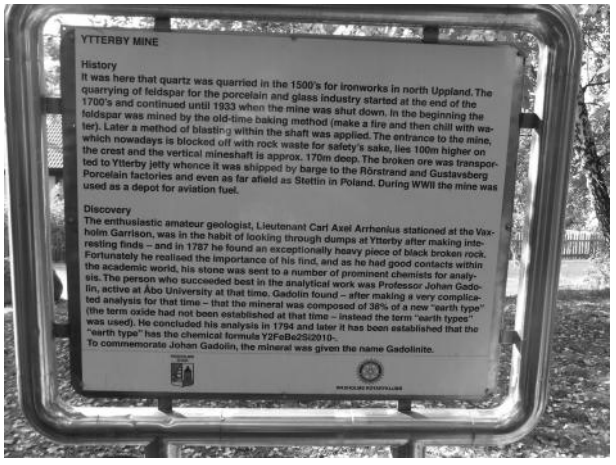
lain factories and even as far afield as Stettin in Poland. During WWII the mine was used as a depot for aviation fuel.

Discovery

The enthusiastic amateur geologist, Lieutenant Carl Axel Arrhenius stationed at the Vaxholm Garrison, was in the habit of looking through dumps at Ytterby after making interesting finds – and in 1787 he found an exceptionally heavy piece of black broken rock. Fortunately he realised the importance of his find, and as he had good contacts within the academic world, his stone was sent to a number of prominent chemists for analysis. The person who succeeded best in the analytical work was Professor Johan Gadolin, active at Åbo University at the time. Gadolin found – after making a very complicated analysis for that time – that the mineral was composed of 38% of a new "earth type" (the term oxide had not been established at that time – instead the term "earth type" was used). He concluded his analysis in 1794 and later it has been established that the "earth type" has the chemical formula $Y_2FeBe_2Si_{20}O_{10}$.

To commemorate Johan Gadolin, the mineral was given the name Gadolinite.

It is interesting to note that even on this notice there is no specific reference to new elements and that is only acknowledged on the ASM plaque at the mine entrance.



The Rotary notice at the path leading to the mine

The Wrap-up

The significance of the area is acknowledged in street names such as Yttriumvägen and Terbiumvägen.

Street name

Coincidentally Noela found an article in the September 2013 issue of *Business Life* which was in the seat pocket of one of our British Airlines flights. Title; *Rare earth element of the month: Yttrium*. It included the statement:

"*When it comes to the discovery of elements on the periodic table you can divide the world into two parts – Ytterby and everywhere else*".

It doesn't quote the source but it's from Sam Kean's blog

http://www.slate.com/articles/health_and_science/elements/features/2010/blogging_the_periodic_table/ytterby_the_tiny_swedish_island_that_gave_the_periodic_table_four_different_elements.html or just google 'elements from Ytterby'.

Even more coincidentally on the final leg from Auckland to Christchurch of our epic trip I was keeping half an eye on the trivia quiz AirNZ screens. One question was "What is the rock that is composed of quartz, mica and feldspar and used in curling stones?" The answer is granite and I immediately thought of the main notice at the start of the Ytterby gruva track.

I have been intrigued by the Ytterby story for years but I am surprised at the number of teachers, even experienced ones, who look at me blankly when I mention Ytterby. Maybe it's a story that is not well known.

Letter to the Editor

With my friend and collaborator Professor Graeme Wake of Massey University, I published last year two pieces in *Chemistry Education in New Zealand* (*ChemEd NZ*) on carbon sequestration by trees.[1,2] I recently sent in a third part, to discover that *ChemEd NZ* has gone into demise. Catherine Nicholson, Editor of *Chemistry in New Zealand*, has kindly agreed to consider a précis of part three as a letter.

It was previously emphasised[1,2] that the low population of New Zealand in relation to its landmass gives it a higher trees-to-persons ratio than the international average, and that this converts into carbon sequestration potential which can be expressed in monetary terms. The third part was to have addressed the matter of oil refining in New Zealand and its carbon footprint. It is pointed out that this is on a small scale and the carbon footprint is correspondingly low. A contrast is made with Japan, which has a landmass exceeding that of NZ only by about 50% yet has a refining carbon footprint colossally larger than that of NZ. A sufficiently interested reader is encouraged to contact me by email for full details.

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Feature

The 2013 Nobel Prize in Chemistry

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The Royal Swedish Academy of Sciences awarded the 2013 Nobel Prize in Chemistry to ***Martin Karplus*** of the Harvard and Strasbourg Universities, ***Michael Levitt*** of Stanford University School of Medicine, and ***Arieh Warshel*** of the University of Southern California, Los Angeles *for the development of multiscale models for complex chemical systems.*



Left: Martin Karplus (courtesy of Public Affairs, Harvard University); centre: Michael Levitt (from Wikimedia); right: Arieh Warshel (courtesy of Prof Warshel)

Summary

The developments in chemistry and biochemistry over the past 50 years have been rapid and significant. Older members of the Institute will recall with affection making models of molecules from plastic balls and sticks, tasks that are now routinely performed on the computer. The structure of a protein is obtained from X-ray crystallography or spin-spin couplings and nuclear Overhauser (nOe) measurements available from nuclear magnetic resonance spectroscopy. Programme development has been such that numerable protein structures have been solved and the results made available and accessible for download from a range of data bases. The viewer is now able to see the individual atoms of the substrate and rotate the 3D structure almost at will. Yet, computer programmes not only interpret experimental data, they can predict structures using models for the interactions between atoms that are based on the quantum mechanical electronic structure.

Emphasis today is not so much on structure as function. The: *What does it look like?* is now less important than *How does it happen?* Sophisticated experimental and spectroscopic methods can provide answers of function for some simple molecules but they are unable to solve the detailed questions pertinent to biochemical processes. Thus, the computer and its ability to model chemical processes is all-important to current day research. An experimental scientist requires input from specialist theoretical calculation – and the field of theoretical chemistry is itself growing rapidly, perhaps faster than any other sub-discipline of chemistry.

Chemical reactions are characterized by a transition state, the minimum (free) energy that a substrate must obtain for the given process to occur. It is that energy which links the product to the reactant. Experiment has yet to evolve adequately to gain transition state information for most reactions but the computational chemist can using theory. Theory is now an essential adjunct to experiment.

Classical theoretical methods gave us good information on groups of atoms by connecting them with springs, obeying Newton's laws of motion that allow the springs to stretch and compress. However, such simulations are unable to let the bonds actually break. In order to examine a reaction where bonds break and form the involvement of the electrons is vital - quantum mechanical equations that describe electron motion are needed. Even today's most powerful computers rapidly run out of storage space when these are used for molecules of even a few hundred atoms. The 2013 Nobel Prize in Chemistry awards three individuals who laid the foundations for detailed molecular modelling by combining classical and quantum mechanical theory.

The work for which the 2013 award was made focuses on the development of theoretical models that combine classical and quantum mechanical methods to allow modelling of large complex molecules and their reactions. The quantum mechanical approach concentrates on the atomic nuclei and the electrons of interest, while classical mechanics models atoms or groups of atoms. This latter procedure employs much simpler physics and far fewer degrees of freedom to describe the particles and this leads to a computational evaluation which is fast. To thoroughly assess aspects of reactivity in any complex molecule a combination of the two theoretical methods is needed. The laureates have provided the wherewithal now to do this so that the reactivity of a complex molecule can be better understood. Indeed, as a result of their studies, a computer may be able to simulate exactly how one complex biological molecule reacts with another in a cell at some point in the future.

The development of quantum mechanics stems from the early pioneering work of Planck, Bohr, de Broglie, Heisenberg, Schrödinger and Dirac who were awarded the Nobel Prize in Physics over the 1918-1933 period. It is from these studies that from about 1965 the construction of inter- and intramolecular potentials for complex systems was developed with Lifson and Warshel pioneering the Consistent Force Field (CFF) method in 1968.[1] Lifson, now with Levitt, used the method to give the first stable conformation of two macromolecules from experimental model co-ordinates, myoglobin and lysozyme. Here they found the deviations of peptide bonds from planar conformation, and the deviations in various bond angles from their respective average values, to contribute significantly to the refined protein conformation. A set of non-bonded potential functions, applicable to the equilibrium of a folded protein in an aqueous medium, were described and tested on myoglobin.[2] The advantage of such potential-based methods is that the calculations provide the energy easily and large molecules can be studied.

Given a complex molecule, the classical potential-based methods will provide the molecular energy of the complex molecule but not its conformation. Allinger was able to generate one characteristic conformation of a molecule with his molecular mechanics (MM) methods while statistical mechanics methods such as molecular dynamics (MD) or Monte Carlo (MC) generate many configurations, ideally with correct statistical weighting. The work of the laureates is independent of which method is chosen to obtain the conformation to be studied. What the 2013 Prize concentrates on are the ways changes in energy of the real system are accurately and efficiently assessed when there are relatively large changes in geometry (or electronic configuration) in a small part of the molecule that is coupled strongly with a surrounding that is only weakly perturbed. This can best be achieved using the Car-Parinello approach[3] but it is too demanding of computer time for large biomolecules. The solution is to combine classical modelling of the large surrounding with quantum mechanical (chemical) theory to model the core where the chemistry takes place.

It was Martin Karplus with Arieh Warshel who made the first breakthrough in 1972.Warshel had a background in inter- and intramolecular potential modelling and Karplus had the quantum chemical experience. Between them a computer programme was constructed that provided the ground and excited state potential surfaces of conjugated molecules by formally separating the σ- and π-electrons.[4] The σ-electron framework was computed using a (classical) empirical potential function and the π-framework by a semi-empirical (quantum chemical) model of the Parriser-Parr-Pople (PPP) type. Initially this was applied to 1,3-butadiene, 1,3,5-hexatriene, 1,3-cyclohexadiene and 1,8-diphenyloctatetraene with excellent results. This early procedure was limited to planar molecules whose symmetry provided a natural separation of the σ- and π-electrons. However, in 1976 Warshel and Levitt constructed a general scheme that partitioned the electrons included in the classical model from those of the quantum chemical method and they applied it to an enzyme reaction by studying the stability of the carbonium ion intermediate formed in the cleavage of a glycosidic bond by lysozyme.[5] They had, in particular, to evolve coupling terms for the interaction between the classical and quantum chemical system and each of these with the surrounding dielectric. Their procedure considered the whole enzyme-substrate together with the surrounding solvent system and it included all the energetic factors[6] that might contribute to the reaction. This allowed them to evaluate all the different quantum mechanical and classical energy factors that could affect the reaction pathway. Incorporation of the polarizability of the atoms of the protein into the calculation allowed them to reproduce, for the first time, the energetic balance found in hydrogen transfer reactions and deal properly with electrostatic interactions.

The electrostatic polarization of the enzyme atoms and the orientation of the dipoles of the surrounding water molecules were simulated by a microscopic dielectric model. Warshel and Levitt found that the solvation energy resulting from this polarization was considerable and, therefore, that it had to be included in any realistic calculation of every chemical reaction involving more than an isolated molecule *in vacuo*. Without it, acidic groups never became ionized and the charge distribution on the substrate was never reasonable. They found that this same dielectric model could follow the reaction of the substrate in solution that then allowed appropriate comparison with the enzymic reaction. In this early study the electrostatic stabilization was important in increasing the rate of the step that led to the carbonium ion formation while steric factors, such as the strain of the substrate on binding to lysozyme, did not contribute significantly.

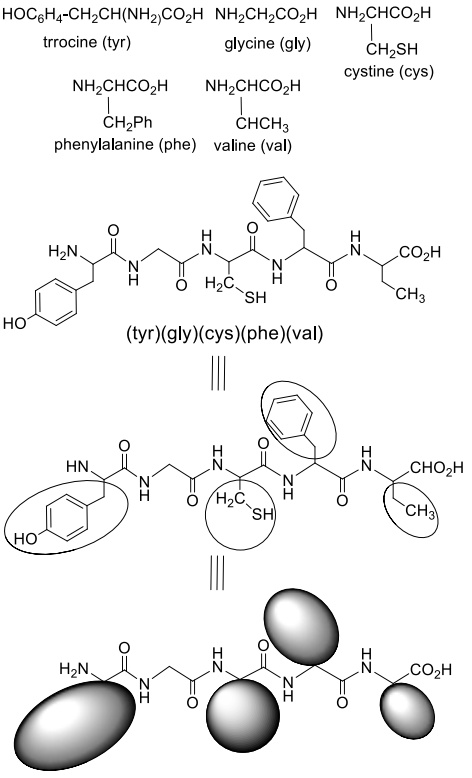

Fig. 1. The amino acids (upper) can give the polypeptide chain (tyr)(gly)(phe)(val) that is simplified by assigning each residue acid an interaction volume that results in the string of pearls structure (lower).

A further step by Levitt and Warshel in 1975 made possible the study of larger systems.[7] Here the pair examined the folding of the protein Bovine Pancreas Trypsin Inhibitor (BPTI), one of the smallest and simplest globular proteins comprised of a single-chain polypeptide with 58 amino acid residues and a molecular mass of 6512. It contains both α helical and β-sheet regions, as well as three disulfide bonds, which help to stabilise the tertiary structure of the molecule. Levitt and Warshel simplified the wrapping of the protein from an open to a folded conformation by assigning each amino acid residue in the chain an interaction volume. This led to a string of pearls-like structure that treated the atoms as rigid units for use as pseudo atoms in the classical simulation (see Fig.1). As will be appreciated, the approach sped up the computation even more.

With the larger part of the biomolecule now able to be treated appropriately and with the classical and quantum chemical procedures coupled, the pathway was opened for advances in big molecule computation by other chemists. Many have advanced the field not simply for organic and biochemical study but also to deal with heterogeneous catalysis and a number of molecules together in a liquid. It is due to the early observations and advances made by Karplus, Levitt and Warshel that computational chemistry is now better able to deal with the complexity of modern chemistry.

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Additional information is available from: *www.nobelprize.org*

Chemistry in the News

Anthea Lees

Dr Jonathon Sperry awarded a Rutherford Discovery Fellowship 2013

The Science and Innovation Minister Steven Joyce announced the names of the 2013 recipients of the Rutherford Discovery Fellowships at the end of September 2013.

Congratulations goes to Dr Jonathon Sperry who is one of ten of New Zealand's top early to mid-career researchers have been awarded Rutherford Discovery Fellowships in 2013. Dr Sperry is a Senior Lecturer in the School of Chemical Sciences at the University of Auckland and his award was entitled: 'Inert C-H Bonds: A gateway to molecular complexity'.

These prestigious five-year awards provide funding of up to $160,000 per annum to support researchers who are between three and eight years post-Ph.D. The awards are funded by the Ministry of Business, Innovation and Employment and are administered by the Royal society.

Steven Joyce stated: "The Rutherford Discovery Fellowships provide our emerging scientific leaders each with a funding package of $800,000 over five years that will allow them to undertake important research that will be valuable for New Zealand's future. The Fellowships will help attract and retain our most talented early-career researchers and encourage their career development in this country."

MarinLit acquired by The Royal Society of Chemistry

The Royal Society of Chemistry made an announcement on 19th September 2013 that it had acquired the marine natural products database MarinLit, which was developed and has been maintained up to the present time, by Professors John Blunt, Murray Munro and co-workers at the University of Canterbury.

MarinLit is a database of the marine natural products literature containing bibliographical data together with information relating to taxonomy, trivial names, compound information, structures, collection location coordinates, UV data, functional groups and molecular masses. The number of references in the database currently stands at 26,400 with information pertaining to over 24,200 marine natural products.

Prof Blunt stated "After spending 25 years developing and maintaining the MarinLit database we were very keen to see it continue to be available to the many users around the world who have found it such a useful support in their research. Having the RSC take over production seemed a logical step as it would fit very well into their growing stable of eScience and ePublishing offerings servicing the scientific community."

Prof Munro also commented ""In my wildest dreams I never thought that my large unwieldy stack of filing cards from the 60s and 70s could be translated to an electronic version, let alone to something used world-wide. The transfer now of MarinLit to the Royal Society of Chemistry seems an appropriate way for us to bow out"

The Executive Director of Strategic Innovation at the Royal Society of Chemistry Dr David James, quotes: "We are delighted to announce that we have completed the acquisition of MarinLit. Over the last 25 years John Blunt, Murray Munro and their colleagues at the University of Canterbury have developed the leading marine natural product (MNP) database, a powerful tool in support of the varied areas of MNP research and we are very excited to welcome MarinLit into the Royal Society of Chemistry's portfolio. It makes an excellent strategic fit with our current activities and natural product research. We are looking forward to working with John and Murray to manage this transition and continue to develop MarinLit's future. We will continue to support and enhance MarinLit, our first development will be to produce a web based version, which will be ready in early 2014."

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.

Alexander Porfirevich Borodin (1834-1887)

Brian Halton

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Alexander Borodin (1834-1887)

The name Borodin has little or no meaning to many, but to others it conjures up the sounds of the Polovtsian Dances from the opera *Prince Igor*. The 1953 musical *Kismet* popularised the themes most notably with "Stranger in Paradise" (credited to Wright and Forrest) that came from the "Gliding Dance of the Maidens" and for which Wright, Forrest and Borodin (posthumously) gained a 1954 Tony Award. Alexander Borodin was, and remains, a highly respected composer. He was one of the Russian group called "The Mighty Handful" - "Moguchaya kuchka" in Russian - a group of five Russian composers [Mily Balakirev (leader), César Cui, Modest Mussorgsky, Nikolai Rimsky-Korsakov and Alexander Borodin], who in 1862 banded together in St. Petersburg in an attempt to create a truly national school of Russian music. They were all young self-trained amateurs at that time; Balakirev was 25 years of age, Cui 27, Mussorgsky 23, Borodin the eldest at 28, and Rimsky-Korsakov just 18 years old. Their objective was to free Russian music of the stifling influence of Italian opera, German lieder, and other western European forms. In a sense, they were a branch of the Romantic Nationalist movement in Russia.

The Mighty Handful from top-bottom (L to R) Mily Balakirev, César Cui, Modest Mussorgsky, Nikolai Rimsky-Korsakov, and Alexander Borodin

Despite becoming a recognised and highly respected musician, Borodin simply claimed to be a "Sunday musician" with Monday to Saturday occupied with his profession. His most famous quote is "*Respectable people do not write music or make love as a career*" but he is also credited with:[1]

As a composer seeking to remain anonymous, I am shy of confessing my musical activity... For others it is their chief business, the occupation and aim of life. For me it is a relaxation, a pastime which distracts me from my principal business, my professorship. I love my profession and my science. I love the Academy and my pupils, male and female, because to direct the work of young people, one must be close to them.

Alexander Borodin was a chemist!

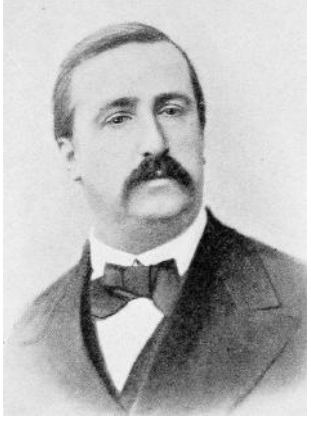
The Early Years

Alexander Porfirevich Borodin was born on February 12, 1834, in St. Petersburg, the illegitimate son of Prince Luka Gedianov, a 62-year old Imeritian and his 25 year old maid Avdotya (Narva) Konstantinovna Antonova. The baby was born in Gedianov's house and continued to live there with his natural father and mother until 1839, when Luka arranged a marriage for Narva to an elderly retired army physician in order to gain her an inheritance. Avdotya was a woman of the middle classes whom Luka loved but was unable to marry given the class structure of Russia at that time. As was common then, the boy was given the name of one of Gedianov's servants, Porfirevich Borodin, and registered as his son. Thus, Alexander was raised in a privileged household where he always addressed his mother as Auntie or Aunt Mimi. She had two other illegitimate sons with Prince Luka but it seems that they were not given the same treatment.[1]

Alexander's father was in receipt of a liberal government pension following the 1810 annexation of Imeritia (Georgia) by Russia and was able to live a life of luxury. He devoted monies for his son's education, which was organised by his mother. Alexander remained his father's serf until 1840 when, sometime before his death Luka Gedianov released him. Alexander was a weak and unhealthy child, a constitution inherited from his parents that remained with him throughout his life. Largely because of this he was home tutored until he was 13 years old. By then he was fluent in German, French and English, and subsequently mastered Italian to the extent that he could write scientific papers in the language. He had an impressive memory and excelled in all academic subjects. As a boy he studied the flute, cello and piano and wrote his first composition

when he was nine, the polka *Helene* that was dedicated to a woman named Elena; he could reproduce on the piano what he had heard a military band play. In addition, he performed creditably on the oboe, the clarinet and several brass instruments. At 13 years of age he composed a concerto for flute and piano and a trio for two violins and cello. The oriental heritage from his father seems to account for his looks and the themes that pervade so much of his subsequent music. However, it was not so much music as chemistry that was his passion and Alexander fitted up a small laboratory in his room and performed experiments making fireworks and performing chemical magic for his friends. One of these, Mikhail (Misha) Shchiglev (who became a noted music teacher), has said:[2] *Almost the entire apartment was filled with jars, retorts and all sorts of chemicals. Tubes with crystalline solutions were on the windows everywhere. The whole house smelled of his chemical preparations and his visiting teachers were afraid of a fire*. Prince Luka did not think a musical career appropriate for a person of royal lineage and discouraged Alexander from it, pressuring him to a medical career that was supported by the step-father. Borodin became attracted to organic chemistry.

The young Borodin was sent to school to prepare for his professional career where Misha was also a pupil. Between classes the two boys would go to a piano and play the symphonies of Hayden and Beethoven in duet arrangements.[3] In 1850, Alexander entered the Medico-Surgical Academy of the University of St. Petersburg making friends with many of the German students. Although his coursework was full-time, Borodin still attended concerts and practiced his flute and cello, even spending all night with like-minded friends.[4] In his first year of study he took classes in botany, zoology, anatomy and crystallography while in his second year he narrowly escaped death from an infection acquired during an autopsy. Throughout this time his main efforts were in chemistry where the noted Nikolay Nikolaevich Zinin was professor. It was Zinin who discovered the reduction of nitroaromatics to anilines with sodium sulfide (the Zinin reaction) and is the reputed grandfather of Russian organic chemistry. In his third year Borodin asked if he could study under his direction and was allowed to do so. However, on one occasion he spent almost 24 hours playing uninterrupted concert music and for this he was severely reprimanded for "trying to hunt two hares at the same time".[3]



Alexander Borodin

Russian Zinin stamp

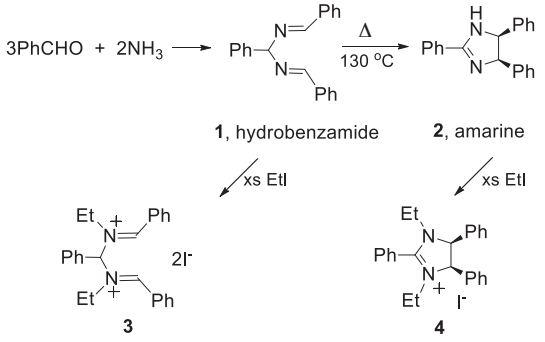
In 1856 Borodin completed his courses at the Academy, by which time he had gained the respect of Zinin and the other academics, and was highly praised. He was immediately appointed a junior officer in the Preobrazhensky Regiment, one of the oldest and elite regiments of the Russian army, as assistant in general pathology and therapy at the Second Military-Land Forces Hospital.[3,5] It was here that he met Modest Mussorgsky, who was then a 17-year old military officer and the Duty Officer.[2] Their friendship and their music grew. Apparently the sight of blood was not to Borodin's taste but he pursued his studies for the completion of his medical degree. In August 1857, he travelled to Brussels with a senior oculist to attend an international ophthalmic congress and then, in March 1858 presented a paper "On the action of ethyl iodide on hydrobenzamide and amarine" to the Russian Academy of Sciences,[5] which was published later that year[3] giving him his first paper.[6] This was from work carried out at the military hospital.[7] Two months later he was awarded his medical doctorate by the academy for his thesis "On the analogy of arsenic acid and phosphoric acid in chemical and toxicological behaviour".[5] Apparently, his was the first thesis at the academy to be written and defended in the Russian language rather than Latin.[8]

The Professional Chemist

After a short time, Borodin returned to Zinin's laboratory as his assistant and not too long afterwards was appointed to a position in the academy. Then in 1859, Zinin arranged for him and other young Russian chemists, including Mendeleev, to gain experience in Europe, and this at the government's expense. The idea was to ready the young men for academic careers on their return home. For Borodin, study was to be in Heidelberg with Bunsen but he found the conditions in his laboratory unsuitable and so he worked under Erlenmeyer instead.[7] Here his studies involved the benzidenes, which became important materials in the dye industry, and he published five papers from his 12-hour work days (starting at 5 am!)[9] in Erlenmeyer's journal, *Zeitcshrift für Chemie und Pharmacie*.[10] It is interesting to note that in work published in Russia and France at that time, 6 was used as the molecular weight of carbon whereas the value of 12 was used in Erlenmeyer's laboratory and it appeared in the Heidelberg papers.

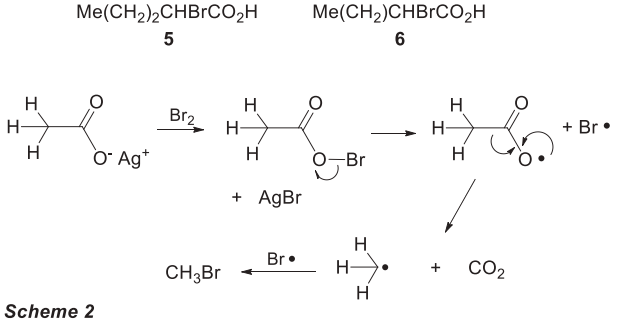
The first piece of work published by Borodin[6] defined above was his attempt to settle the formulae of hydrobenzamide **1** and amarine **2**, and especially the number of N-H units in each compound. Hydrobenzamide, first synthesised in France in 1836, was known to give ama-

rine on heating to 130 °C. By allowing each compound to separately react with ethyl iodide, we now recognise that the imine nitrogen atoms are quaternised and the H of the >NH group replaced by an ethyl giving rise to the corresponding salts **3** and **4** (Scheme 1). Although Borodin did not reach these conclusions,[9] he returned to the compounds later, presenting his final results at a meeting in Kazan in 1873 when he gave the correct number of NH moieties as zero for **1** and one for **2**.[11] This latter work was published by Borodin that year and reported in *Berichte der Deutschen Chemischen Gesellschaft* (1873) by von Richter and from there to the *Journal of the Chemical Society* in 1874.[11]



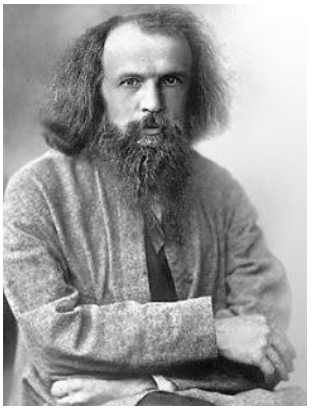
Scheme 1

In his next published work, Borodin reported the syntheses of bromo-butyric **5**, and -valeric **6** acids using the 1836 method of Péligot,[12] which involved treating the silver salt of the acid with bromine vapour. He found the compounds decomposed on distillation in contrast with the stability of bromoacetic acid, which he could not prepare in the same way. Treatment of silver acetate with bromine vapour led only to silver bromide and other gaseous products from which carbon dioxide was isolated and the other was thought to be either *methyl* (or ethyl) *bromide* (Scheme 2).[9] This study was reported on a visit to Paris in late 1860, where Adolphe Wurtz was carrying out his studies at the École de Medicine. It was published in French the following year and then in German in *Liebig's Annalen*.[13] The formation of an alkyl bromide from the silver salt of the derived acid has been routinely described as the Hunsdiecker reaction[14] reported only in 1942. Borodin's 1860 contribution more than 80 years earlier, received scant recognition in the chemical literature[9] until recently; the account on *Google* notes that the reaction now also is called the Borodin reaction, the name commonly used in Russia.



Scheme 2

It was very soon after arriving in Heidelberg that Borodin first met Dmitri Mendeleev who also was to work with Bunsen. Mendeleev did work with Bunsen but took to setting up his own private laboratory rather than use the facilities available in the university. The two young men became lifelong friends and took holidays together while in Germany. The year after arriving in Heidelberg the pair went on a Southern German holiday with Zinin prior to attending the famous[15] 1861 International Chemical Congress at Karlsruhe early in September 1860. This was the first ever international chemistry conference, called by Kekulé so that European chemists could discuss matters of nomenclature, notation, and atomic weights. It attracted some 126 chemists.[15] The problems facing the delegates were enormous as illustrated by the fact that values of 6/12 and 8/16 were commonly in use for the atomic weights of carbon and oxygen, respectively, and that multiple designation for the formula of a compound were common (see Fig. 1).



Dimitri Mendeleev

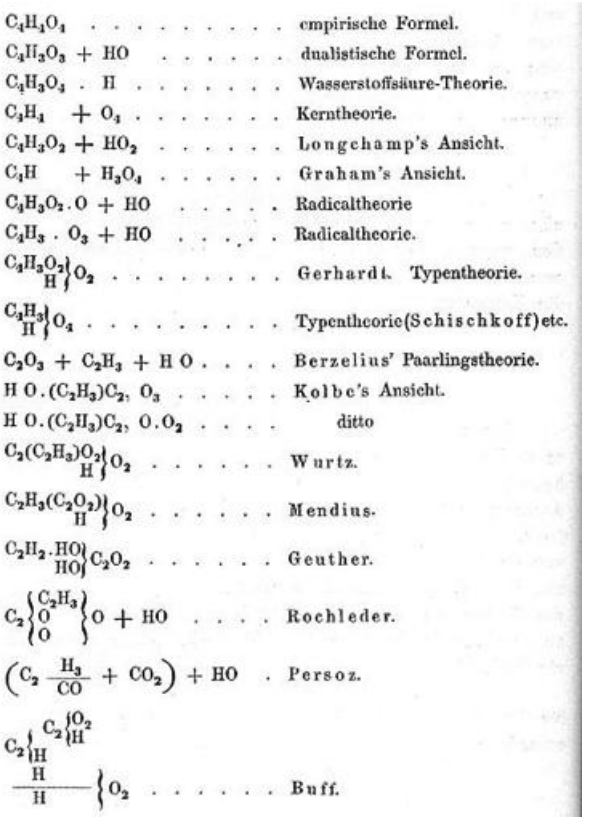


Fig. 1. The 19 formulae for acetic acid, CH_3CO_2H, in Kekulé's 1861 *Lehrbuch der Organischen Chemie*.

It was in May of 1861 that Borodin first met the acclaimed 29-year old Russian pianist Ekaterina Sergeyevna Protopopova, who was in Heidelberg recovering from tuber-

culosis. They attended concerts together and met other musically oriented people in a friendship that turned to love. When Ekaterina's health deteriorated and she was required to go to Italy in October for the winter months, Borodin chose to escort her there. Once in Piza neither of the pair wanted to separate and on visiting Sebastiano de Lucca and Paolo Tassinari at the university, Borodin found first class facilities much more attractive than those in Heidelberg.

He was invited to stay and work there, which he did.[5] He even had his (by then) fiancé living in the same apartment during the 1861-62 winter and through the spring of 1862.[5]

Ekaterina Protopopova (Borodina)

It was during the period in Pisa that Alexander carried out some of the work for which he became renowned, though not completely justifiably. The laboratory was equipped with very expensive platinum retorts,[16] indispensible for any work with highly corrosive materials and his intent by then was to study fluorine and its salts. He studied potassium hydrogen fluoride (KHF_2) among other fluorides and compared these salts with their simpler bases (KF) and then continued the work to organofluorine compounds. He could perform these experiments avoiding the toxic vapours by using the retorts in the open, even in the Italian winter. This led to the preparation of benzoyl fluoride (PhCOF) from the acid chloride, the first replacement of a chlorine substituent by fluorine. The results were published in the Italian journal *Il Nuovo Cimento* and *Comptes Rendus* in 1862 and *Liebig's* Annalen in 1863.[17] However, this was not the first synthesis of an organofluorine compound as was popularly thought. Methyl fluoride (MeF) had been reported in 1835/36 by Dumas and Péligot and the higher homologue, ethyl fluoride, by Frémy in 1854 (Scheme 3), but their studies were not well recognised. Thus, Borodin's work was popularly, but incorrectly, accredited as first synthesis of an organofluorine compound.[18] It was this that gave him much recognition and kudos. His true fame here comes from showing that fluorides tend to form double fluorides, that sodium and potassium fluorides readily do this with a weak acid (as in Eq. 1), and in his use of the double salt to effect the first 'F for C' halogen substitution (Scheme 3). He showed that the organic fluorides were more akin to their chloro analogues than were the inorganic fluorides to their chloride equivalents.

Borodin and Protopopova returned to Russia in the late summer of 1862 arriving back on September 20th. However, financial difficulties prevented their marriage at that time and Ekaterina went back to the warmer Moscow to live in her mother's house. Alexander returned to St. Petersburg where their marriage took place on April 17 the following year. At this time Borodin was involved with the building of a new chemistry laboratory that included an apartment for the pair. Immediately on his return to the academy Alexander had become fully occupied, and in early December he was appointed as adjunct-professor[5] and began to teach organic chemistry. He was much admired by his students: a handsome man, over 1.8 metres tall of a slightly oriental appearance with large deep eyes and a warm smile.[4] When working in his laboratory students felt as if they were in their own home. When Borodin was working and active in his laboratory, he never forgot music, humming tunes and talking of his new works. When he retired to his adjacent apartment the sounds of his piano could be heard by them.[8]

$$MeCO_2H + 2KF \longrightarrow MeCO_2K + KF.HF \quad \text{.... Eq. 1}$$

Dumas & Péligot, 1835-36:

$$(MeO)_2SO_2 + 2KF \longrightarrow 2MeF + K_2SO_4$$

Frémy, 1854:

$$EtOSO_3^- K^+ + KHF_2 \longrightarrow EtF + K_2SO_4 + HF$$

Borodin, 1863:

$$PhCOCl + KHF_2 \longrightarrow PhCOF + KCl + HF$$

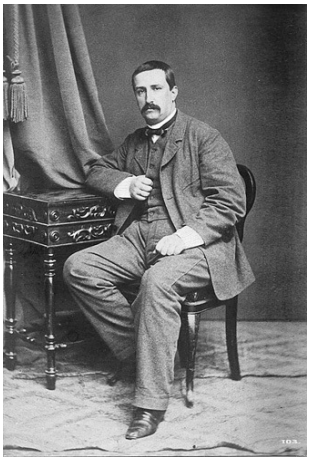
Scheme 3

It was shortly after his return to St. Petersburg that Borodin was introduced to Mily Balakirev, the Russian pianist, conductor and composer who inducted him to the inner circle of composers that became known as the "Mighty Handful" (see above). As the proficiency of the musicians increased they played their works-in-progress for the group to critique.[8,19] Borodin's life took a decisive turn from the first meeting of this group as he accepted Balakirev's challenge to continue writing music in his limited spare time under the man's tutelage. He began work on his first symphony then, the first performance of which was in 1869 under the baton of Balakirev.

Although something of an outpost of culture and academic prowess, St. Petersburg in the 1860s was an exciting place to be.[19] Borodin was starting to establish himself at the Medico-Surgical Academy of the University. He became full professor in 1864 and subsequently Zinin's successor. His friend Dimitri Mendeleev became a professor at the Imperial (now State) Technological Institute in the same city and, a year later in 1865, moved to the Saint Petersburg Imperial (now State) University. By 1871 Mendeleev had transformed Saint Petersburg into an internationally recognised center for chemistry research. Moreover, through his efforts, and with Borodin's support, the Russian Chemical Society was founded in 1868 by a resolution of the chemical section of the First Congress of Russian Naturalists and Physicians. It elected Zinin as its first president.

Over the years Borodin undertook the range of consultancies expected of a professor and turned his experimental studies to what became his most concerted work. This was on the nature of aldehydes, which above all his other works have been used to rank him with his peers. He

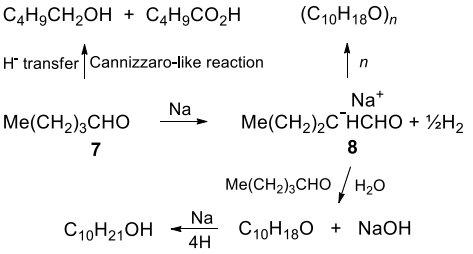
Founders of the Russian Chemical Society 1868; Borodin is back row 5th from left



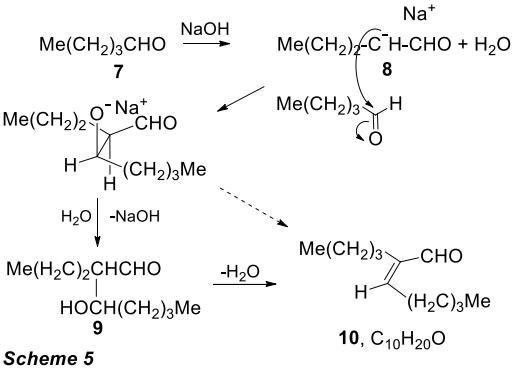
Undated portrait of Alexander Borodin

discovered the aldol reaction almost simultaneously with Wurtz in France but was working on aldehydes before either him or August Kekulé in Germany.[16] Borodin's first published results in this area were two 1864 papers on the action of sodium on aldehydes.[20] These were some five years before Kekulé's first paper appeared, and Borodin felt that it intruded too much on what he then regarded as his area.[16] It was a similar occurrence with Wurtz who also did not acknowledge the Russian studies. In early March 1872, at the Russian Chemical Society meeting, Borodin disclosed three studies that gave more detail to his 1864 papers and included[16] the formation of aldol as also obtained by Wurtz.[21] The issue and disputes with aldol formation lie with kudos and the scientist's place in history, not least because the reaction and the further dehydration (the aldol condensation) became so important in chemistry. So what was it Borodin did?

The first studies concerned the action of sodium metal on valeraldehyde [pentanal **7**, $CH_3(CH_2)_3CHO$] from which Borodin hoped to obtain the sodium salt, presumably **8** in Scheme 4. However, the metal displaced hydrogen and gave a product mixture from which pentanol and pentanoic acid were isolated (Scheme 4). The former could arise by reduction at the metal surface or with the acid by hydride-transfer in a Cannizzaro-like reaction. From the remaining mixture after treating with water, compounds with empirical formulae $C_{10}H_{22}O$ (15-25%) and $C_{10}H_{18}O$ (20-30%) were obtained.[3] The first of these two proved to be an alcohol while the second, although less clearly defined, was consistent analytically with two molecules of **7** combining with loss of H_2O. It can be assumed that proton abstraction from **7** gave the α-anion **8** (Scheme 4) and that this reacted with a second molecule of the aldehyde to give the alcohol-aldehyde (aldol) product **9** (Scheme 5), which would dehydrate to the conjugated enal **10** under aldol condensation conditions. The $C_{10}H_{22}O$ alcohol could be the diol resulting from reduction of the aldehyde function of **9**. Borodin did not establish the nature of **10** other than to state that analysis corresponded (in modern terms) to a dimeric condensation product.

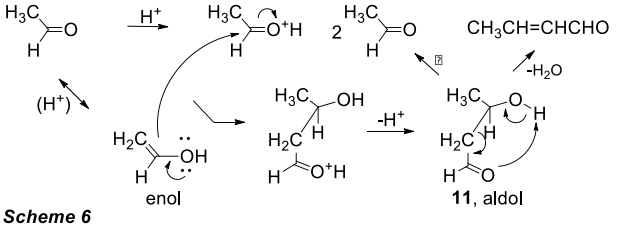


Scheme 4



Scheme 5

His subsequent studies involved castor oil, which on pyrolysis gives heptanal [$CH_3(CH_2)_5CHO$] and undec-10-enoic acid [CH_2=$CH(CH_2)_8CO_2H$]. Borodin found that this aldehyde gave a series of products similar to those from pentanal **7**. It was during this study that he examined the behaviour of acetaldehyde with HCl whereupon he obtained aldol **11** and found that it reverted to aldehyde on distillation (Scheme 6). The isolation of 'aldol' was at about the same time as it was obtained by Wurtz and represents the acid catalyzed version of the reaction. This was the subject of his third announcement at the March 1872 meeting.[22] However, Borodin conceded priority to Wurtz and granted equal priority to the earlier product obtained by Kekulé. He then retreated from the study of aldehydes. Indeed, his chemical output dropped and his researches reverted to the amine chemistry discussed earlier. His educational concerns came to the fore, with his professorial duties in and out of the university placing increased demands on his time. His composing remained a spare time occupation but his music became more serious as he began work on his opera Prince Igor. His final



Scheme 6

chemical works were oriented more towards medicinal chemistry and his last paper concerned improvements to a method he set up for determining the urea content of urine. He had developed hypobromite oxidation of urea (Eq. 2) to the stage where an accurate measurement of as little as 2.25 mL (10^{-4} M) of nitrogen could be made.

$$3NaOBr + H_2NCONH_2 \rightarrow N_2 + CO_2 + 2H_2O + 3NaBr \quad \text{.... (Eq. 2)}$$

There is, however, one other study of Borodin's that deserves mention and this also concerns his medicinal chemistry. At a meeting of the Russian Chemical Society on 1 February 1871, he delivered an account of work performed by Dr Krylov under his guidance.[23] This involved the determination of fat in heart muscles affected by fatty degeneration. Mixed with the fat they found material resembling lecithin (a generic term for any group of yellow-brownish fatty substances occurring in animal and plant tissues). They expected this to give glycerol on hydrolysis but none was found, rather a white solid that was subsequently shown to be cholesterol. Although cholesterol had been discovered in bile and in gallstones by François Poulletier de la Salle as early as 1769 and then rediscovered in 1815 and named "cholesterine" by Eugène Chevreul, its structure was not determined until 1932. The Borodin-Krylov finding of esterified cholesterol in heart lipid received little attention at the time, but it pre-dates the recognition of harmful effects from cholesterol by approximately 40 years and is likely the first linking of the two.

Borodin's dedicated work at the Medico-Surgical Academy was recognised by his promotion to academician in 1877.

Commemorative Borodin coin

The Borodin Family

Borodin's wife Ekaterina, although much affected by ill health, was a keen fighter for women's rights and she converted Alexander to the cause.[1] He was of the opinion that there should be equality of educational opportunity and became convinced that women would make good doctors. He took to opening his laboratory to students, meeting the costs himself and then, in 1872, founded the School of Medicine for Women in conjunction with Professor Rudnev and Mde. Tarnovskaya.[8] This was his proudest achievement. He inaugurated his "Course in Obstetrics" for women, and was professor of chemistry at the women's school teaching courses for some 15 years from its inception until his death. During these years he spent less and less time in the laboratory as the demands of his women's rights campaigns and other philanthropic causes came to the fore. Because of Ekaterina's health each summer was spent in the country with her in simple accommodations as she spent long periods in her mother's home in Moscow where the climate was kinder than in St. Petersburg. Alexander, whose heath also had never been the best,[3] contracted cholera[19] in 1885 and continued to use the confinements to concentrate on his music.

The Borodins had no children of their own but sheltered and cared for many unfortunate and orphaned children. Ekaterina liked to entertain and their charity led to a home that was usually full and happy with the pair showing little concern for wealth. They adopted one girl, Liza Balaneva, who married Alexander Pavlovich Dianin, a former pupil of her father whose work was reported upon by Borodin at the 1873 meeting. Dianin gained a PhD from Jenna in 1777, his medical doctorate in 1882, and joined the faculty of the Medico-Surgical Academy. He was the successor to his father-in-law and is now known for his discovery of bisphenol A and its condensation product with acetone. This latter now has importance in host-guest chemistry and is known as Dianin's compound.

From 1872 until his death in 1887, Borodin worked on his now famous opera, Prince Igor, which was still incomplete at his death. It was finished by his musical friends Rimsky-Korsakov and Glazunov and given its premiere in St. Petersburg on 4 November 1890.[3] Alexander Boron's death came quickly and unexpectedly. On the night of 27 November 1887, the last day of the Russian Carnival, Alexander had arranged for a fancy dress evening in one of the lecture rooms in the academy. He appeared in traditional Russian attire – a deep red woollen shirt, baggy trousers and high boots – showing his usual hospitality and was the life-and-soul-of the party. While involved in one of the many vigorous dances he collapsed and died of a heart attack.

His esteem as a teacher was such that his students carried his coffin from the laboratory to the Tikhvin Cemetery at the Alexander Nevsky Monastery. He is buried there next to his friend Modest Mussorgsky and close to Glinka, Balakirev, Dostoyevsky, Tchaikovsky and Ruberstein. The respect in which he was held by his women students

Borodin's tomb in the Tikhvin Cemetery at the Alexander Nevsky Monastery, St. Petersburg

was shown by a silver plate on his burial casket:[1] "*To the Founder, Protector and Defender of the School of Medicine for Women*". The grave was surrounded by an ornate iron railing that carried at its centre a shield the circumference of which was adorned with the empirical formulae of the compounds Borodin had made.[3] Ekaterina was not in St. Petersburg at the time of Alexander's death or funeral and, when told, she became very distressed. Her health deteriorated and she died some five months later.

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Marsden Awards 2013

Anthea Lees

The Marsden Fund supports research excellence in science, technology, engineering and maths, social sciences and the humanities. Applicants submitted their pre-proposals in February 2013 and if successful were then invited to submit a full proposal at the end of June 2013 with the final funding decisions being announced on 30th October 2013.

The awards were split into two categories - fast-start awards are for early career researchers and worth up to $300,000 over a three-year period, while standard awards are for all applicants and can be worth as much as $850,000 over a three-year period.

A total of 1155 preliminary proposals were submitted in 2013 and of these 229 were called to submit full proposals. 109 proposals were subsequently allocated a share of $59 million, which represented an overall success rate of 9.4%. More than one-third of these awards (40) were Marsden Fast-Starts, designed to support outstanding researchers early in their careers (between zero and seven years after their PhD). Out of the total number of preliminary proposals 88 proposals used the 'Chemical Sciences' code in their 'Fields of research' classifications. At the full proposal stage out of the 229 full proposals invited, 15 of these used the 'Chemical Sciences' code and finally at contract stage 6 of the 109 funded proposals were classified as 'Chemical Sciences'.

The Marsden assessment process comprises a total of ten different funding panels, made up of researchers who are experts in their fields and these panels make their funding recommendations to the Marsden Fund council.

The majority of the Chemistry preliminary proposals (56) were submitted to the Physics, Chemistry and Biochemistry (PCB) panel whilst about one third were submitted to any one of six other panels: biomedical sciences (BMS), Engineering and interdisciplinary sciences (EIS), cellular, molecular and physical biology (CMP), earth sciences and astronomy (ESA), ecology, evolution and behaviour (EEB) and mathematical and information sciences.

The Marsden Fund Council chairperson Professor Juliet Gerrard stated: "The Marsden Fund supports investigator-led research, and plays a vital role in building a healthier, socially more cohesive and economically stronger nation. The Marsden Fund is a unique resource used to support our very best researchers. The research done through investigator-led projects has been shown worldwide to create the most important breakthroughs, which ultimately change the way we operate, think and live. The Marsden Fund is an investment in the long term success of New Zealand.

The huge enthusiasm of New Zealand researchers to engage in basic research means the Fund is always oversubscribed, but this year we were able to fund a larger number of projects from across the country thanks to the increase in government funding. New Zealand produces researchers that are of the very highest calibre and their Marsden-funded research is highly respected internationally. The extra projects will enable more great ideas to be put to the test and showcase New Zealand science on a world stage."

For funding highlights see: *www.royalsociety.org.nz/programmes/funds/marsden/news/articles/2013-highlights/*

Dates of Note

The uranium atom was split for the first time 75 years ago on Jan 22, 1939, using the cyclotron at Columbia University in New York City. ***John Polanyi***, the German-Canadian chemist who shared the 1986 Nobel Prize for Chemistry (with Herschbach and Lee) for contributions to the development of reaction dynamics, has his 85th birthday on Jan 23. On Feb 25, 1839, ***Michael Faraday*** made the first public announcement of the existence of photography as the subject of his *Friday Evening Discourse* at the Royal Institution. ***Alexander King***, the Scottish chemist who was a pioneer in environmental awareness, was born on Jan 26, 1909, the day in 1904 that ***Ancel Keys***, the American nutritionist who was the first to identify the role of saturated fats in causing heart disease, was born. ***Albert Sauveur***, the Belgian-born American metallurgist whose microscopic and photomicroscopic studies of metal structures make him one of the founders of physical metallurgy, died on Jan 26, 75 years ago. Jan 27 marks 50 years since E.I. duPont de Nemours Co. introduced *Corfam* as its hydrocarbon-based, synthetic substitute for leather to be used in shoes, handbags, belts and suitcases, etc. Despite DuPont's predictions, it was snubbed by customers and seems to have been the biggest failure of the company. ***Benoit Clapeyron***, the French engineer who expressed Carnot's ideas on heat analytically in the Clausius-Clapeyron equation, died on Jan 28, 150 years ago; he was born on Feb 26, 1799. ***Fritz Haber***, the 1918 Nobel Chemistry prize winner for his ammonia synthesis, died 80 years ago on Jan 29, 1934. ***Rudolf Ludwig Mössbauer*** (Mössbauer effect) has his 85th birthday on Jan 31. ***George Fownes***, the English chemist who prepared furfurine and benzoline as the first examples of vegetoalkali or organic salt-bases, as they were then known, and coined their names, died on Jan 31, 1849.

On Feb 1, 1944, ***DNA*** was identified as the hereditary agent in a virus and published in a report by Avery, MacLeod, and McCarty. The day also marks 55 years since Texas Instruments was issued a patent on the integrated circuit. On Feb 3, 1879, the first practically usable incandescent filament electric light bulb was demonstrated to an audience of 700 by its inventor Joseph Wilson Swan at the Literary and Philosophical Society of Newcastle-upon-Tyne, England. ***Joseph Priestley***, the English chemist, clergyman and political theorist who discovered the element oxygen and is remembered for his later work on gases, died on Feb 6, 1804. ***Gardner Quincy Colton***, the first to administer nitrous oxide as an anaesthetic, was born on Feb 7, 100 years ago, while ***Hans Jenny***, the Swiss agricultural chemist and soil scientist who developed numerical functions to describe soil in terms of five interacting factors, was born this day in 1899. ***Dmitry Ivanovich Mendeleev*** was born on Feb 8, 1834. Feb 11 marks 75 years since *Nature* published a theoretical paper on nuclear fission, the term coined by authors ***Lise Meitner*** and her nephew ***Otto Fritsch***. It is also the day that ***J. Willard Gibbs***, the American physicist and chemist known for contributions to vector analysis and a founder of physical chemistry, was born in 1839, 175 years ago. ***Vladimir Vasilyevich Markovnikov***, the Russian organic chemist who established the Markovnikov addition rule, died this same day, Feb 11, in 1904. ***Kotaro Honda***, the Japanese metallurgist whose studies of the metallurgy of iron and steel led to the invention of powerful magnetic steels including KS Magnetic Steel and New KS Magnetic Steel, died on Feb 12, 1954, the same day as ***Søren Peder Lauritz Sørensen***, the Danish chemist who introduced the concept of pH, 75 years ago. ***Julius Thomsen***, the Danish chemist who tabulated the amount of heat released or absorbed in 3,500 chemical reactions, died on Feb 13, 1909. ***Heinrich Caro***, the Technical Director of Badische Anilin & Soda Fabrik that commercialized alizarin and (amongst others) indigo, was born on Feb 13, 1834.

Captain ***James Cook*** died on Feb 14, 1779. ***Galileo Galilei*** was born on Feb 15, 1654. ***Robert Kennedy Duncan***, who died on Feb 18, 100 years ago, was the Canadian industrial chemist, teacher and populariser of science who advocated partnering scientific research and industry to create new and better consumer products. ***Svante August Arrhenius*** was born on Feb 19, 1859 while Sir ***Ernest Marsden*** was born on the same day in 1889, 125 years ago. Feb 19 also marks the 250th anniversary of the birth of ***Gottlieb Sigismund Kirchhof***, the German-Russian chemist who applied the first controlled catalytic reaction to produce glucose, developed a method for refining vegetable oil, and also experimented with brewing and fermentation. ***Ludwig Eduard Boltzmann***, the Austrian physicist who founded statistical mechanics, was born on Feb 20, 1844, the day in 1934 that a US patent was issued to Ernest O. Lawrence for his *Method and Apparatus for Acceleration of Ions*- ***the cyclotron***. ***Johannes Nicolaus Brønsted***, the Danish chemist known for the acid-base concept, was born on Feb 22, 1879. ***Casimir Funk***, born on Feb 23, 1884, was the Polish-American biochemist who coined the term *vitamine* from his investigations of the anti-beriberi factor which he showed to be an amine; as all similar substances were not amines, the named changed to *vitamin*. ***Leo Hendrik Baekeland***, the Belgian-American industrial chemist who invented the first thermosetting plastic, Bakelite, died on Feb 23, 1944, the day 60 years ago that the first mass inoculation of children against polio with the Salk vaccine began. ***Glenn T. Seaborg***, the American nuclear chemist for whom element 106 (seaborgium) was named, died on Feb 25, 1999 while ***Phoebus Levene***, the Russian-American chemist who was a pioneer in the study of nucleic acids, was born that day in 1869. On Feb 27, 1879, the artificial sweetener, ***saccharin***, was discovered by ***Constantin Fahlberg***, while he was researching coal tar compounds for Ira Remsen at Johns Hopkins University in Baltimore. ***Edmond Frémy***, the French chemist best known for his discovery of hydrogen fluoride and investigations of fluorine compounds, was born on Feb 28, 200 years ago; he died on Feb 2, 1894.

On Mar 1, 1954, the US hydrogen bomb code-named *Bravo* was detonated at Bikini, in the Marshall Islands, the most powerful of all thermonuclear bomb tests in the area and similar to 1,000 atomic bombs of the kind

dropped on Hiroshima during WWII. The American biochemist ***Elmer McCollum***, who originated the letter system of naming vitamins was born on Mar 3, 1879 while ***Gerhard Hertzberg***, the German-Canadian physicist awarded the 1971 Nobel Prize for Chemistry for his contributions to the knowledge of electronic structure and geometry of molecules and particularly free radicals, died this day 15 years ago. ***Alexander Stanley Elmore***, the British technologist who with his brother jointly developed flotation processes to separate valuable ore, such as copper, from the worthless rock with which it is associated when mined, died on Mar 4, 1944. Mar 6 is the day in 1869 that ***Dmitry Mendeleev*** published his first version of the periodic table. ***Ludwig Mond*** was born on Mar 7, 1839 while ***Otto Diels*** died the same day 60 years ago. ***Ernst Julius Cohen***, the Dutch chemist who researched piezochemistry, electrochemical thermodynamics, polymorphism of compounds and the allotropy of metals, especially tin, was also born on Mar 7, but in 1869. Mar 7, 1799 is the day that the Royal Institution in England was founded. ***Otto Hahn***, the German chemist who (with Strassmann) is credited with the discovery of nuclear fission and who is recognized by element 105 carrying the name hafnium, was born on Mar 8, 1879. ***F. M. Crafts***, of Friedel-Crafts fame, was born this day in 1839. ***Gustav Robert Kirchhoff***, the German physicist who (with Bunsen) established the theory of spectral analysis, was born on Mar 12, 1824, the day in 1924 that Comte ***Hilaire Chardonnet***, the French chemist and industrialist who developed rayon, died.

Mar 14 marks 135 years since the 1879 birth of ***Albert Einstein*** while the 15th is the 10th anniversary of the death of ***John Pople***, who devised the Gaussian suite of programmes. ***Franciscus Sylviu***, the Dutch physician, chemist and physiologist who founded the 17th century school of medicine that related living processes to chemical reactions, was born on Mar 15, 400 years ago. On Mar 19, 1969, the use of radioactive ^{252}Cf in monitoring the sulfur content of coal was announced by the US Atomic Energy Commission. It is also the day in 1474 that the first patent law was enacted in Venice. ***Andrés Manuel Del Rio***, the Spanish-American mineralogist who, in 1801, discovered the element later named vanadium, died on Mar 23, 1849. It was this day 25 years ago that *fusion at room temperature* was claimed by ***Martin Fleischmann*** and ***Stan Pons***. ***Peter Debye***, the Dutch-American physical chemist whose studies of dipole moments, X-rays, and light scattering in gases gave him the 1936 Nobel Prize for Chemistry, was born on Mar 24, 1884. ***Georgius Agricola***, the German mineralogist and scholar regarded as the father of mineralogy, was born on Mar 24, 1494. ***Karl Karlovich Klaus (Claus)***, the Russian chemist who discovered ruthenium in 1844, died 150 years ago on Mar 24, 1864, as did ***Johann Wolfgang Döbereiner*** in 1849. He was the German chemist who identified triads of elements in order of increasing atomic mass; the mass of the central member was approximately the average of the other two, and intermediate in chemical properties between the other two elements. The triads are now found as consecutive members of the groups of the periodic table. ***Friedrich Bergius***, the German chemist who devised a process to convert coal dust and hydrogen directly into gasoline and lubricating oils without isolating intermediate products, died on Mar 30, 65 years ago. The Eiffel Tower was inaugurated on Mar 31, 125 years ago.

On Apr 2, 1889, 125 years ago, ***Charles M. Hall*** patented an inexpensive electrolytic process to extract aluminium from its ore, while Apr 3 marks 80 years since the cats-eye road mark was patented in Britain by Percy Shaw. Sir ***William Crookes***, the English physicist and chemist who discovered the element thallium and showed that cathode-rays were fast-moving, negatively-charged particles, died on Apr 4, 1919. On Apr 6, 1869 celluloid became the first thermoplastic to be patented while the same day in 1889, 125 years ago, the ***Kodak Camera*** was placed on sale by George Eastman. It is the day in 1794 that Joseph Priestley left England for the US. New Zealand-born Australian physician ***Frederick Cossom Hollows*** was born on Apr 9, 1929. ***Michel-Eugène Chevreul***, the French chemist who initiated the study of the chemistry of fats and gave margarine its name, died 125 years ago on Apr 9. ***Jean-Baptiste-André Dumas***, the French pioneer in organic chemistry who laid the foundations for Kekulé's later work, died on Apr 10, 1884. The day also marks the anniversary of the 1944 *synthesis of quinine* by ***Woodward*** and ***von Doering*** at Harvard University. ***Otto Meyerhoff***, the chemist who worked on carbohydrate metabolism and working muscle, was born on Apr 12, 1884. ***Rachel Carson***, the American marine biologist, conservationist and writer who warned the public about the long term effects of misusing pesticides in her 1962 book, *Silent Spring*, died 50 years ago on Apr 14. ***Jean Charles Marignac***, the Swiss chemist whose life work consisted of making many precise determinations of atomic weights suggested the possibility of isotopes and the packing fraction of nuclei, died on Apr 15, 120 years ago. ***Wilhelm Körner***, the German organic chemist who showed how to determine the positions of the substituents on di- and tri-substituted benzenes five years before the van't Hoff-Le Bel hypothesis of tetrahedral carbon, was born on Apr 20, 1839 (175 years ago). ***Charles Friedel***, the French organic chemist and mineralogist who with American James Mason Crafts discovered in 1877 the chemical process known as the Friedel-Crafts reaction, died on Apr 20, 1899. ***Paul Karrer***, the Swiss chemist who investigated the constitution of carotenoids, flavins, and vitamins A and B_2, and was 1937 Nobel Prize Laureate (with Haworth), was born on Apr 21, 1889. *Donald J.* ***Cram***, the 1987 Nobel laureate in chemistry (with Pedersen and Lehn) for host-guest work, was born on 22 April 1919 and atomic scientist ***J. Robert Oppenheimer*** the same day in 1904.

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Article

SciFinder® Future Leaders in Chemistry

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In September 2013, the 15 chemistry PhD students and postdoctoral scientists from 13 countries involved in the *SciFinder® Future Leaders in Chemistry (FLIC)* programme came together to "help shape the future of chemical information". As the NZ representative I had a very enjoyable 10 days of the latest science, fruitful teamwork, and exclusive meetings with senior staff of the Chemical Abstract Service (CAS), and their great US hospitality.

The SciFinder® FLIC provided a wonderful, compact programme which included full expenses, all transportation, US$1,000 cash per person, and attendance at the ACS Fall Meeting & Exposition in Indianapolis as well as the CAS Campus in Columbus, Ohio. Starting with a stroll through the Indianapolis Zoo to whisk away jet-lag and break the ice between the 15 of us, the programme was crowned by two days at the CAS Campus where we found out just how the information goes in the SciFinder® database and the efforts made that keep it one of the best databases for chemists, biologists, and material scientists. Here, we worked in small groups to identify where SciFinder® has potential for advancement and the developments we, end-users, wish for. My personal highlights were a visit to the impressive server room and the workshops with Product Development on the latest SciFinder® prototype.

The ACS Fall Meeting attracted 10,000. Here, I spoke about my VUW/MacDiarmid Institute research on nano-gold as a value-adding colorant for NZ wool fibres and spent three stimulating days learning of the latest colloid research, networking at poster sessions, workshops, and attending a hilarious Alton Brown show about science in cooking.

One of our excursions was to the headquarters of the Battelle Memorial Institute that performs contract research for industry and governments and is the world's largest non-profit research and development organization. Another excursion took us to the business incubator TechColumbus that hosts many small start-up companies which share facilities to decrease fixed costs; collaboration and shared knowledge is encouraged. Imagine, nanofibres are made in your 4 x 4 m^2 clean room facility while next door a designer revolutionises the fashion world!

I gained a new level of understanding SciFinder®, exposure to the latest research in my field, and new friends/colleagues from Australia, Canada, Germany, Italy, Israel, Japan, Poland, South Africa, the Netherlands, the US and UK. Dr. Peter Carlton and Sherri Syfers, the FLIC programme coordinators, were excellent hosts and did an outstanding job in selecting an awesome group of young researchers. I was privileged to represent NZ and become a SciFinder® FLIC.

NOTE: Applications for SciFinder® FLIC 2014 in San Francisco open soon.

Dr Thomas Faust (Sydney) and Andrea Kolb (VUW)

CAS workshop with Michael W. Dennis (Vice-President); bound volumes of Chemical Abstracts are around the walls

Time for a Change

Katherine Hebditch

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It has been a very long time in the making, but the new law governing patents in New Zealand is finally about to come into force.[1] The present New Zealand Patents Act (the law relating to patents) is 60 years old. You could argue it is even older because it was based on the 1949 British Patents Act.

Discussions about updating the New Zealand law started in 1990. A bill was first introduced into Parliament back in 2009. It has been a long and at times tortured path through Parliament, but the Patents Bill finally received royal ascent in September 2013 and will come into force in September 2014. Here we discuss a few of the changes that may (or may not) affect you.

Raising the Standard

In the main the changes to the law are aimed at raising the standard of granted patents in New Zealand. One of the biggest changes is that the Intellectual Property Office of New Zealand (IPONZ) patent examiners will now be able to examine whether an invention includes an inventive step, i.e. whether or not it is obvious. Presently a patent office examiner cannot refuse to accept a patent application on the basis that the subject matter is not inventive. This is an odd quirk of the present system since a granted patent is not valid if it can be proven that its subject matter is not inventive. However, going to court to prove this is expensive and therefore is often not contemplated unless there is a significant monetary drive to do so. The examination process is aimed at reducing this problem, but will never entirely replace the need or desire to challenge some patents.

More Options for Challenging a Patent

At the moment, a patent application in New Zealand is only published once it has been through examination and been accepted by IPONZ. At this stage any *interested party* can oppose the grant of the patent. However, this can be a relatively long and expensive process (though much less so than a Court challenge).

As part of the new law, patents application will be published 18 months after they have been first filed. There is also specific provision that anyone can submit information to the Patent Office regarding the novelty or inventiveness of a pending patent application once the application has been published. This gives the opportunity for experts in a field to review and comment on patent applications should they wish to do so, opening up more opportunity for the public to have a say in which patents are accepted by IPONZ.

There are also new provisions for anyone to request that an accepted patent application or granted patent is re-examined by the Patent Office. The upside and also downside of this option is that beyond providing a reason for the request, for example information on what was already known prior to the patent application being filed, the requestor takes no further part in the re-examination. This makes this option relatively cheap, but also means there is no right of reply to any arguments the applicant makes in support of the application.

Exclusions from what is Patentable

The new law will introduce specific exclusions to patentability for certain subject matter. The exclusion that has received the most media attention relates to computer programs. It is worth noting that patents will likely still be available for inventions that make use of a computer program to achieve a *physical* result. When the new law comes into force there are likely to be challenges in the Courts concerning where the boundaries lie.

Most of the other exclusions merely confirm what is in practice already presently excluded from patentability in New Zealand. Presently methods of medical and surgical treatment of humans, and human beings and biological processes for their generation, are excluded from patentability. This is on the basis that they are either *contrary to morality* or simply not being included in the definition of what is *an invention.* Court decisions over the years have defined what is *contrary to morality* and what is *an invention*. However, this has been the subject of periodic challenges. The new law codifies these exclusions and may limit the ability to challenge them.

It seems unlikely it will be 60 years before the next Law Change

You may be aware of the TPP (Trans-Pacific Partnership) negotiations which are presently taking place (at least at the time of writing this article). Some of the proposals being forwarded, particularly by the United States, would reverse some of the provisions about to be brought into law in New Zealand. For example, the United States is proposing that patents for methods of medical and surgical treatment should be allowable in all countries signing up to the agreement, as is presently the case in the United States.[2] There are also many other changes to patent law being proposed which are not part of the law about to come into force.

It may be that after 60 years of the same law, we are about to go into an age of swift and repeated patent law reform. This seems to reflect the increasing importance of patent law as part of innovation and commercialisation.

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

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Patent Proze
Baldwins Intellectual Property
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References

1. New Zealand Patents Act 2013.
2. Secret TPP treaty: Advanced Intellectual Property chapter for all 12 nations with negotiating positions, WikiLeaks release: November 13 2013.

Katherine Hebditch of Baldwins Intellectual Property in Auckland specialises in chemistry and biotechnology patents. Katherine obtained her PhD in organic chemistry from the University of Manchester in the UK in 2004. She is currently working towards registration as a patent attorney.

Conference Calendar

2nd International Conference on Clean Energy Science (ICCES2)

Dates: 13-16 April, 2014

Venue: HuangHai Hotel, 75 Yan'an Yi Road,Qingdao, China

Themes: Bio and bioinspired systems for energy conversion, Biofuels and biomass conversion, Clean coal and fossil fuels, CO2 capture, storage and utilization, Electrochemical energy conversion and storage, Hydrogen production and storage, Materials and nanotechnology for energy systems, Photocatalysis & environmental catalysis and Solar energy conversion.

See: *http://www.icces.cn/*

Challenges in Inorganic and Materials Chemistry

Dates: 1-4 July 2014

Venue: University of Dublin, Trinity College, Dublin, Ireland

This will be the follow-up event to successful conferences ISACS 3 and ISACS 8 held in 2010 and 2012 respectively, by bringing together leading scientists from across the world to share scientific developments. The Scientific Committee warmly invites you to take part in ISACS 13 and looks forward to welcoming you to Dublin.

Themes: Main Group Chemistry, Metals in Biology, Organometallic Chemistry and Catalysis, Porous and Solid State Materials and Supramolecular Materials.

See: *www.rsc.org/ConferencesAndEvents/ISACS/ISACS13/index.asp*

The Gordon Research Seminar on Green Chemistry

Dates: 26 - 27 July 2014

Venue: Hong Kong.

A Gordon Research Seminar (GRS) is a forum for graduate students and post-docs to present and discuss their cutting edge research among peers and mentors. The small size and focus on young investigators provide an ideal interactive and unintimidating atmosphere. Each GRS immediately precedes an associated Gordon Research Conference (GRC), and topics addressed at the GRS relate closely to the GRC. The focus of this meeting is on novel research in Green Chemistry, with an emphasis on industrial applications (but all interesting and innovative topics using a green chemical approach are welcome to be submitted). This second GRS on Green Chemistry is an excellent chance to build a collaborative network within the Green Chemistry community, working together towards a better, sustainable future.

See: *www.raci.org.au/events/event/the-gordon-research-seminar-on-green-chemistry*

Challenges in Organic Chemistry

Dates: 7-10 August 2014

Venue: Shanghai Institute of Organic Chemistry, China

Themes: Organic and metal based catalysis, Total Synthesis, New Synthetic methodologies, Physical organic chemistry and Bioorganic and medicinal chemistry.

See: *www.rsc.org/ConferencesAndEvents/ISACS/ISACS14/index.asp*

The International Chemical Congress of Pacific Basin Societies (PACIFICHEM 2015).

Call for second round of Symposium proposals

Date of conference: 15-20 December 2015

Venue: Honolulu, Hawaii, USA

The call for the second round of Symposium proposals closes 1 March 1 2014. Before submitting a proposal review the 11 topic areas for Pacifichem 2015 and the topic area descriptions.

Draft your symposium proposal in a subject area not already covered by the Preliminary Program. The Pacifichem Organizing Committee will look specifically for new symposia not already covered.

Submit your proposal following the Symposium Proposal Submission Guidelines.

See: *http://www.pacifichem.org/technical-program/approved-symposia/*