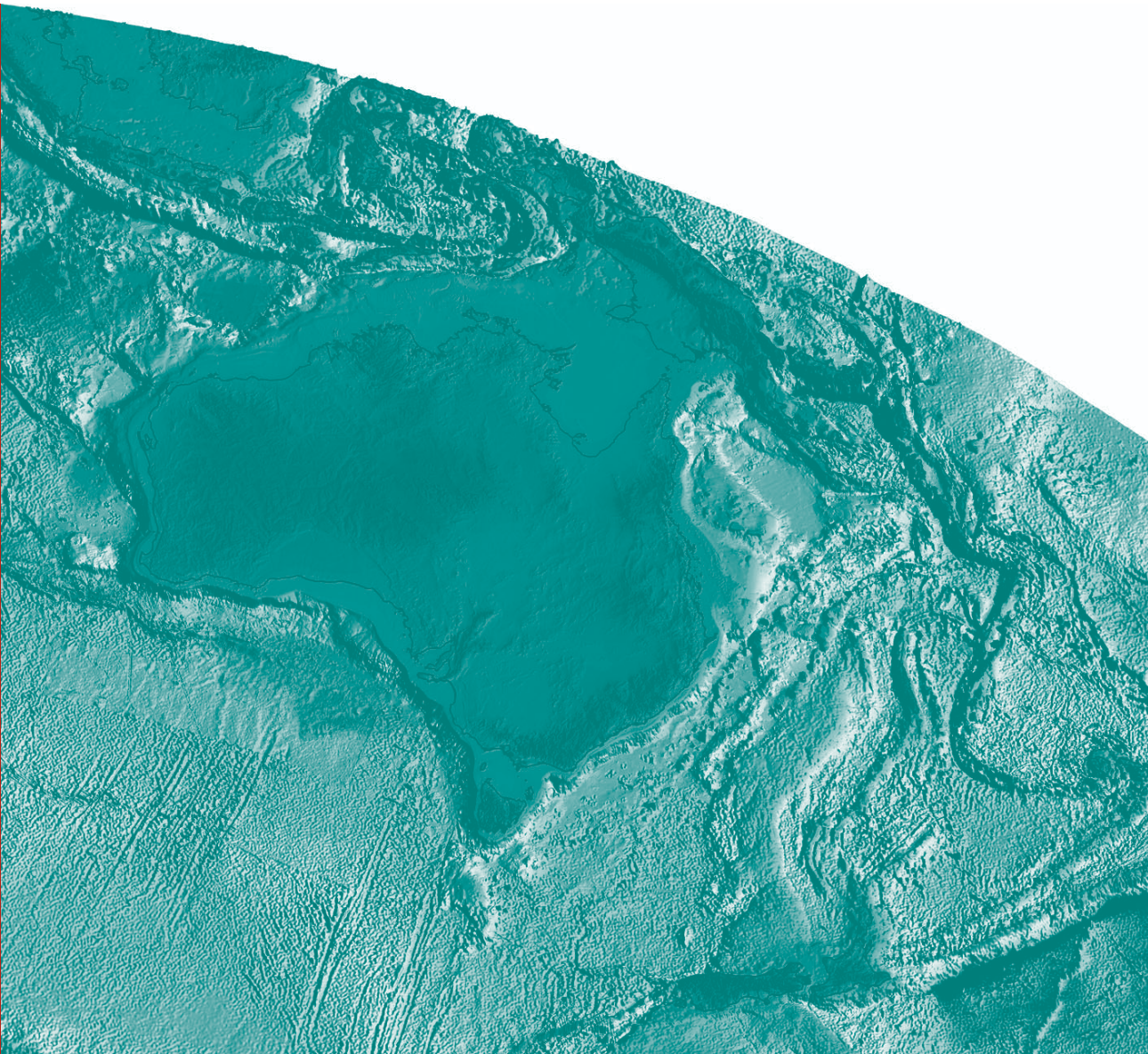**Australian Government**

Geoscience Australia

National Geochemical Survey of Australia: Sample Preparation Manual

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Record

2009/08

GeoCat #
68657

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by

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Executive Summary

The National Geochemical Survey of Australia (NGSA) aims to collect samples from 1529 sites located in 1390 catchments (10 % of which are sampled in duplicate) covering over 90 % of Australia. At each site, two depth ranges are sampled, giving 3058 samples to be processed. Each sample results in 13 individually packaged sub-samples, meaning that 39,754 separate containers will be prepared, labelled, delivered to the laboratories or archived during the sample preparation phase of the project. Any excess fraction in the processing streams is kept for potential future use.

The detailed procedures for preparing the NGSA samples in the laboratory are described. An overview of Quality Assessment/Quality Control and Operational Health and Safety measures is also provided.

There are three main parts or 'streams' to the sample preparation protocol. The first part is the 'Bulk Sample' stream. In this 'stream', the sample is received from the field, weighed, dried (for a minimum of 48 h at 40 °C) and sieved through a 3.35 mm mesh to remove any foreign material. Clay clumps or soil aggregates are gently broken up, with care being taken not to crush rock fragments or hard nodules. The sample is then homogenised and split into two halves. One half is sealed in a labelled plastic bag and set aside for archiving for future analyses/investigations. The other half is split into sub-samples or aliquots for:
1. Laser particle size analysis (LPSA), pH 1:5 (soil:water) and electrical conductivity (EC) 1:5 (soil:water) analysis; and
2. X-ray diffraction (XRD) analysis.

The remainder of the bulk material is sieved through a 2 mm mesh, and split into two portions (~20 % and 80 %), which are processed in the following two 'streams'.

The second part is the 'Coarse Fraction' stream. In this 'stream', the ~20 % split of <2 mm sample prepared above is further split to prepare two aliquots for:
- Platinum group element (PGEs) analysis; and
- Gold (Au) analysis after *aqua regia* (AR) leach.

The remaining material from this 'stream' is then milled to a fine powder, which is further split into aliquots for:
- Fluoride (F) analysis;
- Selenium (Se) analysis; and
- X-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) analysis.

The third part is the 'Fine Fraction' stream. In this 'stream', the ~80 % split of <2 mm sample further sieved through a 75 μm mesh. This sieved material is not milled. It is split into aliquots for:
- XRF and ICP-MS analysis;
- Au analysis after AR leach;
- F analysis;
- Se analysis; and
- PGEs analysis.

Several measures are in place to minimise contamination, cross-contamination and mislabelling of samples. Tests show that low and acceptable levels of variance or contamination are introduced by (1) scooping *versus* rotary splitting of milled samples, (2) sieving with stainless steel *versus* nylon mesh sieves, and (3) milling samples with a carbon steel mill head *versus* not milling.

Introduction

A 5-year Onshore Energy Security Program (OESP) programme 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), will collect transported regolith (sediment) samples from across the Australian continent and analyse 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 supports and adds value to a number of other OESP projects, particularly the Australia-Wide Airborne Geophysical Survey (AWAGS-2; e.g., Minty *et al.*, 2009) project and the Geothermal Energy project. 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 and how they vary spatially; and
- Reports and papers on energy resource prospectivity and other implications.

Samples are being collected over the whole continent from approximately 1400 catchment-based sites (1529 sites including duplicates), giving an average sample density of 1 site per 5500 km^2 (at the time of writing, 75 % of samples have been collected). Collaboration with State and Northern Territory geoscience agencies is critical for the completion of the program, particularly regarding the sampling phase, which is the subject of a previous report (Lech *et al.*, 2007). In the present report, we discuss details of the sample preparation protocol.

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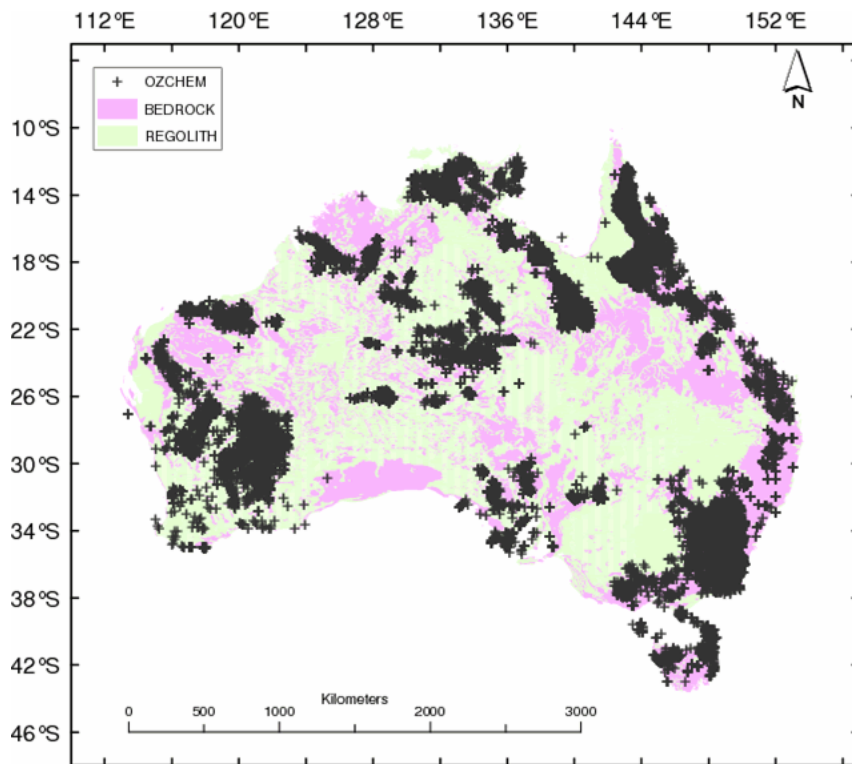
Figure 1. Distribution of whole rock geochemical data in Australia (plus signs) extracted from the OZCHEM national database as at June 2006, overlain on bedrock and regolith coverage.

Similarly, the current airborne gamma-ray spectrometric (radiometric) survey coverage available at a resolution deemed appropriate for exploration does not provide a complete national picture of the distribution of radiogenic elements potassium (K), U or Th (Figure 2). This situation is being remedied by the new AWAGS-2 project discussed above, which, together with NGSA, will result in a significantly improved understanding of the distribution of K, U and Th in Australia.

Some regional geochemical surveys have been carried out in parts of Australia (e.g. Morris *et al.*, 1998; Cornelius *et al.*, 2008), but no national coverage exists. Since the inception of the concept of regional geochemical surveys in the 1960s, they have proven to be a reliable tool for mineral exploration at various scales (Garrett *et al.*, 2008; Smith and Reimann, 2008).

OBJECTIVES
The objectives of the NGSA project are 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.
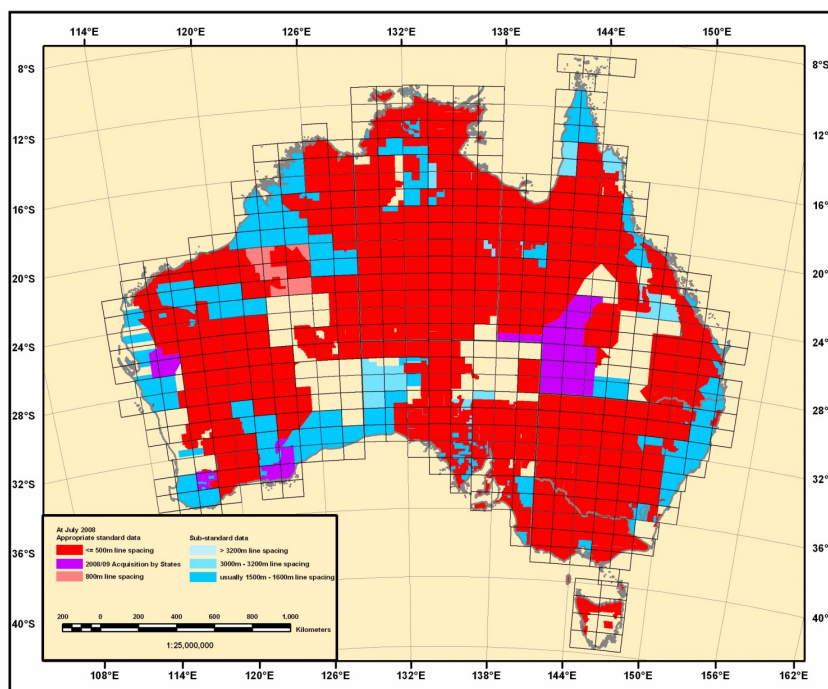
Figure 2. National coverage of airborne gamma-ray data acquired by Geoscience Australia and the State and the Northern Territory geoscience agencies as at July 2008.

STRATEGY

The sampling method has been adapted to Australian landscape and climate conditions. It has been field-tested in the Riverina, Gawler and Thomson pilot projects (e.g. see Caritat *et al.*, 2008b). The cost of a national survey is 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.

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 10 cm interval at a depth of between *circa* 60 and 90 cm).

Sampling sites

1390 catchments covering 91 % (or about seven million km^2) of Australia across all States and Territories have been targeted for sampling (Figure 3). Most catchments are sampled near their outlet, while those exhibiting internal or poorly defined drainage are sampled at, or as close as possible to, their lowest point. Lech *et al.* (2007) give details of the method for determining sampling sites. Catchments smaller than 1000 km^2 (mostly coastal) and small islands are 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.
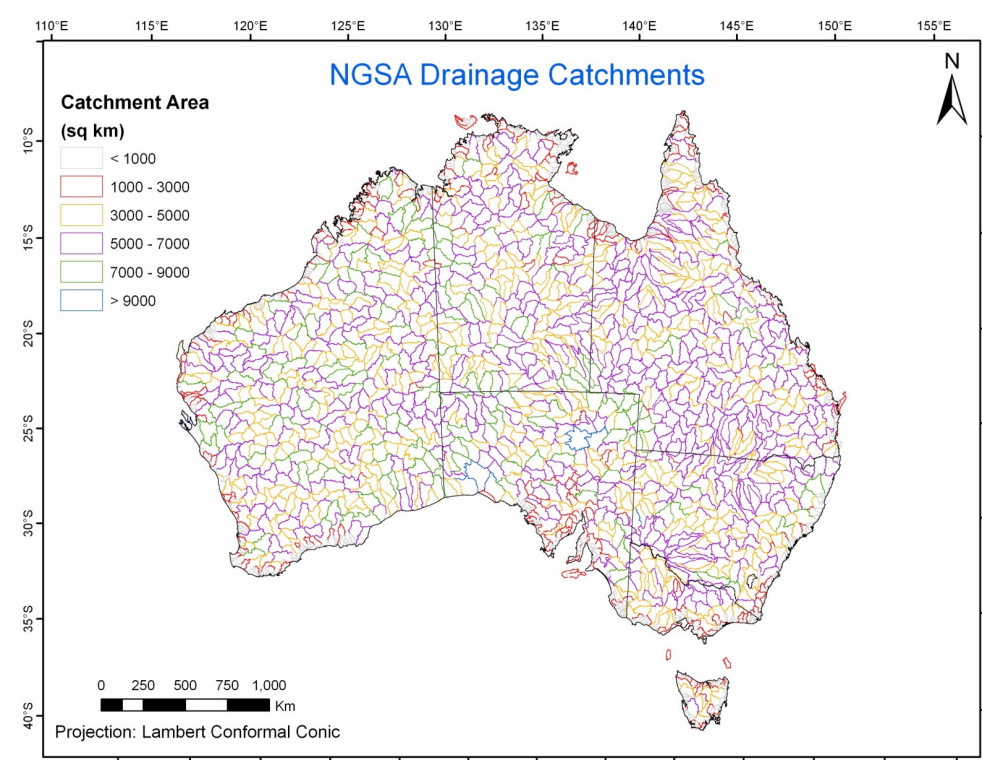
Figure 3. Distribution of catchments for the National Geochemical Survey of Australia.
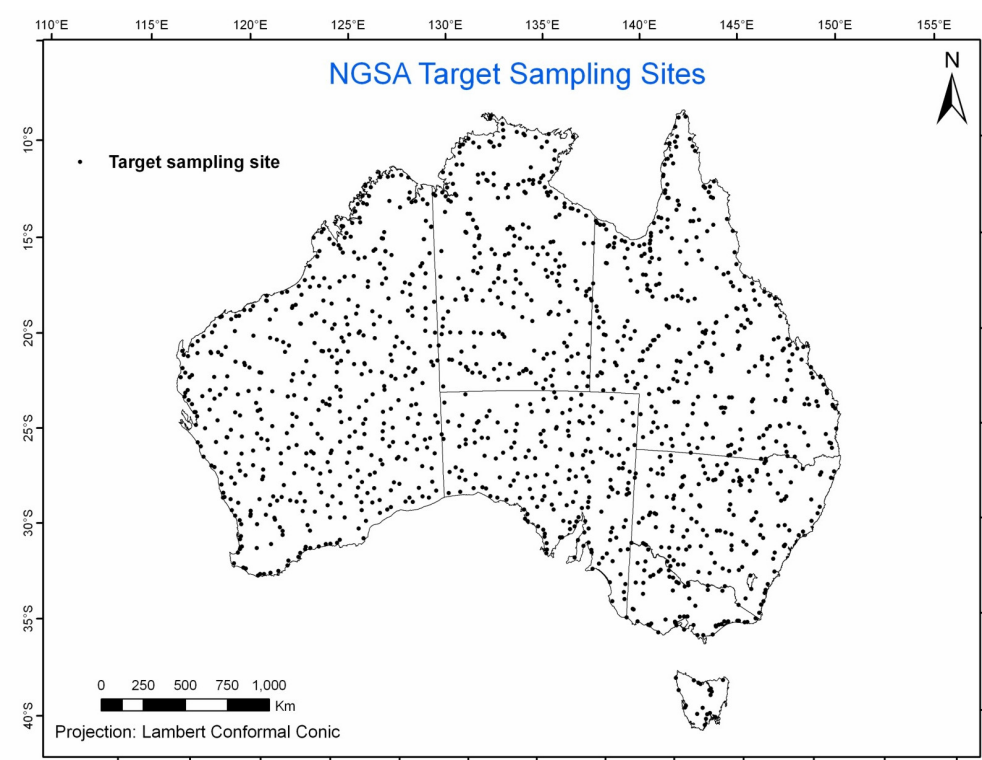

Figure 4. Distribution of target sampling sites for the National Geochemical Survey of Australia.

Sample collection

A detailed Field Manual has been compiled (Lech *et al.*, 2007) and all sampling equipment and consumables have been centrally purchased. At each of the expected 1529 sampling sites (1390 catchments + 10 % of which are sampled in duplicate), a Top Outlet Sediment (TOS) sample is collected from 0-10 cm (below the root zone, if applicable), and a Bottom Outlet Sediment (BOS) sample is collected from a depth of usually between 60 and 90 cm. To reduce natural soil heterogeneity, every sample collected is a composite from several auger holes at a given site (see Lech *et al.*, 2007, for more information). Sample collection is 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 and moist Munsell® soil colours are recorded and several digital photographs are taken. All information is recorded digitally to facilitate subsequent uploading into databases.

Sample preparation

All samples are sent to Geoscience Australia for processing. A bulk split (~50 %) of each sample is archived for future investigations. The remainder is dried, riffle split and dry sieved to <2 mm and <75 μm fractions. The <2 mm fraction is mechanically ground for some analyses, while the finer fraction is not. Details of the sample preparation protocol are discussed later in this report.

Sample analysis

The analysis philosophy is 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 has started 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 to be recorded routinely 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)) will take place externally. Additional digests/analyses (e.g. after *aqua regia* digestion, infrared spectroscopy) are also being carried out.

Quality assessment/quality control

Sample numbers have been 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 standards and certified reference materials are introduced at regular intervals in the analytical streams. Care is taken throughout the project to minimise contamination, cross-contamination and mislabelling risks.

Data analysis

Graphical and statistical data analysis will be carried out at various scales (regional, States/Northern Territory, and National). Non-parametric univariate and multi-variate statistical analysis along with the production of geochemical maps will be carried out.

Timeline

Following planning in the first half of 2007, fieldwork, including initial training, began in mid-2007 and is expected to continue until early 2009 (allowing for the wet season prohibiting field work in northern Australia for six months each year, and for time to obtain access permission in some areas). Figure 5 shows the catchments sampled to 31 December 2008. Sample preparation started in early 2008 and will continue until late 2009. Sample analysis started late-2008 and will continue until mid-2010. Data analysis and reporting are planned to take place in 2010 and early 2011. The project concludes on 30 June 2011.
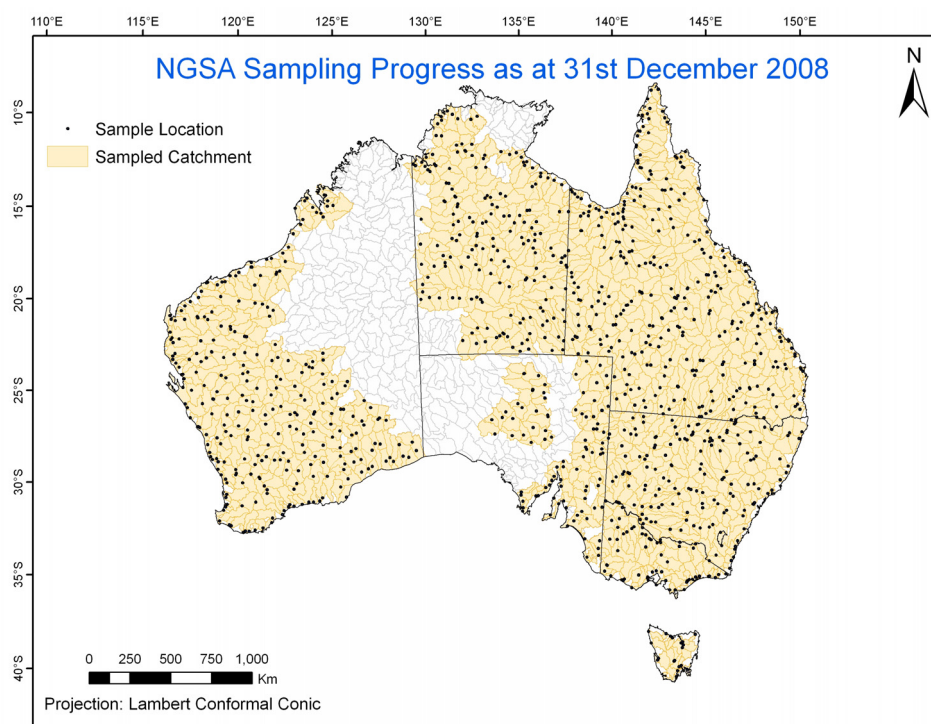
Figure 5. Distribution of catchments sampled for the National Geochemical Survey of Australia, as at 31 December 2008 (1079 catchments, or 78 %, completed).

Sample Preparation

The protocol for sample preparation was based mainly on experience gained from the pilot projects mentioned above, supplemented by knowledge from other geochemical surveys. The protocol consists of three main 'streams':

1. Bulk Sample;
2. Coarse Fraction; and
3. Fine Fraction.

Bulk Sample relates to all processes applied to the totality of the sample material as received from the field. Coarse Fraction refers to the preparation and separation of sample aliquots for the <2 mm grain size fraction. Similarly, Fine Fraction refers to the <75 μm grain size fraction.

The NGSA aims to collect samples from 1529 sites located in 1390 catchments (10 % of which are sampled in duplicate). At each site, two depth ranges are sampled, as explained above, giving 3058 samples to be processed. Each sample results in 13 individually packaged sub-samples, as described below, meaning that 39,754 separate containers will be prepared, labelled, delivered to the laboratories or archived during the sample preparation phase of the project.

The sample preparation is carried out by the Palaeontology and Sedimentology Laboratory group of the Petroleum and Marine Division of Geoscience Australia, in Canberra, Australia. Figure 6 shows the generalised sample preparation flow chart. The three 'streams' introduced above are shown as separate coloured boxes on the chart. The following sections give all the details relevant to each part of the sample preparation process.
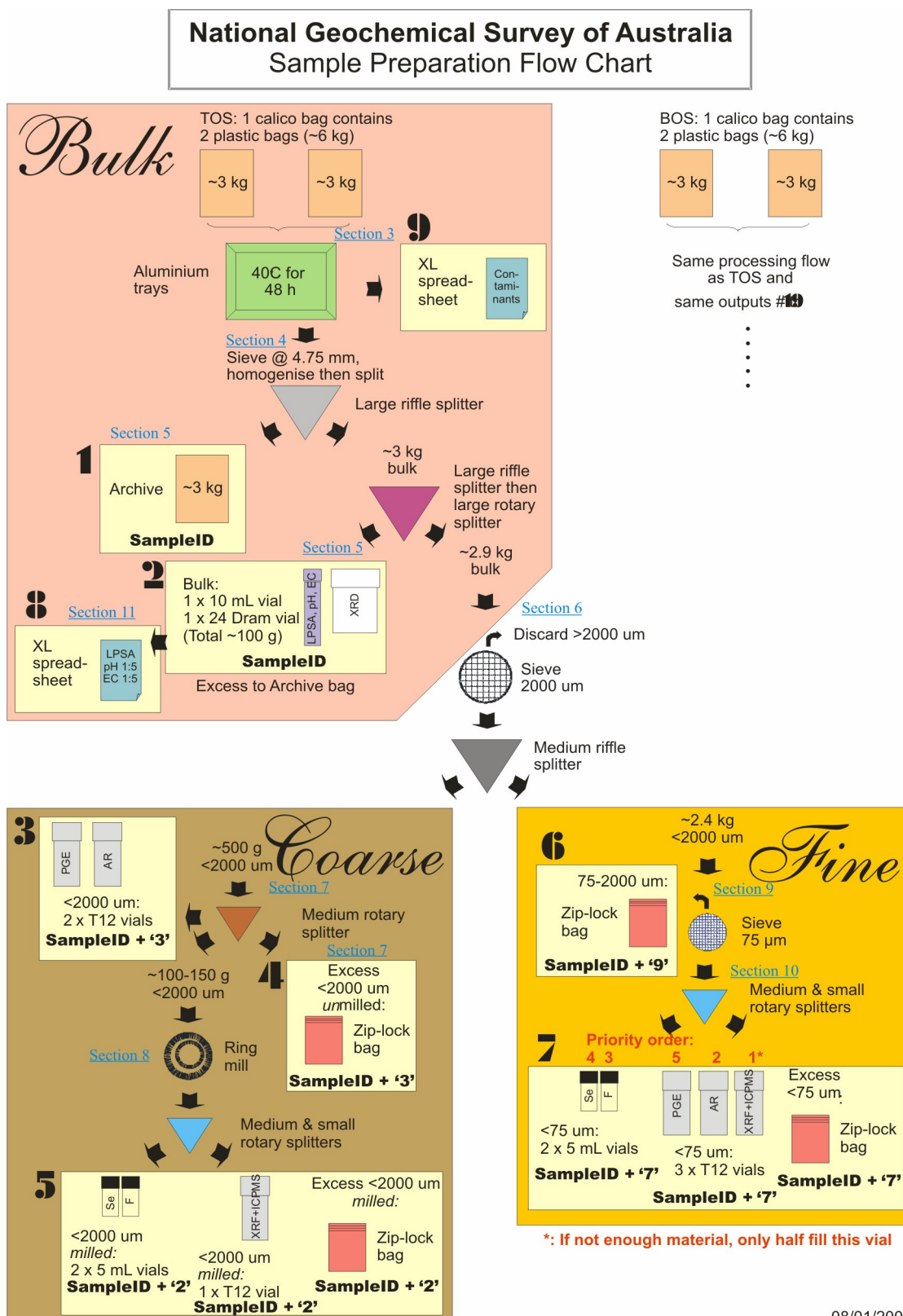
Figure 6. Sample preparation flow chart for NGSA samples. The process is shown for the TOS (Top Outlet Sediment) sample only; an identical process for the BOS (Bottom Outlet Sediment) sample at any given site is also followed.

QUALITY CONTROL/QUALITY ASSURANCE (QA/QC)

The main issues regarding QA/QC in sample preparation are:

- Contamination, including cross-contamination;
- Sample ID mix-up; and
- Segregation or gravitational settling.

Contamination risk is minimised by requiring the sample processing staff to remove any hand jewellery and avoid skin contact with sample material or with those parts of equipment that are in contact with sample (e.g. sieve mesh, inside of milling bowl). Where contact is unavoidable, powder-free, disposable latex or nitrile gloves are worn and changed for every new sample. Of course smoking is prohibited in the processing laboratory (as it is in the whole Geoscience Australia building). Labelling of containers, vials and bags is always done on the outside of the containers, vials and bags to avoid contaminating the sample (only the original Tyvek™ tag from the field is allowed to remain in contact with the sample). Labels are computer generated to minimise errors.

Cross-contamination can result mainly from re-use of equipment/containers and from dust. Only new consumables (e.g. drying trays, vials, bags) are used. Where equipment must be re-used for sample processing, it is cleaned after each sample to avoid cross-contamination. For instance, sieves are cleaned with an air gun, immersed in an ultra-sonic water bath for 15 min (Figure 7), air gun dried then oven dried at ~90 °C. Every piece of equipment is inspected visually for signs of wear and contamination before each use. If necessary, equipment is replaced by new equipment. Dust management in the laboratory is implemented by:

- Using dedicated, well-ventilated laboratories equipped with powerful extraction fans, particularly in conjunction with use of the air gun;
- Vacuuming and wiping work surfaces after every sample with a damp cloth;
- Cleaning equipment, glassware, etc. with water and alcohol-impregnated wipes;
- Vacuuming benches and working surfaces between samples;
- Wiping down and vacuuming entire laboratory (benches, equipment, fume hoods, top of ovens, etc.) on a weekly basis;
- Mopping floors with machine twice a week, and by hand-held mop as often as necessary; and
- Dust coats are changed daily.

Mislabelling risk is minimised by always having a sample label, if possible an original one (e.g. field calico bag, Tyvek™ tag), accompanying the sample through the process. For instance, the Tyvek™ tag is placed in the tray used for drying, or the calico bag is placed under plastic bags or vials containing products. A series of labels for all the products deriving from each sample was prepared electronically and printed on self-adhesive labels in advance of processing (Figure 8).

Figure 7. Ultra-sonic water bath used to clean sieves.

Figure 8. Printed self-adhesive labels for some of the products generated during sample preparation.

Segregation risk is minimised by never pouring/tipping/scooping raw (unmilled) sample material in order to split it. This can result in coarser and finer particles being separated, causing a textural, and thus potentially a compositional, contrast between the original and the split material. To avoid this problem, the raw (unmilled) sample material is always reduced using a riffle splitter (Figure 9). Tests performed early in the project have shown that milled (or ground) material is not significantly affected by this problem (Figure 10). Therefore, for the sake of efficiency, samples milled to the specifications described below are allowed to be split by scooping or pouring.

a)

b)

Figure 9. (a) Medium riffle splitter and (b) small riffle splitter used to split or reduce bulky samples.

Riffle vs scoop splitting of milled sample 2007190202 TOS
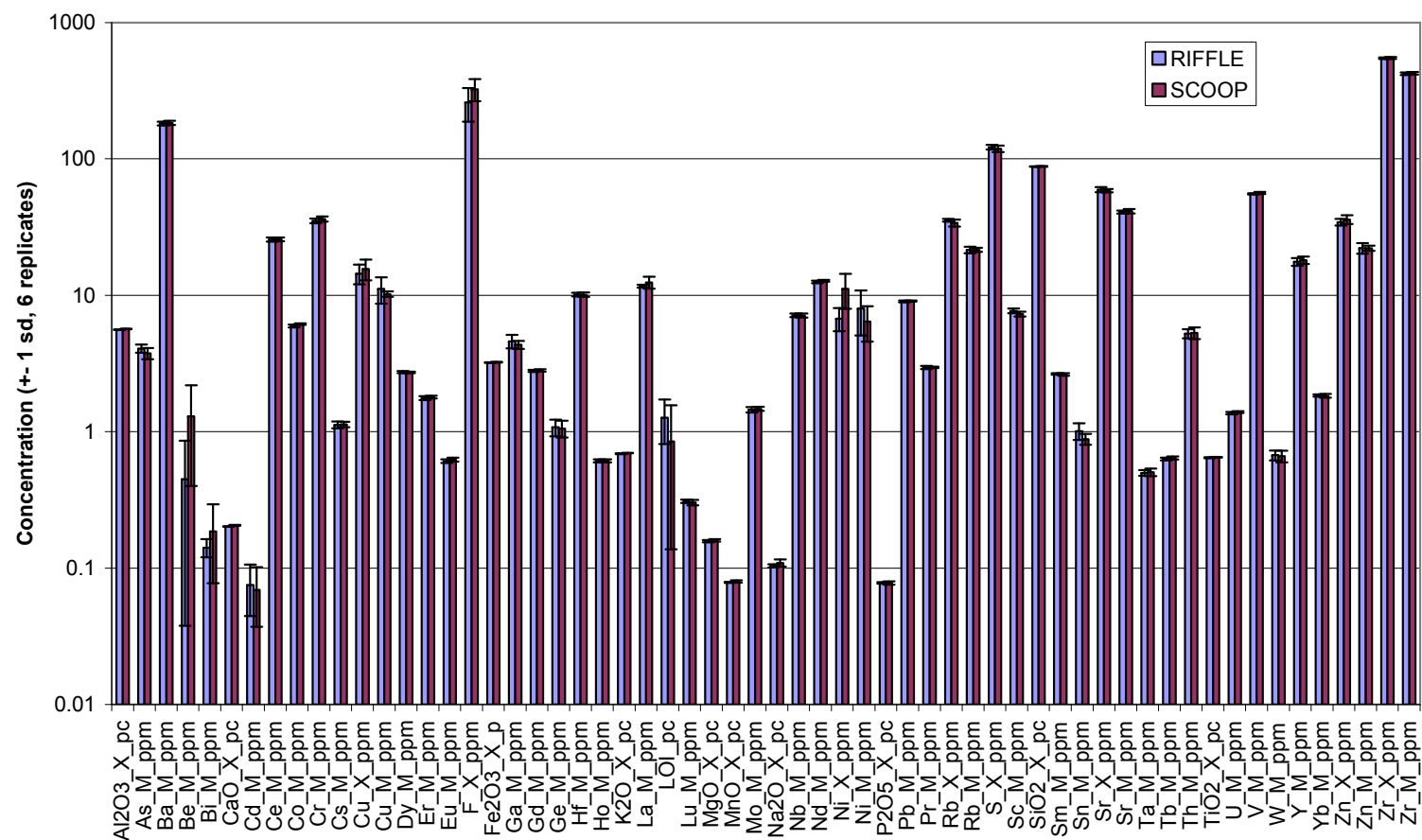

Figure 10. Average concentrations (± 1 standard deviation) of NGSA sample 2007190202 TOS milled to specifications from which 6 replicate aliquots were taken by rotary splitting (first bar) and 6 other replicates were taken by scooping the powder from the milling bowl (second bar). Analyses by ICP-MS (suffix _M) and XRF (suffix _X) expressed in ppm (suffix _ppm) or % (suffix _pc).

OPERATIONAL HEALTH AND SAFETY (OH&S)

OH&S of laboratory staff is ensured by requiring the wearing of:

- Sturdy, closed shoes at all times;
- A good quality dust mask with P2 filter;
- Eye protection where necessary; and
- Ear protection when working with/near noisy machinery, such as the mill, extraction fan, or air gun.

In addition, all laboratory staff undergo training with all equipment, are aware of, and have access to, the Material Safety Data Sheets (MSDS) for all chemicals used, and are First Aid trained. Periodic breaks are taken during the working day and staff are rotated on different tasks within NGSA and also with other Palaeontology and Sedimentology Laboratory and Minerals Laboratory tasks.

PREPARATION OF BULK SAMPLES

Sample receipt and storage

Samples are dispatched by road freight to Geoscience Australia by the field teams as soon as practically possible after completion of a field trip (generally within 2 weeks). The samples consist of two plastic bags for the TOS, which are contained in one tied closed calico bag, and two plastic bags for the BOS, which are contained in another tied closed calico bag. Both calico bags from any given site are placed in one plastic drum or bucket with a sealing lid. Sample identification consists of a loose Tyvek™ tag placed inside each pre-labelled plastic bag, along with a sample identifier written on each calico bag and on each bucket (see NGSA Field Manual by Lech *et al.*, 2007, for more details). A minimum of 6 kg of TOS and 6 kg of BOS was specified in the Field Manual. To date, the average weight of sample received at Geoscience Australia is just over 8 kg for each.

Approximately 450 linear m of shelving space is dedicated to the NGSA samples in Geoscience Australia's stores. As the Sample IDs are randomly attributed to the field teams (see Lech *et al.*, 2007), the samples are rearranged in order of increasing Sample ID in the stores (Figure 11). This allows the analyses to be performed in that order, rather than the order of collection, to avoid regional bias, false anomalies, and improve variance estimates (see Lech *et al.*, 2007).

Figure 11. Complete row of shelf space dedicated to NGSA samples in Geoscience Australia's stores. Note the already dried samples in heat-sealed plastic bags with their field calico bags on top, and the samples partially and completely processed with yellow and pink markings, respectively.

Drying

Upon arrival the samples are prioritised for the drying phase. The wettest samples are dried immediately; dry ones are temporarily stored for later drying. For drying, each plastic bag is opened and its contents emptied into two new, rectangular, food-grade aluminium trays (~250 x 380 x 50 mm or larger). Each tray is labelled externally with the Sample ID of the contained material. At this stage, visual inspection of the sample allows any gross foreign organic material (e.g. twigs, rootlets, animal droppings) or lithic fragments (e.g. gravel, large rock fragments) to be removed and discarded. Any extraneous/anthropogenic material (e.g. glass fragments) is removed, described in a spreadsheet (**PRODUCT 9** in Figure 6) and placed in a zip-lock bag labelled with the Sample ID.

The aluminium trays are placed in a fan-forced oven that is thermostatically controlled to 40 (±5) °C for a minimum of 48 hours, or longer if required, ensuring that there are no signs of moisture left. The temperature is continuously monitored with thermometers placed on the middle shelf of each oven (Figure 12).

Figure 12. Drying of the samples in thermostatically controlled fan-forced ovens at 40 (±5) °C. Note the calico bags on top of the oven; they follow each sample through the process to minimise mislabelling risk.

Once samples have been dried they are either processed further immediately, or, more routinely, the trays are heat-sealed in plastic bags (some of which can be seen in Figure 11), to avoid re-hydration and contamination, and temporarily stored until they can be processed further. The labelled calico bag and the loose Tyvek™ tag accompany each sample throughout the process to provide a cross-check on its identity.

Disaggregation and homogenisation

When the samples are dry, the contents of the two aluminium trays for any given sample are passed through a 3.35 mm (ASTM 6#) stainless steel mesh to further remove unwanted coarse particles (e.g. twigs, animal droppings, gravel, large rock fragments). Any clay clumps or soil aggregates that do not pass through this sieve are gently disaggregated using a porcelain pestle and a thick glass bowl (Figure 13). After this stage, the sample is thoroughly mixed by passing it through a large, steel riffle splitter, re-combining and re-splitting at least 6 times to homogenise the sample.

Figure 13. Disaggregating clay clumps in a sample with a porcelain pestle to ensure it passes through the 3.35 mm stainless steel mesh.

First stage splitting and archiving

After homogenisation, each sample is split into 2 halves using a large riffle splitter. One half is placed in a new plastic bag labelled as archive sample and containing the original Tyvek™ Sample ID tag. The bag is then heat-sealed after excess air has been evacuated. This bag is placed in the original field calico bag, which is then tied closed with its draw-strings and set aside for archiving (**PRODUCT 1** in Figure 6). The archive sample is preserved for future use, for instance when new analyses are suggested or new methods become available.

Other bulk sample products

The remaining half of the bulk sample (theoretically ~3 kg, in practice an average of ~4 kg) is reduced in size by successive riffle splitting (using the medium sized, stainless steel riffle splitter, see Figure 9) into:

- 1 x 10 mL vial (~20 g) for LPSA, and pH of 1:5 (soil:water) and EC 1:5 (soil:water) determinations; and
- 1 x 24 dram vial (~80 g) for X-ray diffraction (XRD) analysis (**PRODUCT 2** in Figure 6).

When these samples are processed, a database of results will be created (**PRODUCT 8** in Figure 6). There are no immediate plans within the NGSA project to systematically analyse all samples by

XRD. If/when XRD analysis is carried out in the future, however, samples for bulk analysis or various size fractions can be separated from the vial prepared as described above.

Sieving at 2 mm

The remainder of the dried bulk sample is then dry sieved through a 2 mm (ASTM 10#) 200 mm diameter x 50 mm height Essa Test Sieve (ISO 3310-1) 316L stainless steel body and stainless steel/RF mesh. Any clay clumps or soil aggregates retained in the sieve are gently broken down further using the pestle and bowl as described above. Care is taken not to crush rock fragments or hard nodules in the process. Sieving is performed using a Retsch AS 200 shaking device (Figure 14) for a period of 30 s.

Figure 14. Stacked sieve ring and pan assemblies clamped in shaking devices.

The remaining material >2 mm in size is removed and stored in a labelled zip-lock plastic bag.

The resulting <2 mm fraction is riffle split (using the medium sized, stainless steel riffle splitter, see Figure 9) into two portions, one (~20 %) for preparation of the 'coarse fraction', the other (~80 %) for preparation of the 'fine fraction' products, as described below.

PREPARATION OF COARSE FRACTION SAMPLES
Second stage splitting

The smaller portion (~20 %) of <2 mm material prepared above is riffle split (using the medium sized, stainless steel riffle splitter, see Figure 9) into:

- 1 x 12 dram vial (~50 g) for PGEs analysis; and
- 1 x 12 dram vial (~50 g) for Au analysis after *aqua regia* (AR) leach (**PRODUCT 3** in Figure 6).

The rationale for doing PGEs analysis on an unmilled <2 mm fraction is to be consistent with other similar recently published studies (Reimann *et al.*, 2007). The rationale for doing AR gold + multi-element analysis on an unmilled <2 mm fraction is that digestion of coarse and poorly AR-soluble

minerals (e.g. quartz, K-feldspar, plagioclase, hornblende, ilmenite, etc.; see Tarvainen *et al*., 1996) is sought to be minimised to reduce the dilution effect that would result and enhance the signal-to-noise ratio of this partial digest. Crushing these normally abundant minerals would result in much smaller anomalies of elements derived from AR digestion of other minerals (e.g. calcite, many clay minerals, goethite, chlorite, biotite, pyrite, apatite, etc.; see Tarvainen *et al*., 1996).

Milling

After samples are taken for PGEs and AR analysis, ~80-100 g of material is separated by riffle splitter (using the medium sized, stainless steel riffle splitter, see Figure 9) and milled using a Rocklabs™ carbon steel bowl (164 mm outer diameter), lid, ring and puck assembly or head (CARB-200-BLRP). Two new, dedicated heads were purchased specifically for this project (Figure 15) and were conditioned with several pure quartz and soil runs before being used on NGSA samples. The choice of the carbon steel head rather than others made from different materials is based on compositional figures of the head materials published by Rocklabs™ (Rocklabs, 2009) and, especially, on results of in-house contamination tests (Webber *et al.*, 2005). These tests indicated that carbon steel results in the most benign contamination given the composition of the samples in this project: 2500-3400 ppm iron (Fe) and <5 ppm chromium (Cr), copper (Cu) and nickel (Ni) for a 50 g charge of acid-washed Merck granular quartz milled for 60 to 180 s.

Figure 15. Two carbon steel mill heads used for NGSA project.

Figure 16 shows that the described milling procedure does not introduce significant contamination or unduly increase the standard deviation on a set of Ovens River Internal Standard (ORIS) sample runs. The NGSA samples were ground in charges of 80-100 g for 2.5 min. Samples were initially tested by a laser particle size analyser to ensure that >75 % of the material was <75 μm in size after grinding. Subsequently, the degree of fineness of every sample was assessed by rubbing the milled powder between two fingers; any discernible grittiness resulted in further milling (material touched by skin is discarded).
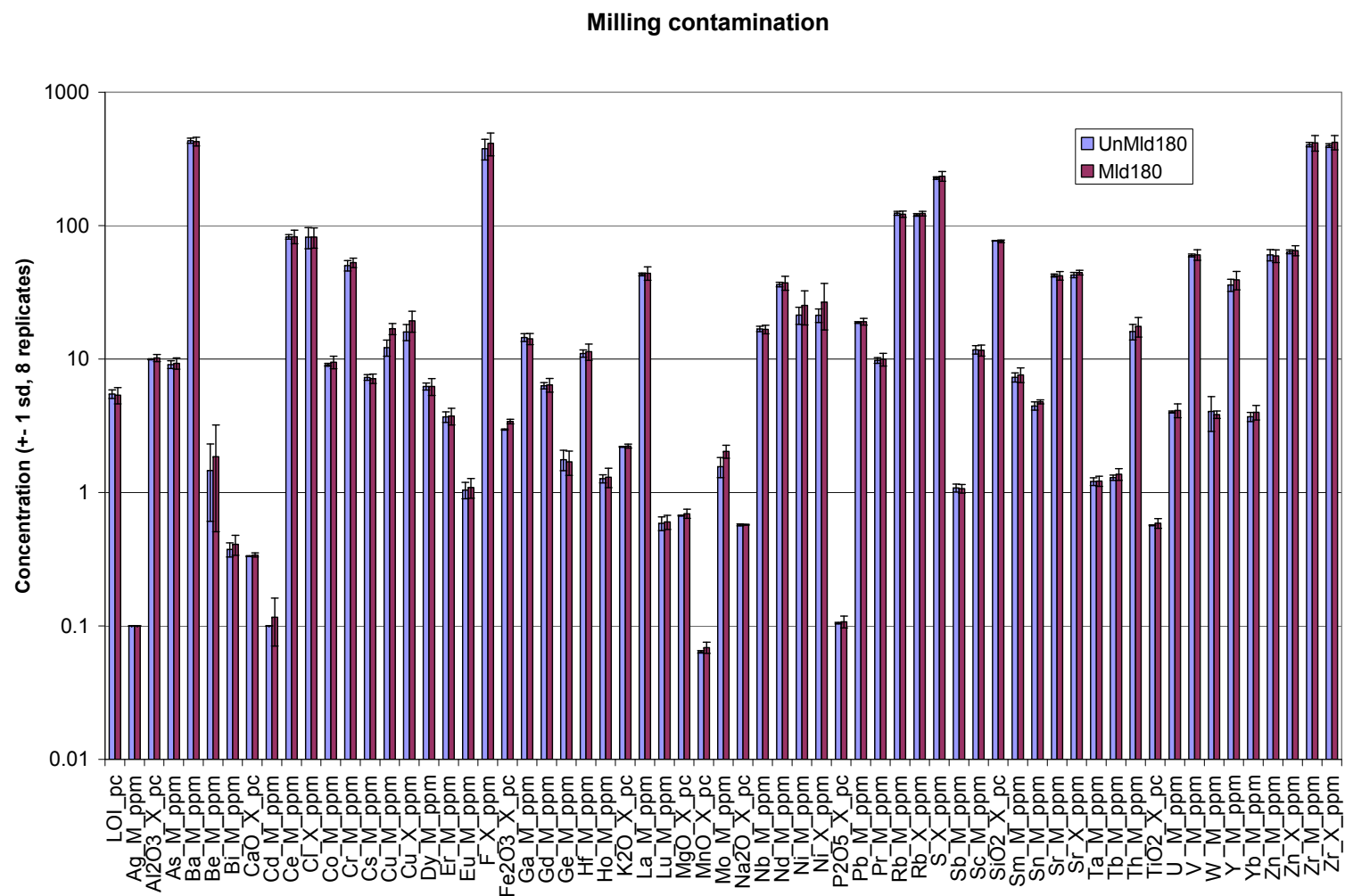
Milling contamination

Figure 16. Average concentrations (± 1 standard deviation) of 8 replicate samples of internal standard ORIS unmilled <180 um fraction (first bar) and milled for 90-120 s in NGSA's carbon steel mill heads (second bar). Analyses by ICP-MS (suffix _M) and XRF (suffix _X) expressed in ppm (suffix _ppm) or % (suffix _pc).

The milled <2 mm material is then divided (here pouring and scooping *is* permitted as the material is very fine and well homogenised in the mill bowl) into:
- 1 x 5 mL vial (~6 g) for F analysis;
- 1 x 5 mL vial (~6 g) for Se analysis; and
- 1 x 12 dram vial (~50 g) for XRF and ICP-MS analysis.

Any excess <2 mm milled material is preserved in a zip-lock plastic bag (**PRODUCT 5** in Figure 6).

Any excess *unmilled* <2 mm material is preserved in a separate zip-lock plastic bag (**PRODUCT 4** in Figure 6).

After each sample, the mill head is 'decontaminated' by grinding a charge of at least 100 g of quartz with water for 90 s, then cleaned by scrubbing under warm water and rinsing, and finally dried with the air gun.

PREPARATION OF FINE FRACTION SAMPLES
Sieving at 75 µm
The remaining (and largest, ~80 %) portion of material sieved at <2 mm as described above is used for the preparation of the fine, <75 µm, fraction. This separation is performed dry using 75 µm (ASTM 200#) stainless steel mesh sieves (200 mm diameter x 50 mm height Essa Test Sieve (ISO 3310-1) 316L stainless steel body and stainless steel/RF mesh). Initially, the intention was to use nylon mesh, but this was found to be incompatible with the scope of the present task, mainly because nylon sieves are mounted in plastic rings, and these are not rated to be used on shaking devices. Thus, if nylon sieves were to be used, the shaking would have to have been done manually, significantly increasing the length of time for sample preparation, and consequently, the cost.

At the beginning of the project, a test was performed to check the degree of contamination potentially deriving from the use of 75 µm stainless steel sieves. This was done by taking 16 identical splits of internal standard ORIS and sieving 8 of them with a 75 µm nylon mesh and 8 others with the stainless steel mesh. Results are shown in Figure 17.
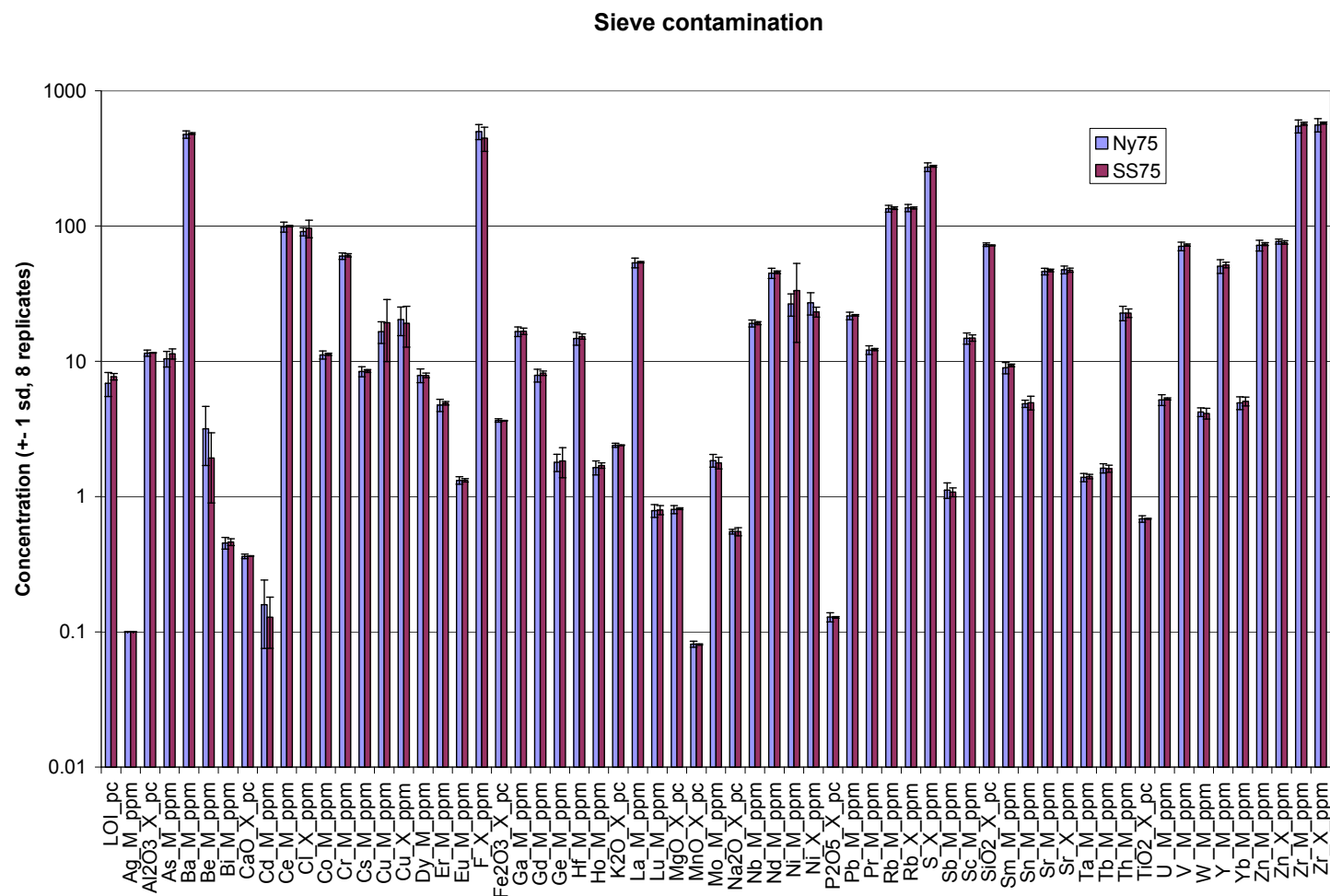
Sieve contamination

Figure 17. Average concentrations (± 1 standard deviation) of 8 replicate samples of internal standard ORIS sieved at 75 µm using nylon mesh (first bar) and 8 other replicate samples sieved using stainless steel mesh (second bar). Analyses by ICP-MS (suffix _M) and XRF (suffix _X) expressed in ppm (suffix _ppm) or % (suffix _pc).

Clay clumps and soil aggregates are further broken down gently (if necessary) at this stage to maximise the quantity of material passing through the 75 µm sieve, without crushing rock fragments or hard nodules, as described previously. Sieving is performed using a shaking device as described above for 3 min (Figure 14). Sieves are cleaned as described in the QA/QC section above. Visual inspection for wear and tear of the sieves is performed at regular intervals. It was found necessary to replace the set of sieves after ~1 year of usage in the NGSA project (or when ~35 % of samples had been sieved).

The material that does not pass through the 75 µm sieves at this stage is preserved in a zip-lock plastic bag and labelled for potential future use (geochronology, heavy minerals?) (**PRODUCT 6** in Figure 6).

Third stage splitting

Using small Endecotts stainless steel riffle splitters (the small sized riffle splitter, see Figure 9) the <75 µm fraction is split into 5 different aliquots (splits) for different analyses. These aliquots are ranked in order of decreasing priority as follows:
- 1 x 12 dram vial (~50 g) for XRF and ICP-MS analysis;
- 1 x 12 dram vial (~50 g) for Au analysis;
- 1 x 5 mL vial (~6 g) for F analysis;
- 1 x 5 mL vial (~6 g) for Se analysis;
- 1 x 12 dram vial (~50 g) for PGEs analysis.

Any excess <75 µm material is preserved in a zip-lock plastic bag (**PRODUCT 7** in Figure 6).

Because this fine fraction can be difficult to obtain for some samples, there occasionally may not be enough material available to fill all of these vials completely. In these cases, it is ensured that just enough material is provided as required by the laboratories (bare minima are ~10 g for XRF and ICP-MS, ~26 g for Au, ~1.5 g for F, ~5 g for selenium Se, and ~30 g for PGEs). If there is not enough <75 µm material to provide enough minimum sample for *all* analyses, then the highest priority ones take precedence; in such cases, PGEs and perhaps also Se, may not be analysed for this fine fraction. At the time of writing, the first 25 % of total samples had been sent for analysis to external laboratories. Of this 25 %, 0.5 % of samples could not be submitted for *aqua regia* (Au) analysis, 4.8 % for PGEs analysis, 1.1 % for Se, and 0.9 % for F because of shortage of the <75 µm material.

List of Products

In summary, the following products are generated during the sample preparation phase of the NGSA project (numbers given are estimates generated at the beginning of the project).

PRODUCT 1:
- 3058 (1529 TOS + 1529 BOS) archive plastic bags, labelled with Sample ID and containing Sample ID tag; each archive plastic bag is placed in its corresponding original calico bag. The bags are to be stored in labelled cardboard boxes in order of increasing Sample ID.

PRODUCT 2:
- 3058 x 10 mL vials (labelled with Sample ID) containing bulk material. The vials are to be stored in labelled cardboard boxes in order of increasing Sample ID.
- 3058 x 24 dram vials (labelled with Sample ID) containing bulk material. The vials are to be stored in labelled cardboard boxes in order of increasing Sample ID.

PRODUCT 3:
- 6116 x 12 dram vials (labelled with Sample ID + suffix '3') containing <2 mm sieved, unmilled material. The vials are to be stored labelled in cardboard boxes in order of increasing Sample ID.

PRODUCT 4:
- 3058 x zip-lock bags (labelled with Sample ID + suffix '3') containing excess <2 mm sieved, unmilled material. The bags are to be stored in labelled cardboard boxes in order of increasing Sample ID.

PRODUCT 5:
- 6116 x 5 mL vials (labelled with Sample ID + suffix '2') containing <2 mm sieved, milled material. The vials are to be stored in labelled cardboard boxes in order of increasing Sample ID.
- 3058 x 12 dram vials (labelled with Sample ID + suffix '2') containing <2 mm sieved, milled material. The vials are to be stored in labelled cardboard boxes in order of increasing Sample ID.
- 3058 x zip-lock bags (labelled with Sample ID + suffix '2') containing excess <2 mm sieved, milled material. The bags are to be stored in labelled cardboard boxes in order of increasing Sample ID.

PRODUCT 6:
- 3058 x zip-lock bags (labelled with Sample ID + suffix '9') containing sieved 75-2000 μm material. The bags are to be stored in labelled cardboard boxes in order of increasing Sample ID.

PRODUCT 7:
- 6116 x 5 mL vials (labelled with Sample ID + suffix '7') containing <75 μm sieved material. The vials are to be stored in labelled cardboard boxes in order of increasing Sample ID.
- 9174 x 12 dram vials (labelled with Sample ID + suffix '7') containing <75 μm sieved material. The vials are to be stored in labelled cardboard boxes in order of increasing Sample ID.
- 3058 x zip-lock bags (labelled with Sample ID + suffix '7') containing excess <75 μm sieved material. The bags are to be stored in labelled cardboard boxes in order of increasing Sample ID.

PRODUCT 8:
- Microsoft Excel spreadsheet(s) containing values for Sample ID, LPSA data and measured pH 1:5 (soil:water) and EC 1:5 (soil:water).

PRODUCT 9:
- Microsoft Excel spreadsheet containing values for sample number, processing date and a record of any observed extraneous or anthropogenic materials identified in the sample.

A description of the analyses performed on the NGSA samples will be the subject of a separate report.

Acknowledgments

The authors are extremely grateful to the NGSA laboratory staff members Matthew Brown, Jessica Byass, Nounou Chanthapanya, Zia Husain, Bozana Krsteska, Andris Lukss, Ador Makuei, Greg O'Connor, and Kylia Wall for their dedication, perseverance and reliability in processing all these samples.

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