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

Prajusha V. Velayudhan and Michael R. Mucalo*

Chemistry Department, Faculty of Science and Engineering, The University of Waikato, Private Bag 3105, Hamilton 3240 (email: *m.mucalo@waikato.ac.nz*)

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) ($G = 18 \pm 2\ \mu s$) 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, Staffordshire

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 °C – 24 °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° 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

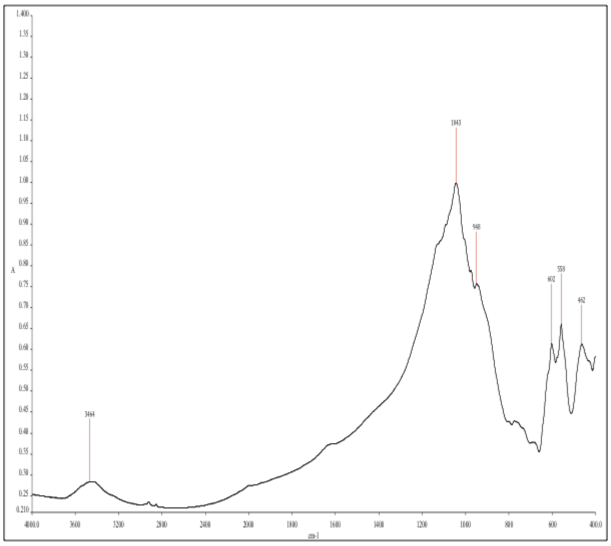

Fig. 1(a). FTIR spectrum of Wileman bone china (B2) of the Victorian era.

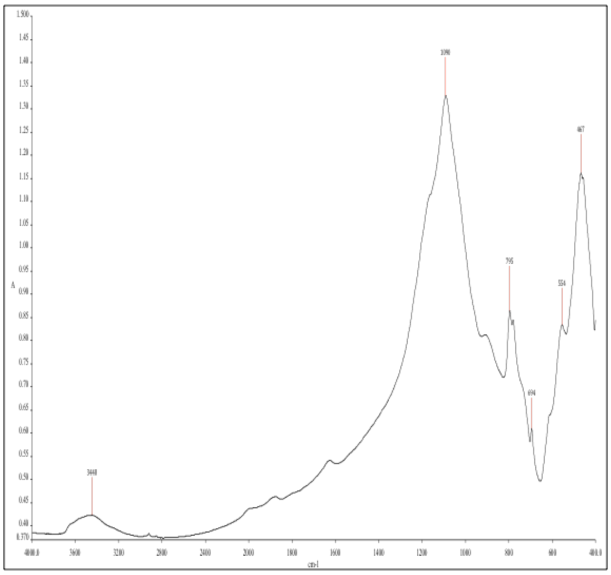

Fig. 1(b). FTIR spectrum of sample C5, a Crown Lynn manufactured item.

$CaAl_2Si_2O_8$ 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

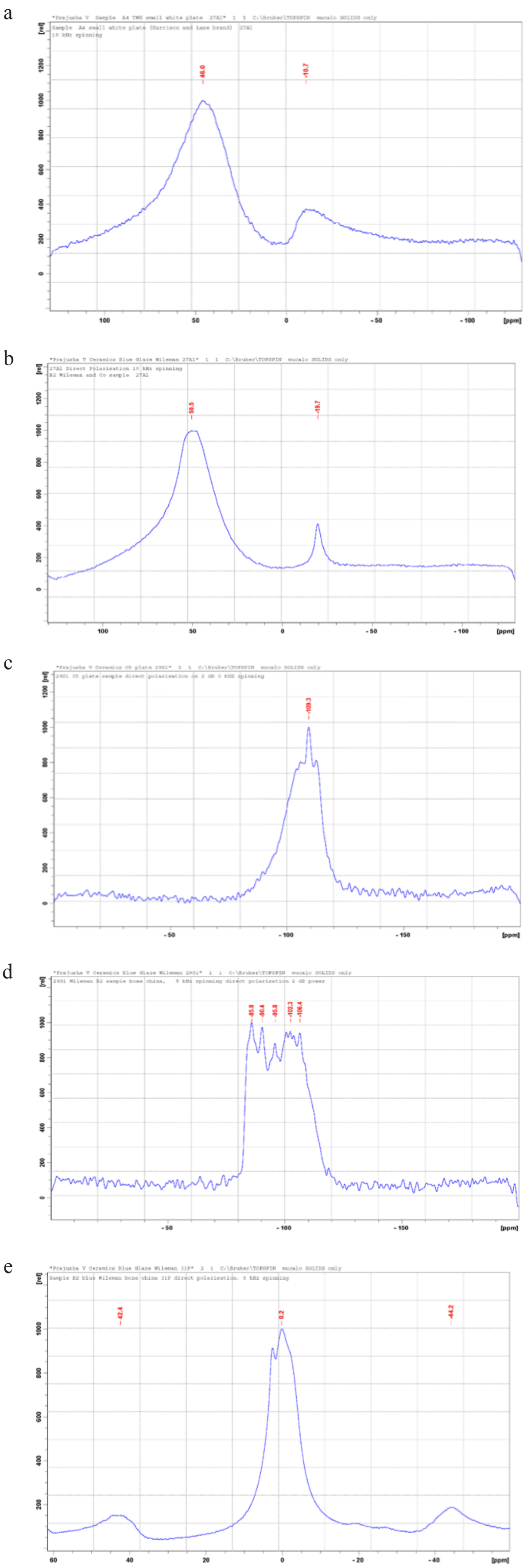

Fig. 2. Solid state NMR spectra of ground domestic ceramic ware: (a) ^{27}Al MAS NMR of a Chinese made white ceramic (A4) sample, (b) ^{27}Al MAS NMR of sample B2, Wileman and Co bone china manufactured in Britain in Victorian/Edwardian times (1892-1911), (c), ^{29}Si MAS NMR of a Crown Lynn "Fleurette" 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 considered 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	**A1**			**A2**			**A3**		**A4**
Elements	**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	**A5**			**A6**	**A7**	**A8**		**A9**
Elements	**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	**A10**			**A11**	
Elements	**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.

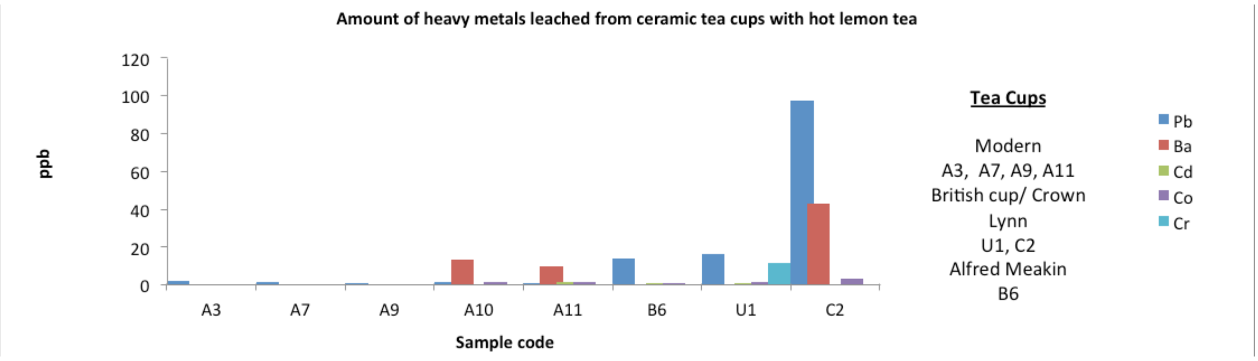

Fig. 3. Leaching results for ceramic mugs/teacups exposed to hot lemon tea

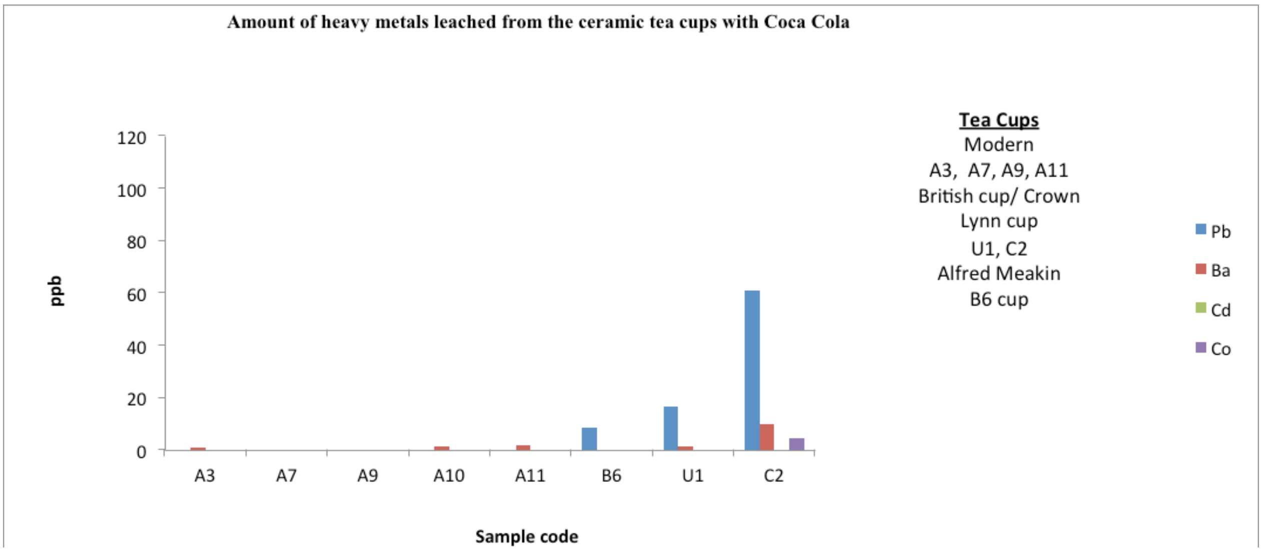

Fig. 4. Leaching results for ceramic mugs/teacups exposed to Coca-Cola.

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.

References

1. OED online, http://www.oed.com/
2. Wu, X.; Zhang, C.; Goldberg, P.; Cohen, D.; Pan, Y.; Arpin, T.; Bar-Yosef, O. *Science* **2012,** 336 (6089) 1696-1700.
3. Packer, J.E.; Robertson, J.; Wansbrough, H. (Eds) *Chemical Processes in New Zealand, Section IX Inorganic Materials C (Ceramic Products),* 2nd ed. 1998
4. Council Directive 85/500/EEC of 15 October 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs, 85/500/EEC, *Official Journal of the European Communities*, No. L 277/12, 20. 10.**84**
5. Commission Directive 2005/31/EC of 29 April 2005, amending Council Directive 84/500/EEC as regards a declaration of compliance and performance criteria of the analytical method for ceramic articles intended to come into contact with foodstuffs, *Official Journal of the European Union,* 30.4.2005.
6. http://www.stuff.co.nz/the-press/business/the-rebuild/8828392/Rebuild-a-boom-time-for-archeologists (accessed 23/10/13)
7. http://www.thepotteries.org/ (accessed 23/10/13)
8. Monk, V.R. *Crown Lynn, A New Zealand Icon,* Penguin Books, Auckland, 2006.
9. http://www.alibaba.com/
10. Lehmann, R.L. *Lead Glazes for Ceramic Foodware*, The International Lead Management Center, Triangle Park, NC, USA, 2002, http://www.ilmc.org/Publications/ILMCFinalCombo8-02B.pdf (accessed 23/10/13)
11. Technical factsheet on Barium, http://www.epa.gov/ogwdw/pdfs/factsheets/ioc/tech/barium.pdf (accessed 23/10/13)
12. Goldstein, J.I.; Yakowitz, H. (Eds). *Practical scanning electron microscopy: electron and ion microprobe analysis,* Plenum Press, New York, **1975**.
13. ASTM C738-94(2011), Standard Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces, *ASTM Volume 15.02 Glass; Ceramic Whitewares*, published April 2013.
14. Elliott, J.C. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*, Elsevier, Amsterdam, 1994.
15. St Pierre, P.D.S. *J. Amer. Ceram. Soc*. **1956**, *39(4),* 147-150.
16. Schneider, H.; Komarneni, S. *Mullite*, Wiley VCH, Weinheim, 2005.
17. Mackenzie, K.J.D.; Smith, M.E. *Multinuclear Solid-State NMR of*

Inorganic Materials, Pergamon, Oxford, 2002.

18. MacKenzie, K.J.D.; Brown, I.W.M.; Meinhold, R.H.; Bowden, M.E. *J. Amer. Ceram. Soc.* **1985**, *68*, 293-297.
19. Colomban, P.; Sagon, G.; Faurel, X. *J. Raman Spectrosc.* **2001***, 32*, 351-360.
20. Castilone, R.J.; Sriram, D.; Carty, W.M.; Snyder, R.L. *J. Amer. Ceram. Soc.* **1999**, *82(10)*, 2819-2824.
21. Moezzi, A.; McDonagh, A.M.; Cortie, M.B. *Chem. Eng. J.* **2012**, *185–186*, 1-22.
22. Wainwright, I.N.M., Taylor, J.M., and Harley, R.D., 'Lead antimonate yellow' in Artists' Pigments: A Handbook of Their History and Characteristics, Volume 1, ed. R.L. Feller, National Gallery of Art, Washington DC (1986) 219-254.
23. Eppler, R. A., *Colorants for Ceramics. Kirk-Othmer Encyclopedia of Chemical Technology* John Wiley and Sons, http://onlinelibrary.wiley.com/doi/10.1002/0471238961.0315121505161612.a01.pub3/abstract (accessed 23/10/13)
24. Chin, T.W.; Loeb, M.; Fong, I.W. *Antimicrob. Agents Chemother.* **1995,** *39(8)*, 1671-1675.
25. Simpson, A.; Shaw, L.; Smith, A.J., *British Dental Journal* **2001**, *190*, 374-376.
26. http://www.ilpi.com/msds/ref/carbondioxide.html (accessed Oct 2013)
27. Elliott, H.A.; Herzig, L.M. *Journal of Soil Contamination* **2010**, *8(1)* 105-116