

Appendix 3A

Sample preparation, analysis and discussion of quality assurance – quality control (QA/QC) for regolith and spinifex chemistry

Sample collection

Regolith

Regolith samples were collected using a Tanaka power auger fitted with a 10 cm diameter auger bit, which can penetrate to a maximum depth of 90 cm. At each sample site, about 4 kg of regolith was collected from the bottom of the augered hole, and split between two plastic bags; one for geochemical analysis and one for archiving. Both plastic bags were secured with a nylon cable tie and placed in a drawstring calico bag. All three bags were labelled with the site number. On completion of sample collection, the augered hole was backfilled. At some sites, regolith was on or close to areas of outcrop, the regolith was cemented, or regolith had a high proportion of lithic or carbonate clasts. At these sites, regolith was collected from the maximum penetration depth of the auger, or (where augering could not be carried out) excavated using a small shovel. The sample depth was recorded on each site form (Appendix 3B, 3C).

Ferruginous lag, consisting of a surface veneer of subrounded to rounded iron-rich granules, nodules and ferruginized lithic fragments, was collected by sweeping the material into a plastic dustpan using a nylon brush. Approximately 400 g of material was collected where available, and placed in a paper geochemistry sample packet, then sealed using the paper-covered wires. The packet was labelled with the site number and placed in the calico bag with the regolith samples.

At every tenth site, a site duplicate (i.e. a second sample of regolith and, if available, lag) was collected 50 cm to 1 m from the primary sample. Site duplicates were labelled with the site number suffixed with 'd'.

Spinifex

Spinifex samples were collected from healthy plants using Bosch Li-ion grass shears. At each site, several bunches of spinifex were harvested from each plant, detached about 4 cm above the ground to exclude any root material and adhered regolith. Seed-bearing heads and dead strands were removed before or after sampling. Leather riggers' gloves were worn when handling plant material, and any dust or resin build up, and extraneous spinifex spines, were cleaned off the shears between samples. At two sample locations (SR8 and SR12), and at the Wolfe Creek Crater (approximately 180 km north of Yagga Yagga), a second sample (sample duplicate) was taken from the same plant to test for within-plant homogeneity. Within-site homogeneity was assessed by analysis of spinifex from six plants within a 50 m radius at Zone 52 388016E and 7698776N.

Spinifex samples were placed in a 37 x 31 cm drawstring calico bag. This bag was tied off and placed in a second calico bag (labelled with the site number). Samples were put in 20 litre white plastic pails, sealed with a tight-fitting lid and labelled with the numbers of the contained samples. At the field base, pails were stored in a cool, dust-free room and the lid loosened to encourage air circulation. For transportation to Perth, lids were firmly reattached, and all pails were stored in a dust-sealed trailer.

Nett spinifex sample weights (i.e. taking into account the weight of the calico bags) ranged from 115 to 315 g. Each sample was oven dried at 80°C for 24 hours at GSWA's Carlisle Laboratory. Between 40 and 50 g of this dried material was packed in plastic bags and freighted to BV Minerals in Vancouver, Canada, for analysis.

Sample analysis

Regolith

Sample preparation and analysis was carried out by Intertek Genalysis Laboratory Services (Intertek-Genalysis, Maddington, Perth). A representative split of each regolith sample was dry screened for 30 minutes using a Retsch AS2000 sieve shaker, to provide sufficient <50 µm material for analysis. Clean nylon sieve cloth was used for each sample. Samples were analysed in six batches of between 96 and 123 samples. A second aliquot of the <50 µm fraction of 90 samples (i.e. sample duplicate) was analysed to assess within-sample homogeneity, and analysis of the <50 µm fraction of the 51 site duplicates provided an indication of within-site homogeneity.

For each batch, a number of materials of a known composition (reference materials; Kane, 1990; Brand, 2015) were inserted as blind samples, including four aliquots of the GSWA reference materials BB1 (basalt; Morris, 2007) and IQC47 (laterite; Morris, 2000), and the certified reference material granodiorite OREAS 24b. Several reference materials and analytical blanks were inserted by Intertek-Genalysis.

Each sample was digested with aqua regia — a 3:1 mixture of hydrochloric (HCl) and nitric (HNO₃) acids — and analysed for 63 elements by a combination of inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectrometry (ICP-OES). Units of measurement and detection levels are shown in Table 5. An aliquot of the <50 µm fraction of 45 samples was analysed at a second laboratory (LabWest, Malaga, Perth) using a similar approach.

Quality control

Sample duplicates

The level of agreement between the parent and duplicate samples has been assessed using the Half Absolute Relative Difference (HARD; Stanley and Lawie, 2007) expressed as a percentage (Table 3.1).

$$\text{HARD} = 100 \times [(\text{analysis1} - \text{analysis2}) / (\text{analysis1} + \text{analysis2})]$$

The level at which HARD becomes unacceptable is not fixed, but in this Record a value <10 has been adopted, as long as the concentration of the analyte in either the parent or duplicate is >10x the lower level of detection (LLD), which takes into account increased analytical imprecision at lower concentrations.

Eight analytes (Al, Cs, Hf, Li, Rb, Sb, Ti and Zr) have HARD values >10 for more than 10 parent–duplicate analyses. The association of Al, Li, and Rb indicates that, despite aqua regia being a partial digest that is relatively ineffective in dissolving silicates (Chao, 1984; Mann, 2010), there could have been some variable digestion of clay. This may also account for higher HARD values for Ga and K in some samples. Higher HARD values for high field strength elements such as Hf, Ti and Zr reflect the resistance of minerals such as zircon and rutile, which are persistent during the weathering process (Scott and Pain, 2008), to digestion by aqua regia. Gold concentrations of most samples is <1 ppb, and generally show good agreement for sample duplicates. Exceptions are M697 (Liveringa Group, duplicate analyses of 4 ppb and <1 ppb), M893 (Hidden Basin beds; 6 and <1 ppb) M869 (Redcliff Pound Group; 5 and 1 ppb) and M823 (Liveringa Group; 4 and <1 ppb), which suggests some minor micro-nugget effects.

Five duplicates have HARD values >10 for 20 or more analytes, and the duplicate from site M884 (Liveringa Group) has 43 analytes with HARD >10. This level of disagreement is difficult to explain. Site information records an area of sheetwash with a high proportion of lithic fragments, located in a slight depression in an area of outcrop.

Site duplicates

HARD is >10 for Al, Ba, Ca, Hf, K, Li, Mn, Sr, and Zr for 10 site duplicates (Table 3.2). Similarly to variations in sample duplicates, the association of Al, K, and Li, indicates some variable digestion of clay, whereas Ca and Sr variations could be related to inhomogeneously distributed calcrete. Variations in Ba could reflect patchy gypsum distribution. The influence of minor resistate phases, such as zircon and rutile, may account for variations in Hf and Zr.

At 12 of the 51 sites, HARD is >10 for 10 or more analytes, including 36 analytes at M606 (Hidden Basin beds), and 37 analytes at M687 (Noonkanbah Formation). The reason for this higher level of within-site heterogeneity is unclear. The higher HARD values are spread across most element groups, in particular the REE and HFSE, and site information lists a higher carbonate content at M606, but homogeneous quartz-rich sand at M687.

Reference materials

Reference materials covering a wide compositional range from unmineralized to mineralized samples have been analysed in each batch (Table 3.3), but only four (OREAS 504b, OREAS 45e, OREAS 24b and OREAS 501b) have certified values for aqua regia digestion, limiting any assessment of accuracy. For these reference materials, HARD values are generally low if either the obtained or certified values of one or both analytes are >10x the LLD. However, Ba, Hf, Nb, Sb, Ti, W and Zr in OREAS 504b, Th, Ti, Y, and Zr in OREAS 24b, and Au and Mo in OREAS 501b show poorer agreement between obtained and certified values. However, in some cases, concentrations are low, and pertain to elements that are typically difficult to accurately analyse using a partial-digestion approach. For example, Hf and Nb in OREAS 504b have certified values of 0.5 ppm and 0.81 ppm, respectively. In other cases, there is an underestimation of analyte concentration (such as Ba for OREAS 504b), or an overestimation (e.g. Au in OREAS 501b). In these cases, concentrations are well above the LLD.

Multiple analyses of reference materials can be used to gauge analytical precision, regardless of whether values are certified. The percent covariance (COV%, also known as percent relative standard deviation, or RSD%) is <10 for all analytes in laterite IQC47 (Morris, 2000), where concentrations are more than 10x the LLD. For the basalt reference material BB1 (Morris, 2007), precision is poorer for Hf, Nb, Zr, and Au, and in some cases for Cs, Al and Sb. Similarly, Hf and Zr show poorer precision in OREAS 24b, along with Sb.

Assessment of accuracy is compromised by the small number of reference materials with certified values. In common with sample and site duplicate data, HFSE and other elements that are found in resistate phases are not as precisely or accurately analysed as other elements when aqua regia digestion is used. The validity of some reference materials for assessment of certain elements (e.g. Ba in OREAS 504b, Au in OREAS 501b) is questionable. Precision also suffers for elements typically contained in resistate minerals.

Blanks

Analytical blanks have been assessed by comparing blank analyses to a value equal to three times the LLD (Table 3.4). Of the 30 blank determinations, most values are less than the 3x LLD threshold, apart from Sr (maximum 0.45 ppm; n = 17) and Ce (maximum 0.09 ppm; n = 5).

Umpire analyses

The <50 µm fraction of 45 samples has been analysed at LabWest (Malaga, Perth) following microwave-assisted aqua regia digestion and ICP analysis. In most cases, concentrations determined by LabWest are higher than those determined by Intertek-Genalysis, which can be attributed to the more aggressive microwave digestion approach used by LabWest (Table 3.5). An example of this is Zr values of 42 ppm for two analyses of the reference material OREAS 24b, compared to a certified values of 24.5 ppm. In contrast, Au determinations by LabWest are either similar to or at lower concentrations than those determined by Intertek-Genalysis. The sample with highest Au content of 63 ppb (221058 M91) determined by Intertek-Genalysis returned a value of 10.7 ppb at LabWest.

Discussion

For both sample and site duplicates, even small amounts of resistate phases in the fine fraction, such as zircon, rutile, and chromite (which are resistant to aqua regia digestion), can result in heterogeneity of some elements, in particular HFSE. Although aqua regia is relatively ineffective in terms of digesting silicates, heterogeneity in Al, K, Rb and Li points to some clay digestion, possibly facilitated or promoted by the high surface-area/volume ratio. Gold is at low concentrations in most regolith samples, and in general there is good agreement both within sample and within site, suggesting that gold is both fine grained and evenly distributed. Umpire laboratory analyses illustrate how changes in sample preparation conditions can affect analytical results, as discussed by Bisrat et al. (2011) who showed how variations in pH, time and temperature can affect the leaching of soil samples.

Spinifex

Between 50 and 100 g of dry spinifex was ashed at 475°C under controlled conditions. An ash weight of 0.25 g was digested in modified aqua regia (equal parts of HCl, HNO₃ and deionized water) for one hour in a heating block or hot water bath. The sample was made up to volume with dilute HCl. Each sample was analysed for 64 elements by either ICP-ES (emission spectrometry) or ICP-MS.

In addition to site and plant duplicates, a duplicate of ash sample SR9 was analysed, and three samples of the multiply analysed spinifex material ASH-5 were also analysed. The reference materials OVEN STD-2, ASH-1, DS10, and analytical blanks were also measured.

Quality control (Table 3.6)

Plant duplicates

Due to low analyte concentrations (<10x LLD for either the parent or duplicate), a number of elements could not be assessed, although in many cases, the low concentrations were reliably duplicated (e.g. As, U, Au, V, W, Te, Ta, In, Re, Be, Eu, Ho, Tm, Yb, Lu, Pd). Elements that showed acceptable agreement at higher concentrations for at least two of the three duplicates included Cu, Pb, Ni, Mn, Fe, Sr, Ba, Na, S, Ce and Pr.

The one ash duplicate (from SR9) shows good agreement for a wide range of elements.

Within-site variation

Analyses of spinifex from six plants within a 50 m radius show a high level of heterogeneity in terms of the percent relative standard deviation (%RSD). However, there is some agreement for elements at low levels of concentrations, such as some REE and HFSE.

Reference materials and blank analyses

Three analyses of the multiply analysed spinifex ash ASH-5 have low and acceptable %RSD values, and agree well in terms of HARD for an average analysis (C Dunn, written

comm., 2015) where the analyte concentration is at least 10x the LLD. A single analysis of ASH-1 compares well in terms of HARD for the average of 20 analyses of this material (C Dunn, written comm., 2015). Blank analyses are acceptably low (less than three times the LLD).

Taking all the QA/QC data together, there are a limited number of analytes that could be useful in assessing regolith chemistry in the Ngururupa area. These include Sr, Cu and P, and to a lesser extent Ni, Mn, Ba, Pb, B and S.

Discussion

Due to low concentrations of a number of analytes in spinifex, it is difficult to objectively assess analytical precision within individual spinifex samples, although the close agreement of a number of analytes at concentrations either close to or less than the LLD points to good reproducibility at low concentrations. Where analyte concentrations are higher, a number of elements show acceptable precision. The relative standard deviation for analyses of six spinifex samples collected over a 50 m radius shows a high level of heterogeneity at the metre to tens of metre scale, although (as for within plant duplicates) a number of elements at low concentrations show good agreement.

In contrast to sample and site duplicates, quality control data for ashed material is of a higher quality, both in terms of reproducibility (ash duplicate from SR9) and agreement between suggested and obtained data for multiply analysed ash material. Three analyses of an ashed spinifex material also produced low %RSD values <5 for most elements.

References

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