RECOMMENDED PROCEDURES FOR GEOCHEMICAL SAMPLING AND ANALYSIS

K.G. McQueen
CRC LEME
Department of Earth and Marine Sciences
Australian National University, ACT 0200
Ken.McQueen@canberra.edu.au

GENERAL CONSIDERATIONS

The following are some general rules applicable to all geochemical sampling programs:

- Remove all jewellery, particularly rings when sampling for low level gold, silver and PGEs;
- Take a sufficient number and type of duplicate/replicate samples for quality control;
- Submit standard samples to check laboratory accuracy.

GUIDELINES FOR SAMPLING SOILS

Soil samples are a widely used geochemical sampling medium, including in the Cobar area.

Soil sampling is generally recommended in the following situations:

- Areas of residual soil over saprock;
- Areas with soil developed on *in situ* regolith;
- Areas with soil developed over transported regolith that is less than 5 m thick.

Soil sampling may be appropriate in areas of deeper transported cover (up to 10 m thick) where deep-rooted vegetation has been active.

Most soils in the region contain a transported component (e.g. wind-blown dust/silt, alluvium/colluvium, lag transported by sheetwash) and some consideration needs to be given as to whether this component is likely to be a significant dilutant or contaminant and the extent and direction of transport. Calcrete nodules or finely dispersed carbonate are commonly present in the alkaline soils of the region (particularly in the lower part of the soil profile) and may affect partial extraction techniques that are pH sensitive. Carbonate-bearing zones may have higher gold concentration.

Sampling program
Parameters that need to be decided are:

- Sample spacing;
- Soil horizon to be sampled, which broadly relates to the depth of sampling;
- Soil fraction to be sampled and analysed (generally either bulk soil or a particular size fraction);
- Method of sample digestion and analysis.

Sample spacing
Soil samples are generally collected on a rectangular pattern, generally with closer spacing of sample sites along more widely spaced sample lines. Theoretically, the sampling lines are oriented normal, or at a high angle, to the expected longer dimension of the target, but the

orientation of a geochemical dispersion pattern is generally not well known, if at all, before sampling.

The optimum spacing between sampling lines and sample sites will depend on the purpose of the survey and the expected size of the dispersion halo to be detected. Generally the aim is to obtain at least 2 samples from the anomaly on a sampling line. Common sample spacings for reconnaissance soil sampling are 400m by 400m or 200m by 400m. For detailed anomaly detection samples are commonly collected at 100m intervals on 200m spaced lines with infill sampling down to 50m on 100m spaced lines.

Soil horizon to be sampled

Many soil sampling programs in the Cobar region have taken shallow soil samples (10-20 cm depth) for ease of sampling and speed. The near surface layer (< 50 cm) of many of the soils has a large component of wind blown dust or has been partly eroded and disturbed by agricultural activities. Near surface samples may have advantages in areas of deep transported or leached regolith where the target and pathfinder elements have been taken up by deep-rooted vegetation to be deposited and accumulated in the humus component of the upper soil layer (although in some areas this has been eroded away). The near-surface zone of the soil may also contain ferruginous lag fragments which retain a geochemical signature from their source.

In very shallow soils (e.g. skeletal soils on bedrock rises) it is probably best to sample as close to the base of the soil as possible. For deeper colluvial and alluvial soils (particularly where they have been ploughed) sampling below the plough hard pan (about 50 cm) will give a less disturbed or contaminated clay-rich sample.

As with most sampling methods, it is important to be as consistent as possible in terms of the type of material collected (but not necessarily the depth of sampling).

Soil fraction

Traditionally, soil geochemical surveys have targeted the finer fraction (<120 μm), clay-rich B horizon, in the belief that cations present will be largely adsorbed onto clays. This will be influenced by the type of clays in the soil, for example kaolinite and illite have very low cation exchange capacities, whereas smectites have high cation exchange capacities. In the deeply weathered regolith of the semi-arid Cobar region, most of the cations are probably hosted in iron and manganese oxides/oxyhydroxides, carbonates and residual rock and quartz grains (as occluded particles of other host minerals). The coarser fraction (up to 2-3 mm) will target these soil components and a number of studies have shown that the 0.1-2 mm fraction generally gives a stronger response for most target and pathfinder elements. The simplest option is to take a bulk sample of material less than 3 mm in size, which will include grains of lithic and ferruginised lithic material and the finer clays and granular carbonate. The wind blown component is generally in the 60-80 μm size range so selecting the 100 μm to 3 mm fraction will largely remove this dilutant (mostly quartz and kaolinite) although it may also remove much of the residual clay component, powdery carbonate and fine organic matter.

Method of sample digestion and analysis

The sample digestion method will depend to some extent on the elements being targeted and their host phase/s. A strong acid digest is most suitable for all round multi-element detection where the target and pathfinder elements are both weakly and strongly bound in ferruginous and weathered lithic components.

Aqua regia is commonly used because it will dissolve elemental gold, as well as breakdown iron and manganese oxides/oxyhydroxides, carbonates, sulphates, sulphides and many clays. It will not release elements or minerals included within quartz (including silcrete) or other insoluble silicates nor dissolve resistate minerals such as chromite, rutile, cassiterite, ilmenite, zircon.

Near total digestion of samples, including the silicates (but not resistates), can be achieved with a multi-acid digest of hydrofluoric-perchloric-nitric acids. This is not suitable for gold analysis and has the other disadvantage of producing solutions with high total dissolved solids, which can affect the sensitivity of the analytical method.

Less aggressive digests are designed to take up only weakly bound ions, but there are many documented cases where such an approach gives good anomaly definition. Dilute hydrochloric acid has been used in this way, particularly for gold exploration, where the gold is thought to be very finely dispersed (e.g. in carbonate or organic matter). Hydrochloric acid will dissolve gold, but the AuCl species is not stable, except for very small particles of gold. There are also a range of proprietary partial leach and selective extraction methods designed to target elements weakly bound to specific materials (e.g. MMI, Regoleach, Enzyme Leach). These digestions have the advantage or producing solutions with very low total dissolved solids, which increases the sensitivity and detection limit of the analytical method. This is probably their main advantage.

Solutions obtained from acid digests, partial leach and selective extractions can be analysed using a number techniques. Currently the most popular, efficient and cost effective technique for multi element analysis is a combination of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) and Inductively Coupled Plasma Mass Spectrometry (ICP MS). Graphite Furnace Atomic Absorption Spectroscopy (GF AAS) following aqua regia digest and solvent extraction (concentration) may be used for low-level gold analysis.

Instrumental neutron activation analysis (INAA) or X-ray fluorescence analysis (XRF) can be used for true total multi-element analysis. These methods cover a wide range of elements and have the advantage that the elements do not have to be taken into an aqueous solution. These techniques are also commonly used to independently check analyses obtained by other methods.

The various options for sample digestion and analysis should be carefully discussed and negotiated with the analytical laboratory providing the service.

Sample location and sampling methods

Historically, soil samples have been collected on a surveyed and pegged grid. The current accuracy of portable GPS receivers is sufficient for sample sites to be located using this method, but always establish a physical datum and peg a baseline at sufficient intervals to allow samples to be relocated if there is a problem with the GPS (user error, drift etc). Location, sample numbers and site descriptions can be entered into a suitable data base or GIS platform.

Shallow samples are conveniently collected using a pelican pick (or similar). A planting shovel (with narrow straight blade) may be more efficient in hard soils (common in the Cobar region).

Deeper samples can be collected with a hand auger (e.g. standard 20 cm diameter soil auger). Practitioners in the region prefer a small diameter (6.5 cm) Jarret or Dormer auger for deep sampling in hard clay-rich soils. Four wheel drive mounted, motorised spiral augers have also been used. These can have difficulties when layers of pisoliths are intersected in the soil.

For most soil sampling surveys, 300-500 g samples are sufficient, although larger samples (up to 5 kg) may be collected for bulk leach extractable gold (BLEG). Collected samples should be placed in chemical-free paper (geochemical bags) suitable for drying in the sun or a drying oven.

Sample preparation and sieving should be conducted in areas free from any wind blown contaminants and particularly away from active mine sites.

GUIDELINES FOR SAMPLING LAG

Lag fraction

Different size fractions of lag can be sampled, depending on the purpose of the survey (i.e. regional reconnaissance, using the generally smaller size of transported lag, or detailed target location using the larger less transported and worked sizes). A common size used is 3-15 mm. In theory and for special surveys it is possible to separate out a particular compositional component (e.g. highly ferruginous, lithic, quartz) but apart from selecting the magnetic fraction, most surveys would not find this practical, because of the extra time involved.

Bulk lag is probably the best material to sample. There have been a number of surveys targeting the magnetic lag. This material generally is more ferruginous and contains greater than 5% maghemite. It is easy to sample using a simple plunger type, hand held magnet. However, the magnetic fraction is generally enriched in hematite (a good host mineral and scavenger for As, Pb, Bi, Sb) and in many cases goethite-rich lag and goethitic lithic lag may be a better medium. Goethite is good host for Cu, Zn and other target and pathfinder elements and goethitic lithic lag is more likely to reflect a close or underlying source. Maghemite forms at the surface from the other iron oxides/oxyhydroxides and so there is a greater probability that maghemite-bearing (magnetic) lag has been at the surface longer and hence subjected to possible transport. Removing the magnetic fraction or analysing it separately may be to advantage if you are interested in understanding the more ferruginous transported component.

Sequential digestion studies have indicated that most target and pathfinder elements are strongly bound in ferruginous lag, particularly in the hematite component. This means that this material will generally retain its geochemical signature under surface conditions.

Sampling Steps

- Locate sample sites with GPS receiver and enter into data base or GIS platform.
- Record the regolith landform setting.
- Estimate the proportions of the main lag types, for example: highly ferruginous (including magnetic and non magnetic); ferruginised lithic; lithic; quartz; calcrete; other.
- Estimate the range in clast size.

- Estimate the proportion of transported and in situ lag (based on degree of clast rounding, size of clasts, composition of clasts).

- Sweep up lag with plastic dust pan and brush over about a 5 m diameter area. About a 2 kg sample is sufficient.

- Sieve out the coarse pebbles, sticks etc (greater than 1 or 2 cm) on to a plastic sheet and quickly pick out any obvious organic material. An alternate approach is to float off any light organic material by washing the lag in water prior to sample preparation.

- Extract the magnetic fraction, if this is to be removed from the final sample or targeted separately. In cases where it is possible that only small amounts of magnetic material are present, this should be done in the field to ensure that a sufficient magnetic sample has been collected.

Sample preparation and analysis

- Select the desired size fraction/s or compositional component/s by sieving or hand picking.

Most regional surveys will target the bulk lag over a particular size range (e.g. 3-15 mm) and the sieving can be done on site as the samples are collected.

- The sample will need to be pulverised (this is generally done by the commercial laboratory) before analysis using the most appropriate method (see description of ***Method of sample digestion and analysis*** for soils). An aqua regia digest is commonly used. Instrumental Neutron Activation Analysis is a good method for total analysis.

GUIDELINES FOR THE SAMPLING OF PLANT MATERIALS IN A BIOGEOCHEMICAL PROGRAM

S.M. Hill
CRC LEME
School of Earth & Environmental Sciences
University of Adelaide SA 5005
steven.hill@adelaide.edu.au

Increasingly mineral explorers are considering the advantages of taking plant samples in mineral exploration programs when trying to explore through transported cover. Some of the advantages of this technique include:

- Widespread and in some places abundant cover across the landscape;
- Easy access to samples that in many cases are convenient to take;
- An ability for plant organs to provide chemical expressions that have penetrated through the transported cover;
- The ability to selectively extract and concentrate some elements (e.g. hyper-accumulators);
- A potential ability to homogeneously amalgamate a chemical signature from an enlarged and potentially heterogeneous substrate;
- Environmentally passive exploration approach, with minimal site disturbance and need for remediation; and;
- Some proven exploration success and expression of buried mineralisation.

The following is a short account of how to take a plant sample as part of a biogeochemical program.

Sampling Program

The following are aspects recommended for your consideration:

- Decide upon the nature of the survey required, including the area, sample spacing and sample location. Some localities allow for plants to be sampled conveniently along a transect or a grid, whereas others need to be sampled opportunistically (e.g. in sparsely vegetated areas) or along a restricted landscape setting (e.g. trees along creek lines). Sample spacing will depend upon variables such as the plant species targeted, the size of the exploration target and associated dispersion halo;
- Choose a target plant species or several plant species. The best results are obtained when plants of the same species are sampled because their assay results are more comparable. This typically includes one of the most widespread and abundant plant species from the project area. If there is existing knowledge on particular plant species in your area, then this may also influence the choice of target species. Choosing a plant species that is distinctive and easy to identify can make your job easier.You need to be confident that the chosen species will be reasonably deep rooted. In most cases a small orientation program testing a range of species in different landscape, regolith and geological settings is recommended if time and money allow;
- For your chosen species, a uniform plant organ (e.g. leaves, twigs of similar diameter, bark, wood, fruits, flowers, roots) is recommended for sampling. The more uniform and consistent that your sample is the more valuable the comparisons between sample assay results will be. As a general rule plant leaves can be the easiest to sample and

prepare for analysis. Try to target leaves of uniform age / maturity in order to reduce sample variability;

- Temporal variations (especially time of year with respect to seasons or rainfall events in arid areas) can have an impact on the variability in your assay results. Try to sample within a limited time period, and be very careful comparing assay results from samples taken at different times of year or in different climatic context; and,
- Plant sampling duplicates are important for QA/QC measures. The degree of duplication will depend upon your own protocol, however depending on total sample population size, duplications in the order of 1 in 10 are typical.

Plant Sampling

The general rule here is to obtain uniform and therefore comparable samples between your population of target plants. Assuming that you are targeting a consistent plant species and plant organ, some general considerations include:

- Before sampling, record the sample location (GPS coordinates), type and description of plant, and regolith-landform site information;
- Be cautious of sources of environmental contamination such as dust (e.g. from roads, ploughed pastures, drill rigs and mine sites). If possible it is best to avoid samples that may be excessively influenced by dust, particularly because later washing of the sample is typically less than effective and may leach or further contaminate for some elements;
- Recommended sample bags are made of unbleached paper (e.g. brown paper lunch bags are ideal).g These minimise sample sweating and decomposition and add minimal contamination to the sample. The opening of these bags can be folded over once the sample has been collected (avoid metal fasteners for the bags, such as staples or pins, because these can be a source of metal contamination);
- It is recommended to have clean hands, remove jewellery and preferably wear powder-free latex or nitrile gloves for each sample. This minimises contamination while sampling;
- Try to take samples from a uniform height and from around the plant canopy; and,
- The optimal sample size is still debated between some researchers, and will depend to some extent upon the analyticl technique used. Typically your sample should be no less than 20 g, and ideally several hundred grams (which usually comes to about half to three quarters a bag full).

Sample Storage and Preparation

Sample decomposition and contamination are to be minimised during storage. A sheltered well-ventilated site is recommended. Samples may need rotation during short-term storage to avoid irregular sweating and decomposition. Low temperature, clean oven drying will desiccate and stabilise the sample. An oven temperature of <60° C for approximately 48 hours is recommended. Higher oven temperatures may volatilise some important chemical components from your samples. Once thoroughly dried, samples can be stored in snap-seal plastic bags for longer periods.

The type of preparation required will ultimately depend on the type of plant analytical technique to be performed. A standard technique suitable for most approaches is as follows:

- Thoroughly clean a mill using a combination of high purity ethanol, paper towel and compressed air. It is important to use the same degree of care to reduce contamination in the laboratory as was used in the field (e.g. wear powder-free latex or nitrile gloves);

- Preferred mill types are quite variable between different people. Suitable results have been obtained using household stainless steal coffee and spice mills with rotating blades. The contamination from these mills is less significant for soft plant organs such as leaves;
- Pre-contaminate the mill with a small amount of the sample to be prepared. Use a short milling time and discard this preliminary material before adding the main part of the sample;
- Once the sample is milled to a fine powder (typically a consistency approaching that of talcum-powder) then this can be removed from mill and stored in a labelled, snap-seal plastic bag; and,
- Re-clean mill.

Sample Analysis

This will depend on time, budget and of course the element suite that you are interested in. Techniques such as ICP-MS, ICP-AES, XRF, INAA and AAS have all been widely and successfully used for the analysis of plant materials.

Standard and certified reference material should be included in your sample batch for submission. These are available for plant material, although presently no materials exist for Australian native vegetation.

For further information please consult CRC LEME's ***Explorer's Guide to Phyto-exploration***, due for release in 2008.