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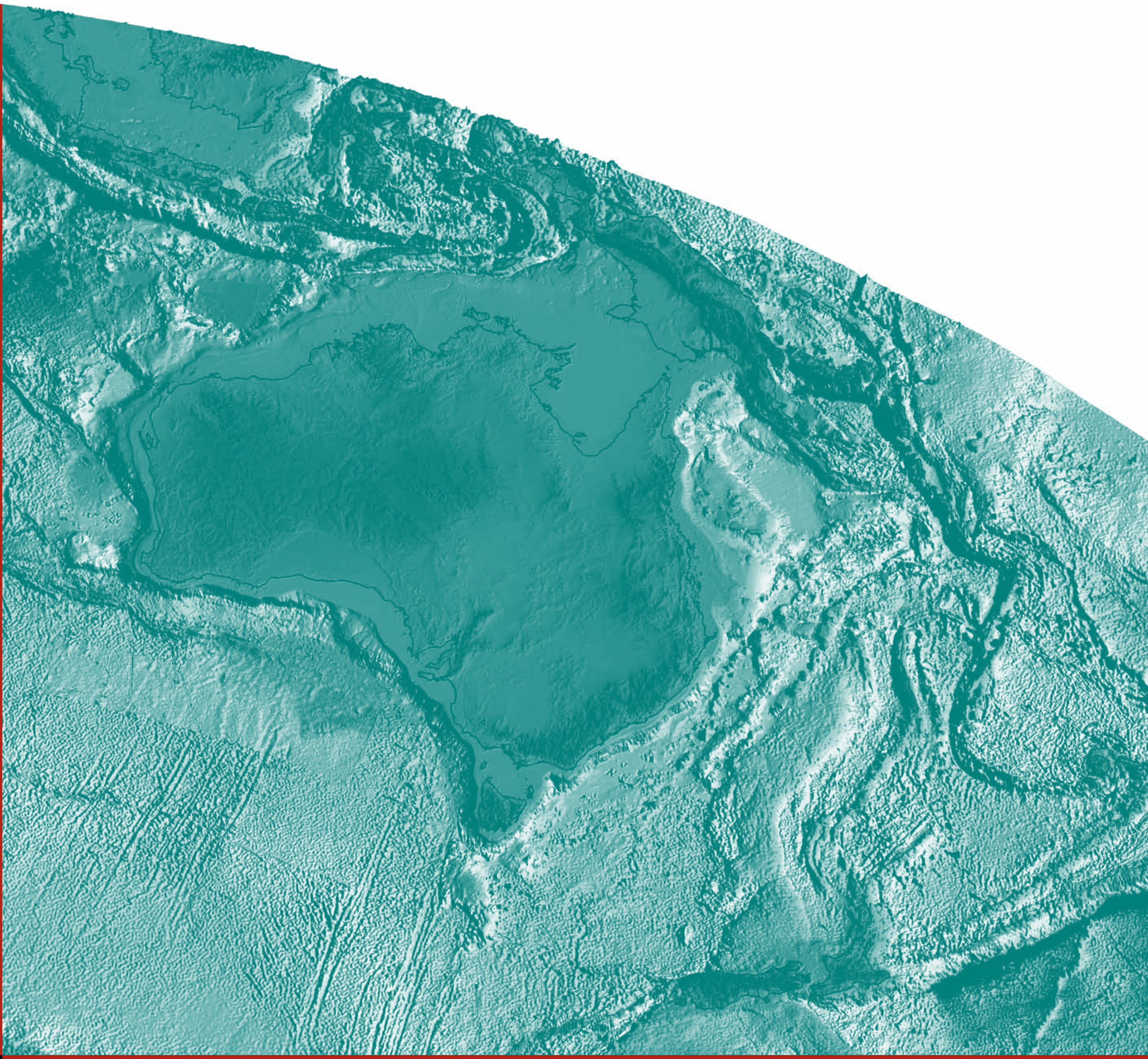

APPLYING GEOSCIENCE TO AUSTRALIA'S MOST IMPORTANT CHALLENGES

National Geochemical Survey of Australia: Analytical Methods Manual

GEOSCIENCE AUSTRALIA
RECORD 2010/15

by

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Executive Summary

The National Geochemical Survey of Australia (NGSA) project has collected samples from 1315 sites located in 1186 catchments (~10 % of which were sampled in duplicate) covering over 80 % of Australia, in a collaborative venture between Geoscience Australia and the geoscience agencies of all States and the Northern Territory. At each site, two depth intervals were sampled and two grain size fractions were separated, giving 5260 samples to be analysed.

Samples were analysed for:

1. total content of multiple elements, analysed by x-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS)
2. aqua regia soluble content of multiple elements, including low-level gold (Au), analysed by ICP-MS
3. aqua regia soluble content of selenium (Se), analysed by ICP-MS
4. ligand extractable content of multiple elements, analysed by ICP-MS
5. fluoride (F) after alkaline fusion, analysed by ion specific electrode (ISE)
6. platinum group elements (PGEs) after fire assay, analysed by ICP-MS
7. pH, electrical conductivity and particle size distribution of bulk samples

Nearly 750,000 analyses were carried out according to the methods described herein for the National Geochemical Survey of Australia.

Introduction

A 5-year Onshore Energy Security Program (OESP) was announced in 2006 to enable Geoscience Australia to deliver high quality, pre-competitive geoscience information relating to onshore energy prospectivity (Johnson, 2006). The National Geochemical Survey of Australia (NGSA), which is part of this programme (Baldwin, 2007), collected transported regolith (sediment) samples from across the Australian continent and analysed their inorganic chemical composition. The NGSA will provide the only nation-wide, internally consistent geochemical dataset with state-of-the-art detection limits. It aims to:

- Help calibrate and ground-truth the airborne radiometrics coverage of Australia (including addressing mother-daughter disequilibrium in the uranium-decay chain);
- Fill gaps in the existing airborne radiometric and geochemical coverages of Australia with quality data;
- Permit multi-element characterisation and ranking of radiometric anomalies (e.g. differentiation of uranium signatures from ‘hot’ granites, black shales or palaeochannels); and
- Provide fundamental data to enable first-order characterisation of geothermal hot-spots.

As such, the NGSA project (http://www.ga.gov.au/minerals/research/national/geochemical/index.jsp) supports and adds value to a number of other OESP projects, particularly the Australia-Wide Airborne Geophysical Survey project (http://www.ga.gov.au/minerals/research/national/radiometric/index.jsp; Minty *et al*., 2009a) and the Geothermal Energy project (http://www.ga.gov.au/minerals/research/national/geothermal/index.jsp). Additionally, the NGSA will have spin-off outcomes in mineral exploration for other commodities and natural resource management.

By its completion in 2011, the NGSA will deliver:

- A geochemical dataset that is national in scope, internally consistent and acquired through the application of state-of-the-art methods and instrumentation;
- A web-delivered geochemical atlas of Australia for some 60+ elements/parameters showing for the first time what the concentrations of these elements are in surface materials at the national scale and how they vary spatially; and
- Reports and papers on energy resource prospectivity and other implications.

Samples have been collected from 1186 catchments (or 1315 sites, including duplicates), which together cover over 6M km^2 or ~80% of Australia at the average sample density of 1 site per 5500 km^2. Approximately 200 catchments in South Australia and Western Australia could not be sampled during this project due to access limitations. Collaboration with State and Northern Territory geoscience agencies was critical for the completion of the project, particularly regarding the sampling phase.

Field procedures were reported in Lech *et al.* (2007) and sample preparation protocols were documented in Caritat *et al*. (2009). In the present report, we discuss details of the sample analysis methods.

Background to the Project

The NGSA project aims to provide pre-competitive data and knowledge to support exploration for energy resources in Australia. In particular, it will improve the existing knowledge of the concentrations and distributions of energy-related elements such as uranium (U) and thorium (Th) at the national scale.

The project is underpinned by a series of pilot geochemical surveys carried out in recent years by Geoscience Australia and the Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME) to test robust and cost-effective protocols for sample collection, preparation and analysis. Examples of these are the Riverina (Caritat *et al.*, 2005; Caritat *et al.*, 2007), the Gawler (Caritat *et al.*, 2008a) and the Thomson (Caritat and Lech, 2007; Lech and Caritat, 2007) pilot geochemical surveys. Selected results from these pilot projects have been summarised in Caritat *et al.* (2008b).

The current national project, briefly described below, is being conducted in collaboration with all the State and the Northern Territory geoscience agencies.

RATIONALE

The national geochemical survey was initiated because of the realisation that there is no complete geochemical coverage available for Australia and because such a data layer is an important complement to national-scale geological and geophysical datasets (Caritat *et al.*, 2008c).

The distribution of geochemical data available through the national repository (OZCHEM database) at the time NGSA was initiated is shown in Figure 1. The map shows that there are vast areas of the country (>60 %) that lack any geochemical information. Also, where geochemical data are available, they are often not comparable as a result of:

- Inconsistent sampling material (e.g. rocks of various types and/or degree of alteration, mineralisation or weathering);
- Inconsistent sample preparation methods (e.g. total analyses *versus* partial digests with weak acids);
- Differences in instrumentation used, leading to variable lower limits of detection between datasets (e.g. older *versus* state-of-the-art instruments);
- Lack of metadata on data quality (e.g. instrument calibration, bias, precision, sample type description, replicates, etc.); and
- Variable suite of elements analysed (e.g. sometimes a very limited suite such as gold (Au) only or Au + copper (Cu)).

Although a significantly improved nation-wide, levelled coverage of airborne gamma-ray spectrometric (radiometric) data (Minty *et al.*, 2009a,b) became available (Figure 2) during the course of the NGSA project, field calibration of radiogenic elements potassium (K), U or Th is perhaps not as systematic as it could be and the question of disequilibrium in the radiogenic decay chain is poorly constrained as a result. It is hoped that the NGSA data, in combination with the new radiometric coverage, will yield insights into this problem.

Some regional geochemical surveys have been carried out in parts of Australia (e.g. Morris *et al.*, 1998; Cornelius *et al.*, 2008; the pilot geochemical surveys mentioned above), but no national coverage exists. The modern concept of regional geochemical surveys was first developed in the 1960s, and it has since proven to be a reliable tool for mineral exploration at various scales (Garrett *et al.*, 2008; Smith and Reimann, 2008).

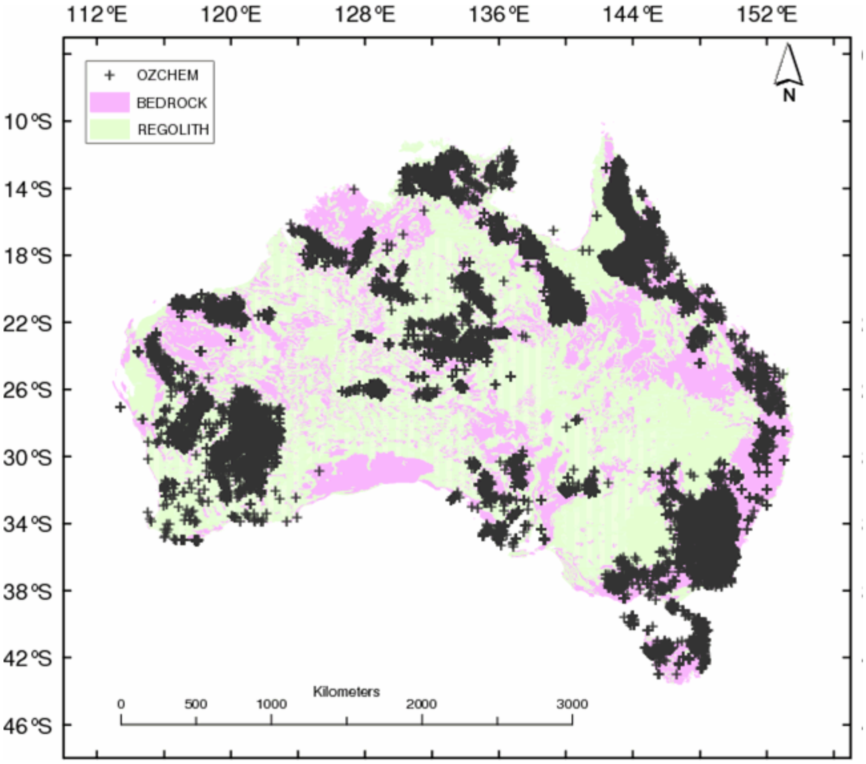

Figure 1. Distribution of whole rock geochemical data in Australia (plus signs) extracted from the OZCHEM national database as at June 2006, overlain on bedrock and regolith coverage.

OBJECTIVES

The initial objectives of the NGSA project were to:

- Collect transported regolith samples at the outlet of large catchments covering >90 % of Australia using an ultra low sampling density approach;
- Prepare and analyse the samples to extract the maximum amount of geochemical information (60+ elements/parameters) using internally consistent, state-of-the-art techniques;
- Populate the national geochemical database with the resulting new data; and
- Compile an atlas of geochemical maps for use by the mineral exploration industry to identify areas of interest in terms of energy-related resources and other mineral commodities, which can then be the focus of targeted exploration efforts.

STRATEGY

The sampling method has been adapted to Australian landscape and climate conditions (e.g., importance of aeolian landforms in some areas, climate ranging from tropical to arid). It has been fine-tuned and field-tested during the Riverina, Gawler and Thomson pilot projects (e.g. see Caritat *et al.*, 2008b). The cost of a national survey was kept reasonably low by applying an ultra low sampling density approach (generally accepted to mean between 1 site/1000 km^2 and 1 site/10,000 km^2).

The strategy adopted for the national geochemical survey is briefly described below.

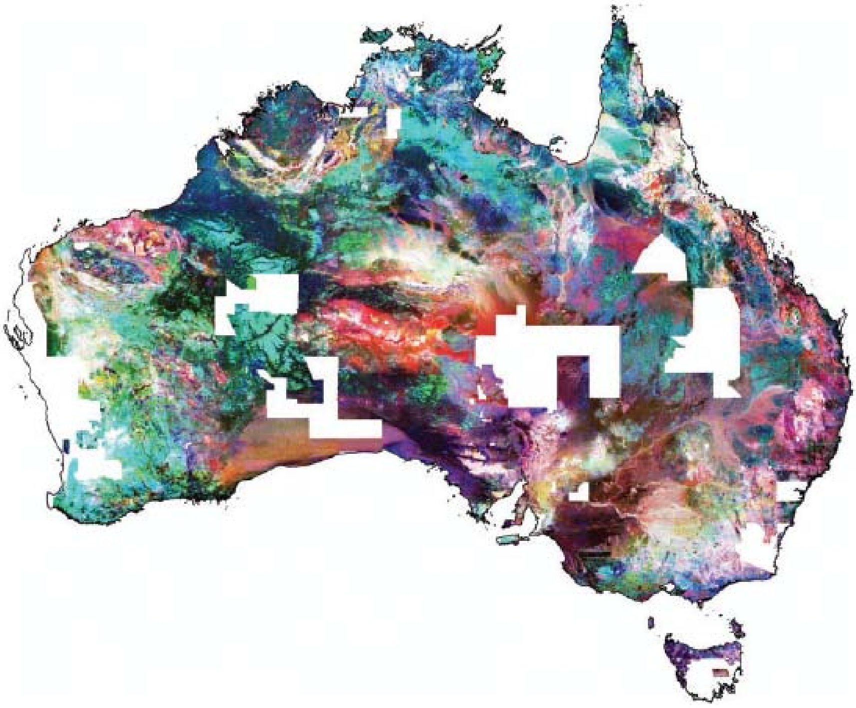

Figure 2. Ternary image (K-red, eU-blue, eTh-green) of Australia derived from the new levelled National Radioelement Database (Minty et al., 2009b).

Sampling media

Catchment outlet sediments (similar to floodplain sediments in most cases) were sampled at two depths (0-10 cm below the surface as well as a ~20 cm interval at a depth of between ~60 and 80 cm). The term 'catchment outlet sediment' was deliberately chosen because it is more general than 'floodplain sediment' to allow for those cases where aeolian influence is important in the regolith formation process.

Sampling sites

Initially, 1390 catchments covering 91 % (or about seven million km^2) of Australia across all States and Territories were targeted for sampling (Figure 3). In total, it was expected that 1529 samples (1390 catchments + 10 % of which are sampled in duplicate) would be collected. Most catchments were sampled near their outlet, while those exhibiting internal or poorly defined drainage were sampled at, or as close as possible to, their lowest point. Lech *et al.* (2007) gave details of the method for determining sampling sites. Catchments smaller than 1000 km^2 (mostly coastal) and small islands were not included in the survey. The resulting distribution of catchment outlet sites targeted for sampling is shown in Figure 4 and translates to an average sampling density of around 1 site/5500 km^2.

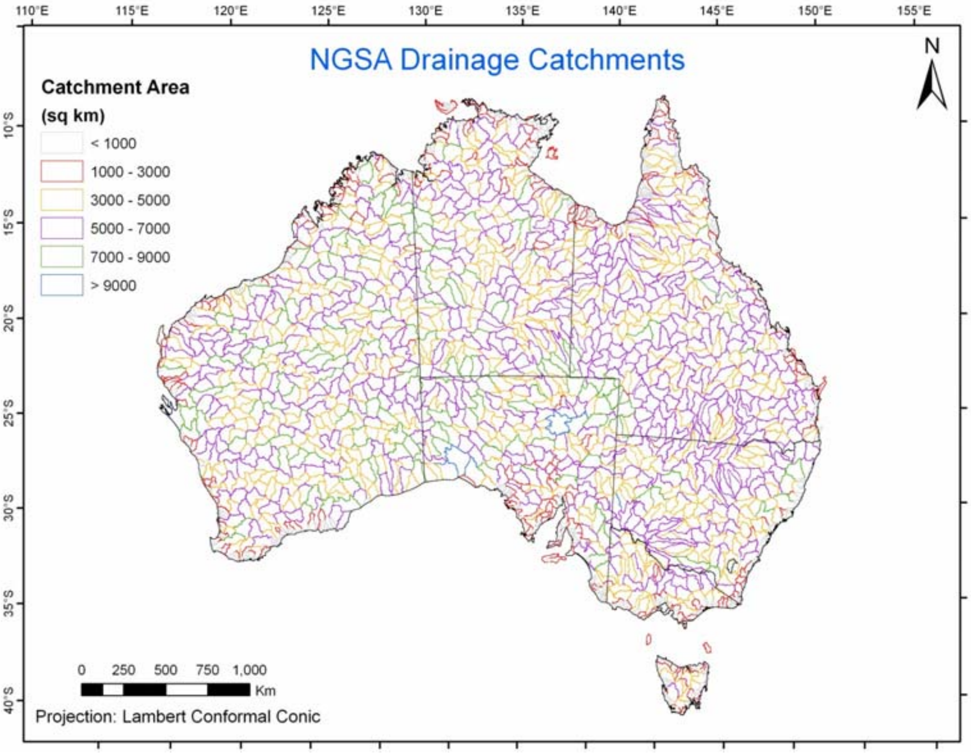

Figure 3. Distribution of catchments for the National Geochemical Survey of Australia.

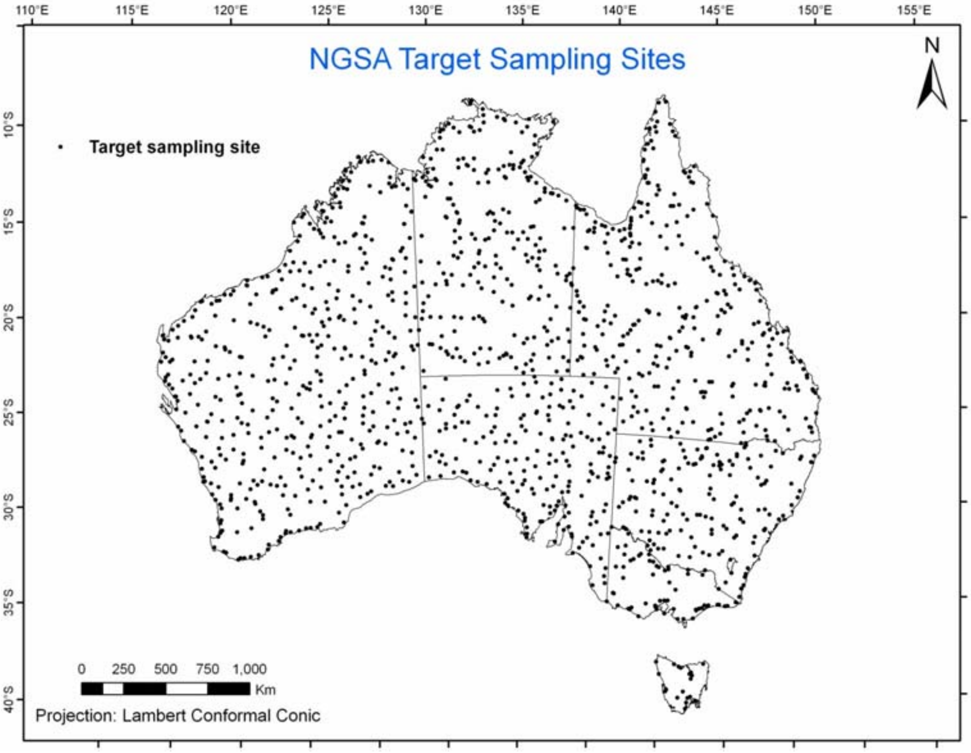

Figure 4. Distribution of initial target sampling sites for the National Geochemical Survey of Australia.

Sample collection

A detailed Field Manual was compiled (Lech *et al.*, 2007) and all sampling equipment and consumables were centrally purchased. Despite best efforts to access all the target sites, only 1186 catchments could physically be sampled before the deadline for field work was reached. Of these 1186 catchments, 124 were sampled in duplicate (on average 365 m away from the original site), and five of the largest catchments were sampled at two widely separated locations (on average 79 km apart), yielding a total of 1315 sampled sites (Figure 5). At each of these sites, a Top Outlet Sediment (TOS) sample was collected from 0-10 cm (below the root zone, if applicable), and a Bottom Outlet Sediment (BOS) sample was collected from a depth of between 60 and 80 cm on average. To reduce natural soil heterogeneity, every sample collected was a composite either from a shallow soil pit (TOS) or from at least three auger holes (BOS) at a given site (see Lech *et al.*, 2007, for more information). Sample collection was carried out by the State and the Northern Territory geoscience agencies following a hands-on, in-field training period with the Geoscience Australia NGSA team. At each locality a detailed site description, field pH, and dry (if possible) and moist Munsell® soil colours were recorded and several digital photographs were taken. All information was recorded digitally to facilitate subsequent uploading into databases.

Sample preparation

All samples were sent to Geoscience Australia for processing. A bulk split (~50 %) of each sample was archived for future investigations. The remainder was dried, riffle split and dry sieved to <2 mm and <75 µm fractions. The <2 mm fraction was mechanically ground for some analyses, while the finer fraction was not. The sample preparation protocols were discussed in detail in the NGSA Sample Preparation Manual (Caritat *et al.*, 2009).

Sample analysis

The analysis philosophy from the outset was to apply a multi-element approach on two grain-size fractions prepared by two digestion methods, in order to maximise the amount of geochemical information delivered. At the time of writing, sample analysis was nearing completion for 60+ elements/parameters using mainly X-ray fluorescence (XRF) and (reaction cell) inductively coupled plasma-mass spectrometry (ICP-MS) at Geoscience Australia. The ICP-MS analyses are carried out on a total digest ($HF + HNO_3$) of fragments of the XRF beads (Pyke, 2000). Other parameters being recorded at Geoscience Australia are pH 1:5 (soil:water), electrical conductivity (EC) 1:5 (soil:water), and laser particle size analysis (LPSA). Analyses for selected elements not available at Geoscience Australia (e.g. Au, fluorine (F), selenium (Se), and platinum group elements (PGEs)) took place externally. Additional digests/analyses (e.g. after *aqua regia* digestion, ligand-based extractions, near visible-infrared spectroscopy) were also carried out externally. Details of the sample analysis protocols are discussed in further detail later in this report.

Quality assessment/quality control

Sample numbers were randomised to minimise regional bias, help separate false from true anomalies and obtain meaningful estimates of the variance of duplicates. Field duplicates, analytical duplicates, internal project standards and certified reference materials were introduced at regular intervals in the analytical streams. Care was taken throughout the project to minimise contamination, cross-contamination and mislabelling risks.

Data analysis

The production of national-scale geochemical maps will be carried out and they will be released as a web-based atlas. Reports providing preliminary interpretations and including graphical and statistical analysis will be prepared and released on Geoscience Australia's website.

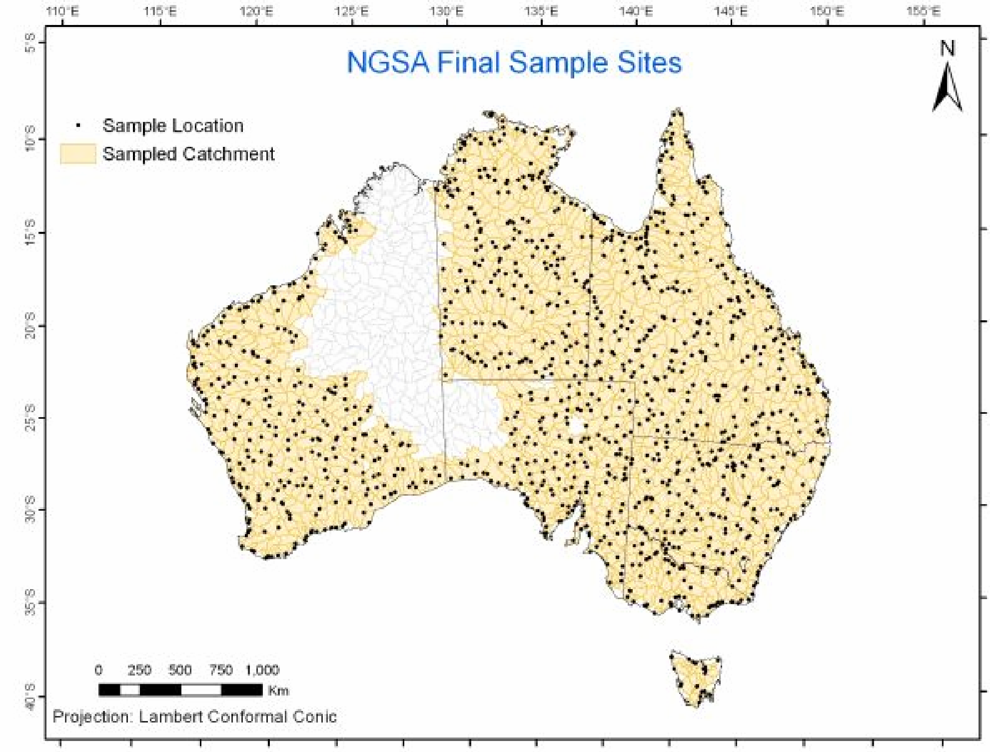

Figure 5. Distribution of catchments actually sampled for the National Geochemical Survey of Australia (1186 catchments, or 86 %, completed).

Timeline

Following planning in the first half of 2007, fieldwork, including initial training, began in mid-2007 and concluded in late 2009. Figure 5 shows the final distribution of catchments actually sampled for NGSA at the end of fieldwork (December 2009). Sample preparation started in early 2008 and continued until late 2009. Sample analysis started late-2008 and is scheduled to finish in mid-2010. Data analysis and reporting are planned to take place in 2010 and early 2011. The project concludes on 30 June 2011.

Sample Analysis

A summary of the analyses for 73 parameters/elements performed on NGSA samples is presented in Table 1. Unless otherwise indicated, the analyses are all performed on 4 samples from each site:

- TOS <2 mm
- TOS <75 µm
- BOS <2 mm
- BOS<75 µm

Nearly 750,000 analyses were determined for the NGSA project. The following describes the analytical methods used. For details on sample preparation, please refer to Caritat *et al.* (2009).

TOTAL ELEMENT CONTENT

Multi-element analysis by x-ray fluorescence

X-ray fluorescence (XRF) spectrometry at Geoscience Australia was carried out on a Philips PW2404 4kW sequential wavelength dispersive spectrometer fitted with a rhodium X-ray tube. It was used to measure the major elements present in samples analysed by the laboratory and a range of the routinely more abundant trace elements to complement those analysed by the ICP-MS.

Sample preparation

The method used was a variation of Norrish & Hutton (1969). No heavy absorber was added to the flux in this procedure.

Depending on the sample composition, the Geoscience Australia laboratory used one of three lithium borate fluxes:

- LM100: lithium metaborate, used for samples with >75% SiO_2 content
- 12:22 Flux: 12 parts lithium tetraborate and 22 parts lithium metaborate, used for ‘normal’ silicate samples
- 57:43 Flux: 57% lithium tetraborate and 43% lithium metaborate, used for carbonates

The default method for NGSA samples was LM100. A number of samples, thought to contain elevated calcium and/or organic matter, did not produce a homogeneous glass bead using this flux and were instead fused using 12:22 flux. Several samples with moderately elevated calcium that did fuse with LM100 were also fused with the 12:22 flux to check on consistency of results for calcium and other elements between the two preparation methods. A small number of samples thought to contain very high calcium and/or organic matter did not fuse properly with the 12:22 flux either and were consequently fused with the 57:43 flux. Again, several samples that did fuse with the 12:22 method were also fused with the 57:43 method to check the consistency of results for calcium and other elements between the two preparation methods.

Glass fusions, or beads, were prepared by accurately weighing approximately 0.6 g of sample and 4.80 g of the selected flux into a platinum/gold (95%/5%) crucible. Subsequently, 0.5 mL of a 20% lithium nitrate solution was added and the mixture sintered at 400 °C for 15 minutes to oxidise any sulfide present. A pellet of blended cellulose and ammonium iodide was added and the crucible was then transferred to a Bradway rocking furnace and heated at 1000 °C for a further 8 minutes without rocking followed by 7 minutes with rocking. The molten mix was then poured into a preheated mould and cooled in an air stream.

Table 1. Summary of 73 parameters/elements analysed for in the NGSA project.

Parameter/ Element	Total XRF	Total ICP-MS	AR ICP-MS	MMI-ME ICP-MS*	FA AR-PGEs	ISE-F	AR-Se	pH meter^	Conductivity^	Laser particle size analysis^	Titration#	Gravimetry#
pH 1:5								☑				
EC 1:5									☑			
Grain size										☑		
FeO											☑	
LOI												☑
Ag		☑	☑	☑								
Al	☑		☑	☑								
As		☑	☑	☑								
Au			☑	☑	☑							
B			☑									
Ba		☑	☑	☑								
Be		☑	☑									
Bi		☑	☑	☑								
Ca	☑		☑	☑								
Cd		☑	☑	☑								
Ce		☑	☑	☑								
Cl	☑											
Co		☑	☑	☑								
Cr		☑	☑	☑								
Cs		☑	☑	☑								
Cu	☑	☑	☑	☑								
Dy		☑	☑	☑								
Er		☑	☑	☑								
Eu		☑	☑	☑								
F	☑					☑						
Fe	☑		☑	☑								
Ga		☑	☑	☑								
Gd		☑	☑	☑								
Ge		☑	☑									
Hf		☑	☑									
Hg			☑	☑								
Ho		☑	☑									
In			☑									
K	☑		☑	☑								
La		☑	☑	☑								
Li			☑	☑								
Lu		☑	☑									
Mg	☑		☑	☑								
Mn	☑		☑	☑								
Mo		☑	☑	☑								
Na	☑		☑									
Nb		☑	☑	☑								
Nd		☑	☑	☑								
Ni	☑	☑	☑	☑								
P	☑			☑								
Pb		☑	☑	☑								
Pd				☑	☑							
Pr		☑	☑	☑								
Pt				☑	☑							
Rb	☑	☑	☑	☑								
Re			☑									
S	☑											
Sb		☑	☑	☑								
Sc		☑	☑	☑								
Se			☑	☑			☑					
Si	☑											
Sm		☑	☑	☑								
Sn		☑	☑	☑								
Sr	☑	☑	☑	☑								
Ta		☑	☑	☑								
Tb		☑	☑	☑								
Te			☑	☑								
Th		☑	☑	☑								
Ti	☑			☑								
Tl			☑	☑								
Tm			☑									
U		☑	☑	☑								
V		☑	☑	☑								
W		☑	☑	☑								
Y		☑	☑	☑								
Yb		☑	☑	☑								
Zn	☑	☑	☑	☑								
Zr	☑	☑	☑	☑								
Total	**19**	**43**	**60**	**54**	**3**	**1**	**1**	**1**	**1**	**1**	**1**	**1**

*: Only on TOS <2 mm samples

^: Only on bulk samples (TOS and BOS)

#: Only on 10% of samples

Sample analysis

The XRF instrument was calibrated using a range of United States Geological Survey (USGS), South African Reference Material (SARM) and other international standards. The 'Classic Model' as outlined in the 'Philips SuperQ/Quantitative Users Guide' was used to calculate alpha coefficients and line overlap factors.

Reference monitor standard Si3 was used to measure instrumental drift. Depending on the element, current varied from 66 to 125 mA, potential from 32 to 60 kV, and counting time from 8 to 200 seconds (totalling 710 seconds per sample).

For the NGSA project, 19 elements were analysed using the method described above, 10 of which are major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si and Ti; reported as oxides in %) and nine trace elements (Cl, Cu, F, Ni, Rb, S, Sr, Zn and Zr; reported as elements in ppm).

Multi-element analysis by inductively coupled plasma-mass spectrometry

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis of total element content was performed at Geoscience Australia.

Sample preparation

The samples for ICP-MS analysis were the same fused samples previously analysed by the XRF for major element analysis as discussed in Pyke (2000); this methods allows virtually total recovery of elements, including zirconium (Zr). The XRF fused samples were prepared as described above. The XRF fused discs were presented to the ICP-MS laboratory in numbered plastic bags. The discs were shattered inside the bags by placing the bags between pieces of clean paper and giving them a sharp blow with a hammer.

200 ± 0.003 mg of chips from the smashed discs were weighed into a Savillex Teflon vessel. 5 mL of internal standard, 1 mL of distilled hydrofluoric acid and 5 mL of distilled nitric acid were added. The vessels were sealed with a cap mould attachment and tension wrench and heated for 12 hours, usually overnight, on a hotplate set at 120 °C. The caps on the cooled vessels were carefully unscrewed and the contents transferred to 200 mL volumetric flasks. Volume was made up with 18 MΩ/cm water.

Sample analysis

A range of trace elements (see below) were determined using an AGILENT 7500ce ICP-MS to complement those elements analysed on the XRF. Ultra high purity helium gas was used in the octopole reaction cell during ICP-MS analysis.

The instrument was calibrated using synthetic standards. The calibrations obtained were verified against a range of USGS Certified Reference Materials (AGV-2, GSP-2), Canadian Certified Reference Materials (TILL-1, 2, 3 and 4) and a Russian Certified Reference Material (DVG-1).

The analytical method divided the elements into four groups. The counts obtained for each analyte were ratioed against one of four isotopes introduced to the solution as internal standards (nickel-61, samarium-147, thullium-169 and thallium-205), one for each of the analyte groups.

Inter-element interference factors were determined using a range of single element solutions.

43 elements were determined by the total ICP-MS method for the NGSA project: Ag, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, U, V, W, Y, Yb, Zn, Zr.

AQUA REGIA SOLUBLE ELEMENT CONTENT

Gold analysis by inductively coupled plasma-mass spectrometry

This analysis was performed in a commercial laboratory, which provided the following information.

Sample preparation

A 25.00 ± 1.00 g aliquot of the sample was digested with an aqua regia solution (50 mL concentrated hydrochloric acid added first followed by 20 mL concentrated nitric acid) at 95 ± 3 °C for 4 hours to leach the acid-soluble components (the leach only partially dissolves silicates and oxides). Once the sample had cooled to room temperature, 180 mL of diluent was added and the bottle was capped and shaken vigorously. The sample was then allowed to settle until a clear solution could be sampled. This aliquot was diluted a further 10 times with 18 MΩ/cm water.

Sample analysis

The solution was introduced into the ICP-MS. The solution was vaporized and ionized within the inductively coupled plasma and the ions were then transferred into the mass spectrometer. The ions were spatially separated according to their mass to charge ratio in a quadrupole mass spectrometer and the intensities of each atomic mass were measured. The concentration of the trace elements in the samples was calculated using calibration standards and blanks.

Au was analysed within the range 0.1-5000 ppb using the aqua regia ICP-MS method for the NGSA project.

Multi-element analysis by inductively coupled plasma-mass spectrometry

This analysis was performed in a commercial laboratory, which provided the following information.

Sample preparation

A 0.50 ± 0.02 g aliquot of the sample was digested with an aqua regia solution (1.8 mL concentrated hydrochloric acid added first followed by 0.6 mL concentrated nitric acid) at 90 ± 3 °C for 2 hours to leach the acid-soluble components (the leach only partially dissolves silicates and oxides). Once the sample had cooled to room temperature, 17.5 mL of diluent was added and the bottle was capped and inverted 10 times to completely homogenise the content. The sample was then allowed to settle over a 6 hour period or longer. The sample was exposed to light for as little time as possible to prevent reduction of silver. The sample was diluted a further 50 times with 18 MΩ/cm water.

Sample analysis

As per aqua regia gold analysis.

59 elements (in addition to Au discussed above) were determined by the aqua regia ICP-MS method for the NGSA project: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Re, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr.

Selenium analysis by inductively coupled plasma-mass spectrometry

This analysis was performed in a commercial laboratory, which provided the following information.

Selenium, after aqua regia digestion, is in the oxidised (Se^{6+}) state. Reduction with citric and ascorbic acids in the presence of cupric copper (Cu^{2+}) converts Se^{6+} to Se^{4+} and finally to Se metal, provided all ferric iron (Fe^{3+}) has been reduced to ferrous iron (Fe^{2+}).

Sample preparation

5.00 g of pulped sample was weighed into a 250 mL beaker, to which nitric and hydrochloric acids were added. The beaker was placed on a hot plate set at 160 °C in a fume hood, until a viscous texture was achieved. The sample was leached with hydrochloric acid then filtered. The selenium was precipitated with ascorbic acid and chilled, before being filtered under vacuum using 0.45 µm cellulose nitrate membrane filters to collect the precipitate. The filtrate was washed thoroughly with doubly deionised water, then digested in aqua regia and volume adjusted to 10 mL.

Sample analysis

The samples were presented in a pre-concentrated form and contained an aqua regia matrix, which was diluted 10 times together with the calibration standards (see below) and then presented to the ICP-MS. Calibration standards used were matrix matched and the stock solutions are as follows:

Standard 1 = 0.5 ppm Se, Standard 2 = 2 ppm Se and Standard 3 = 5 ppm Se in 2% hydrochloric acid and 3% nitric acid.

The resulting solutions were presented to a PerkinElmer Elan 9000 quadrupole ICP-MS fitted with a 40 MHz RF generator used for sample excitation. The settings of the instrument were as follows:

- RF power: 1100 W
- Nebulizer flow: 0.78 L/min
- Pump speed: 8 revolutions per minute
- Nebulizer: micro-bore PFA concentric type

The method setup utilised rhodium and iridium internal standards. Se results were reported from mass 82. The major interference at this mass comes from krypton, which if present would more than likely come from contamination of the argon gas supply. Other interferences at mass 82, although quite small and on most occasions without significance, come from zinc-oxygen, calcium-calcium and copper-oxygen. Other selenium masses such as those at 77 and 78 can suffer from a number of interferences, the worst being the argon-argon dimer at mass 78.

With the aqua regia type digest that was used, many of the interferences on selenium became almost insignificant due to the pre-concentration step that was used in the sample preparation. Internal standards used aided in keeping sample loading under control.

LIGAND-BASED EXTRACTION ELEMENT CONTENT

Multi-element analysis by inductively coupled plasma-mass spectrometry

The determination of Mobile Metal Ions™ by the MMI-ME method relies on a weak, partial, ligand-based extraction followed by analysis of 54 elements by ICP-MS. This analysis was performed in a commercial laboratory, which provided the following information.

Sample preparation

50 g of sample were weighed directly from the original bag/container as received. Mobile metal ions present in the sample were partially extracted using a concentrated MMI™ solution.

Sample analysis

The extracted sample solution was aspirated into a Dynamic Reaction Cell (DRC) ICP-MS where the ion concentrations were measured and quantified according to their unique mass. The DRC-ICP-MS was calibrated with each work order. An instrument blank and calibration check was analysed with each run. One preparation blank and reference material was analysed every 46 samples, one duplicate every 12 samples. All quality control samples were verified using the Laboratory Information Management System (LIMS), with acceptance criteria controlled statistically and control charts used to monitor accuracy and precision. Samples that fell outside the control limits, if any, were investigated and repeated as necessary. The results were exported to the LIMS via a secure audit trail.

54 elements were determined by the MMI-ME ICP-MS method for the NGSA project: Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr.

ALKALINE FUSION ELEMENT CONTENT

Fluoride analysis by ion specific electrode

This analysis was performed in a commercial laboratory, which provided the following information.

Sample preparation

A nominal sample weight of 0.4 g was weighed into a crucible, with weights captured electronically. Samples were fused at 650 °C with sodium peroxide. A 5:1 ratio water extract followed this, with solutions left to stand. A subsample of this liquor was removed and buffered.

Sample analysis

Solutions were presented to a fluoride ion selective electrode (ISE) and results were back calculated based on sample weights/volumes.

FIRE ASSAY ELEMENT CONTENT

Platinum group elements analysis by inductively coupled plasma-mass spectrometry

This analysis was performed in a commercial laboratory, which provided the following information.

Sample preparation

A prepared sample (nominally 30 g to 50 g aliquot) was thoroughly mixed and fused with 170-200 g of flux, which was a mixture of lead oxide, sodium carbonate, borax and silica, inquarted with gold-free silver. This fire assay procedure comprised a reducing fusion at 1025-1100 °C for approximately 1 hour in which two phases, a complex liquid borosilicate slag and a liquid lead phase, were formed. The lead phase collected the precious metals and the gangue elements were separated into the slag. The great difference in density between the two phases allowed easy separation after solidification and isolation of a lead button containing the gold and precious metals.

The second stage involved cupellation (oxidising fusion at 920-1000 °C for approximately 45 minutes) with silver acting as a collector for the gold and platinum group metals. In this process the lead button was oxidised to lead oxide and absorbed into the cupel, leaving a bead of silver plus any gold, platinum and palladium present in the sample.

This silver bead (prill) was added to a test tube and 1 mL of 50% nitric acid was added. The test tube was placed on a hot plate set at 120 °C until the evolution of brown fumes ceased. The test tube was removed from the hot plate and checked to ensure parting was complete, and then allowed to cool for 5 minutes. 2 mL of hydrochloric acid was added to the test tube, which was shaken vigorously before being returned to the hotplate for a further 10 minutes. The tube was checked for complete dissolution of gold and then cooled and bulked with laboratory grade water to a final volume of 10 mL.

Sample analysis

The solution was analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for gold, platinum and palladium. In each fire, one blank, two standards and three duplicate samples were run. The standards most commonly run for this method were ST-321 and ST-381. Performance of each analysis was closely monitored via control charts.

3 trace elements were determined by the fire assay aqua regia PGE ICP-MS method for the NGSA project: Au, Pd, Pt.

BULK ANALYSES

Reduced iron analysis by titration

This analysis was performed in Geoscience Australia's laboratories for a subset (~10%) of NGSA samples, using the following method.

The method used is a modification of that of Shapiro and Brannock (1962) and is described below. Approximately 250 mg of sample was weighed accurately into a 50 mL platinum crucible. The sample weight in mg was entered into the Metrohm Titrino titrator. 10 mL of 1:3 sulfuric acid and 5 mL of 40 % hydrofluoric acid were added to the crucible and sample. The crucible was covered with a platinum lid and digested on a hotplate for 10 minutes. The digest was transferred to a 600 mL plastic beaker containing 200 mL of deionised water, 15 g boric acid and 10 mL of 1:1 phosphoric acid. If necessary, water was added to bring the volume up to approximately 400 mL. The solution was titrated with potassium dichromate ($K_2Cr_2O_7$), prepared by dissolving 6.83 g of $K_2Cr_2O_7$ in 5 L of 18 MΩ/cm water, using a Metrohm 716 DMS Titrino titrator with a Pt wire electrode. The instrument was calibrated against a range of in-house standards and USGS International Standards.

Loss on ignition by calculation

Loss on ignition (LOI) was calculated from Geoscience Australia's XRF results for all samples by subtracting from 100% the sum of XRF major element oxide determinations for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, SO_3 .

Loss on ignition by gravimetry

This analysis was performed in Geoscience Australia's laboratories for a subset (~10%) of NGSA samples, using the following method.

After taring the balance, a porcelain crucible was weighed and the weight entered in a computer spreadsheet. Approximately 500 mg of sample was added to the crucible, and the weight of the crucible plus sample was entered in the spreadsheet. The crucible was then transferred to a furnace, where it was ignited to 1100 °C. When the sample was cool enough to handle safely, it was transferred to a desiccator using tongs. When cool, the crucible plus sample was weighed and that data was entered in the spreadsheet, which calculated the LOI using the formula:

$$\text{LOI Weight \%} = \{(\text{sample + crucible - ignited sample + crucible})/(\text{sample plus crucible - crucible})\}*100$$

pH of 1:5 (soil:water) slurry

This analysis was performed in Geoscience Australia's laboratories, using the following method.

<u>Sample preparation</u>

The sample was dried at 45 °C during the sample preparation process, riffle split and transferred to a clearly labelled container. 10 g (± 0.2 g) was accurately weighed into a clearly labelled plastic vial. 50 mL of distilled water was added to the vial using a bottle top dispenser. The volume of water was accurately measured to ensure 50 mL was dispensed each time. The sample was shaken and transferred to an ultrasonic bath for 5 minutes. The sample was shaken and transferred to a orbital shaker (Barnstead - Lab Line) for 1 hour at 160 revolutions per minute. The sample was shaken and placed in fridge for 24 h. The sample was allowed to warm to room temperature before pH and EC was measured on a TPS smartCHEM – conductivity/pH meter. Between samples, the probes were washed with deionised water and dried using a lint-free tissue. Readings were written and entered into a running spreadsheet. Results were compared to the duplicates and samples retested if the results fell outside error margins.

Sample analysis

Samples are analysed in batches of up to 40 samples. The TPS smartCHEM – conductivity/pH meter was calibrated at the beginning of each batch of analysis against pH 4.0 and 6.88 buffers.

pH buffers were measured at end of each batch to record any instrument drift. Buffer solutions were replaced weekly to minimise dilution and contamination. Laboratory duplicates were prepared and analysed 1 in every 10 samples. An internal project standard (GRIS) was measured once a week. The reported precision from repeated internal project standard measurements was found to be ± 5%.

Electrical conductivity of 1:5 (soil:water) slurry

This analysis was performed in Geoscience Australia's laboratories, using the following method.

Sample preparation

As per pH 1:5.

Sample analysis

Samples were analysed in batches of up to 40 samples. Samples were grouped into similar electrical conductivity values and the TPS smartCHEM – conductivity/pH meter was calibrated at the beginning of each batch of analyses against the appropriate standard, as follows:

- <300 µS: 147 µS standard
- 300 to 2000 µS: 1413 µS standard
- 2000 to 5000 µS: 2760 µS standard
- 5000 to 25,000 µS: 12,860 µS standard
- >25,000 µS: 58,000 µS standard

EC standards were measured at end of each batch to record any instrument drift. Standard solutions were replaced weekly to minimise dilution and contamination. Laboratory duplicates were prepared and analysed 1 in every 10 samples. An internal project standard (GRIS) was measured once a week. The reported precision from repeated internal project standard and duplicate measurements was found to vary as follows:

- <75 µS: ± 21%
- 75 to 175 µS: ± 18%
- 175 to 750 µS: ± 15%
- 750 to 1500 µS: ± 12%
- 1500 to 3000 µS: ± 8%
- >3000 µS: ± 5%

Grain size by laser particle size analysis

This analysis was performed in Geoscience Australia's laboratories, using the following method.

Sample preparation

The sample was dried at 45 °C during the sample preparation process and transferred to a clearly labelled container. The sample was micro-riffle split into weights of approximately 0.15 to 1 g and transferred to a 50 mL glass beaker. The weight was determined by the material type: clays require less material to analyse compared to sand. The objective was to sample enough representative material to allow for the ideal obscuration for the analysis to take place. The sample was placed in 30% hydrogen peroxide to remove organic material and then neutralised. The sample was top cut at 1700 µm to prevent blockages (only the <1700 µm fraction was analysed). The sample was transferred to a 1000 mL beaker and shaken for 30 seconds in an ultrasonic bath.

Sample analysis

The sample was analysed using a Malvern™ Mastersizer 2000 coupled to a Hydro 2000 MU pump unit. Raw data was saved to a project drive and reports printed. Instrument and equipment were cleaned between samples. The basic principles of particle size analysis are summarised by Rawle (undated) from Malvern Instruments Ltd (http://www.malvern.co.uk). The laboratory followed the international standard ISO13320 Particle size analysis – laser diffraction methods, updated 2009.

Quality Audit Standards (QAS3002) were tested weekly. Laboratory duplicates were prepared and analysed 1 in every 10 samples. An internal project standard (GRIS) was measured once a week.

QUALITY ASSURANCE /QUALITY CONTROL (QA/QC)

A number of steps were taken by the NGSA project to allow quantification of the quality of the data at the end of the project. A quality statement will be made when results are reported.

QA/QC was based on one or several of the following steps, depending on the analysis undertaken:

- Field duplicates: every 10th site, a field duplicate sample was collected to help quantify total (sampling + analytical) precision
- Samples were presented to the laboratories in a randomised order, unrelated to the order in which they were collected (as much as practically feasible)
- Certified Reference Materials (CRMs) TILL-1, TILL-2 (Natural Resources Canada) were run with every batch on GA's XRF & ICP-MS to help quantify analytical precision and bias
- Laboratory duplicates (splits), internal project standards (MRIS, WRIS, ORIS, MRIS2, WRIS2), exchanged project standards (GEMAS-Ap, GEMAS-Gr from EuroGeoSurveys; SoNE-1 from United States Geological Survey), and international CRMs (TILL-1, TILL-3, LKSD-1, STSD-3 from Natural Resources Canada) were covertly inserted in the analytical suites for in-house and external analyses to help quantify analytical precision and bias
- Internal project standard (GRIS) for pH 1:5, EC 1:5 and grain size measurements

In addition to these measures, external laboratories applied their own QA/QC measures, which included repeat analyses (replicates), and analysis of blanks, internal standards and CRMs.

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