

Refining fine fraction soil extraction methods and analysis for mineral exploration



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Abstract: Soils are widely used as geochemical sample media. In transported cover, the soils that host the mobile element signature are the smallest size fractions, so we should consider concentrating the clay size fraction (<2 µm) as an improved sample medium. Twenty-seven bulk reference soils were collected in the vicinity of known mineral deposits (including background areas) that reflect common soil types of Western Australia. A selection of these soils was used in replicate testing to assess differences in particle size, sample weight, dispersants, and how this relates to the Au and Cu geochemistry. Using multiple analysis of variance tests, the submicron fractions showed that, although the <0.2 µm fraction was slightly different to the <2 µm and <0.75 µm fractions, there was no additional value in the extra effort required to extract these submicron fractions, and the <2 µm fraction was favoured. Ultrasonics and rinsing were not required for Au analysis, and during wet separation no Au is lost in solution and only a small fraction of the overall Cu (0.5%) is lost. Using a dispersant was critical for solid recovery and Na-hexametaphosphate (technical or laboratory grade) was found to be the most effective reagent. The <2 µm size fraction showed no significant differences for assays of Au using 0.1, 0.2, 0.5, 1 and 4 g ($P < 0.05$) with a microwave-assisted aqua regia digestion being the best analytical method for Au recovery. In addition to the geochemistry, the spectral reflectance variation was investigated with respect to particle size and weight, and showed more variation in the smaller weight fraction of material and a loss of quartz in the fine materials as expected. The integration of results from this study generated a new workflow called UltraFine+™. This workflow provides 40 elements, spectral mineralogy, particle-size distribution, pH, electrical conductivity (EC) and specific surface area, offering more quality data to improve mineral exploration using soil and regolith samples.

Keywords: spectral mineralogy; regolith; UltraFine+™; particle size; geochemistry

Supplementary material: Spreadsheets of soils and regolith data from orientation sites and regional map sites analysed with the UltraFine+ method is available at <https://doi.org/10.25919/5d1058f8b05fc>

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Greenfields exploration in Australia is in decline and directly hindered by the transported cover that blankets the underlying rock and masks ore bodies. The technical challenge of exploring in such deeply weathered and covered regions has not been fully addressed, and yet exploration success in these areas is critical to the future economy. Commonly, near-surface soil sampling is paired with acid digestions and multi-element measurement for mineral exploration. The technology to analyse the solutions has improved (e.g. atomic absorption (AA) to inductively coupled plasma mass spectrometry (ICP-MS)), resulting in lower detection limits and increased numbers of elements measured. The only other irregularly employed change in the approach has been the extraction solutions (partial digestions), which have been used with varied success (Chao 1984; Mann *et al.* 1998; Williams & Gunn 2002; Dalrymple *et al.* 2005; Noble & Stanley 2009). This approach to digest the dry-sieved soils and analyse the solution generally for target element(s) has not significantly changed over the past 30 years.

Commonly, exploration soil samples are sieved to <250 µm or <180 µm to remove larger gravels and coarse sand and, in some cases, then pulverized for analysis, but no other refinements are undertaken on the soil samples. However, are these <250 µm or <180 µm fractions the appropriate ones for mineral exploration? In residual terrains the <250 µm soil fractions may be effective because all materials present are related to the local geology. In covered terrains, where the origin of the surface materials are transported, most materials do not represent the local underlying rocks and so

only a mobile dispersion signature of target and pathfinder elements should be studied, as demonstrated by Anand *et al.* (2014, 2016). These mobile elements of interest are adsorbed onto soil exchange sites and are not part of the matrix. The size of the soil particles is inversely related to the surface area and the associated exchange capacity of the particle: that is, smaller particles have the greatest surface area and ability to adsorb other ions in the soil solution. Clays, organic compounds and various oxides/oxyhydroxides dominate this fine fraction, and have a greater exchange capacity than quartz (Hawkes & Webb 1962; Hall 1998). Hence, the soil fractions that host the mobile element signature are the smallest size fractions, so we would argue that for exploration purposes we should consider concentrating the clay size fraction (<2 µm) as an improved sample medium. Microparticulate (<2 µm) and nanoparticulate (<0.2 µm) separations are performed for clay analysis in engineering- and agricultural-related pursuits. This technique is slow and laborious, and provides the weight of each fraction and sometimes the mineralogy. The related geochemistry has not been tested, yet is essential for applications in mineral exploration.

Small Au particles (<2 µm) in regolith have been observed using scanning electron microscopy (Hough *et al.* 2008; Anand *et al.* 2017), but the amount of micro- and nanoparticulate Au cannot be quantified by this method. Silt and clay fraction (*c.* <50 µm) separation and geochemical analysis has been used for geochemical exploration in several studies, with the <75, <63 or <50 µm size fractions used to enhance target and pathfinder element contents (Scott & van Riel 1999; Morris 2013; Anand *et al.* 2014; Arne &

MacFarlane 2014; Baker 2015). Although intermittently tested by industry and researchers, it is not a routine method

A demonstration study by Noble *et al.* (2013) dealt with the separation and quantification of micro- and nanoparticulate Au in 14 transported soils from the East Wongatha region of Western Australia, where a regional regolith geochemical survey was carried out by the Geological Survey of Western Australia (Morris 2013). The results revealed that the Au was highly anomalous in the micro- and nanoparticulate size range where it was close to, or below, detection limits (1 ppb) in the bulk material. The importance of improving detection limits for Au to avoid so many results below detection has been emphasized (Leybourne & Rice 2013). Quartz, with practically no exchange capacity, commonly makes up much of the sand fraction, is the major mineral in most exploration soil samples and is a major dilutant to the trace element chemistry of interest (Noble *et al.* 2013). Another demonstrative study published by Anand *et al.* (2014) showed that the <53 μm soil fraction had much greater concentrations of Au over the Moolart Well deposit, whereas the frequently used <250 μm fraction was ineffective.

In this paper, we assess method variants of soil weight, dispersants, extraction type and differences in particle size (<2 μm , <0.75 μm and <0.2 μm), and how these relate to the Au and Cu concentrations in soils. In addition to the geochemistry, the spectral reflectance variation is investigated with respect to particle size and the integration of multiple parameters is used to generate a new workflow called UltraFine+™.

Methods

Soil samples

Twenty-seven bulk reference soils were collected from 10 prominent exploration and mining regions in Western Australia to provide a background set of samples to test various separation and analysis techniques. Figure 1 shows the location of these sites.

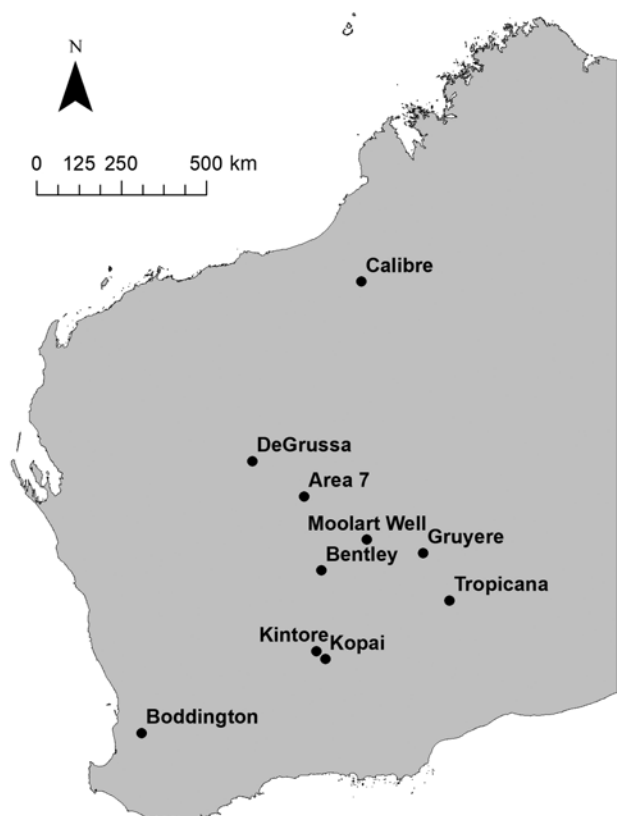


Fig. 1. The location of the bulk reference soil samples used in this study.

Table 1 shows key features of the soil types/target commodity. At each reference site a number of samples from the area (Table 1) were combined to give a soil that was broadly representative of the physicochemical and mineralogical properties of the region. These soils were in background areas, as well as above mineralization. Approximately 20% of the samples used in the composites might be considered proximal to the surface projection of mineralization. Samples were homogenized to provide *c.* 5 kg of material to test.

Clay separation methods and materials

Deionized (DI) water was added to soil at a ratio of 5:1 in 120 or 240 ml high-density polyethylene (HDPE) bottles with screw-on lids. Sodium-hexametaphosphate (35.5 g l^{-1}) with Na_2CO_3 (5 g l^{-1}) was used as a dispersant and added at a rate of 5 ml/100 ml solution. Samples were rolled for 24 h and then stood for *c.* 4 h, dependent on the laboratory temperature. The solution of <2 μm was drawn from the top 5 cm depth based on Stoke's law:

$$F_d = 6\pi\eta Rv$$

where F_d is the frictional force in Newtons ($= \text{kg m s}^{-2}$) acting on the interface between the fluid and the particle, η in Pa s is the dynamic viscosity ($= \text{kg m}^{-1} \text{ s}^{-1}$), R is the radius in metres of the spherical object, and v is the flow velocity relative to the object in m s^{-1} . The solution was then dried at 60°C for *c.* 24 h in the same HDPE bottle.

Variations on the separation method tested different dispersants (none; analytical, laboratory and food-grade Na-hexametaphosphate; 0.5 M ammonium solution; and 0.5 M sodium carbonate: Table 2) and the application of ultrasonic vibration for 30 min and DI rinse steps. Other tests compared the weight of sample used for digestion and the particle-size differences. Experiments are shown in Table 2.

Centrifugation was employed to separate the submicron fractions, also using Stoke's law, with *c.* 14 min at 3000 rev/min for <0.75 μm and 16 min at 8800 rev/min for the <0.2 μm fractions using a Sorvall RC 6+ centrifuge, and accounting for tube shape and rev/min and slow-down conditions.

In addition, all bulk reference soils were subject to dry sieving and weighing of the various larger size fractions based on the methods described by Gee & Bauder (1986).

Laboratory analysis

The standard extraction for the method testing was MAR-04, except where specifically noted. MAR-04 is offered through LabWest Pty Ltd, Perth, Australia as documented below along with additional extractions. All partial extractions of the soils were analysed for a multi-element suite of *c.* 40 elements using inductively coupled plasma optical emission spectrometry (ICP-OES: Perkin Elmer Optima 7300DV) and ICP-MS (Perkin Elmer Nexion 300Q).

Microwave-assisted aqua regia digestion (LabWest MAR-04)

Soil samples (0.2 g) were subjected to an aqua regia digestion with a 100% mixture of 3:1 concentrated $\text{HCl}:\text{HNO}_3$ and heated to 180°C in a closed Teflon tube in a microwave (Anton Paar Multiwave PRO Microwave Reaction System). The detection limit for Au is 0.5 ppb.

Aqua regia digestion (LabWest PL05s)

Soil samples (0.2 g) were subjected to an aqua regia digestion with a 100% mixture of 3:1 concentrated $\text{HCl}:\text{HNO}_3$ for 24 h with some agitation. The samples are centrifuged and supernatant analysed.

Weak aqua regia digestion (LabWest PL05)

Soil samples (0.2 g) were subjected to an aqua regia digestion with a 10% mixture of 3:1 $\text{HCl}:\text{HNO}_3$ for 24 h with some agitation. The samples are centrifuged and supernatant analysed. This partial

Table 1. Bulk reference soils and key parameters

Deposit	Region	Target commodity	Soil colour	% C	%OC	CEC (cmol/kg)	EC ($\mu\text{S}/\text{cm}$)	pH	% Clay <2 μm	% Silt 2-50 μm	% Sand 50–2000 μm	<i>n</i>	% Gravel > 2000 μm	Latitude ($^{\circ}$)	Longitude ($^{\circ}$)
Gruyere	Yamarna	Au	5YR 4/4	0.2	0.2	0.64	39	5.74	1.8	1.1	97.1	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	7.5YR 3/2	0.3	0.3	1.47	99	6.83	1.2	1.0	97.8	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	7.5YR 3/4	0.2	0.2	0.86	44	5.92	1.4	1.1	97.5	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	5YR 4/4	0.2	0.2	0.79	52	5.56	1.2	0.8	98.0	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au		0.2	0.2	0.64	66	5.63	1.3	0.9	97.8	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	5YR 4/4	0.2	0.2	0.54	86	5.48	1.5	0.7	97.8	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	7.5YR 4/2	0.2	0.2	0.75	76	6.29	1.3	0.6	98.2	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	5YR 3/2	0.2	0.2	0.78	47	6.1	1.2	0.8	98.1	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	5YR 3/4	0.2	0.2	0.54	28	5.79	1.4	0.5	98.1	0.0	1*	–27.98	123.84
Gruyere	Yamarna	Au	5YR 3/4	0.2	0.2	0.61	35	5.8	1.3	0.7	98.0	0.0	1*	–27.98	123.84
Calibre	Paterson	Cu–Au	5YR 4/4	0.2	0.2	0.54	47	5.42	0.7	1.4	97.7	0.1	15	–20.77	122.20
Calibre	Paterson	Cu–Au	5YR 4/4	0.1	0.1	0.44	44	5.43	0.6	1.5	97.8	0.0	15	–20.77	122.20
Bentley	NE Yilgarn	Zn	5YR 5/6	0.4	0.2	1.36	341	4.86	2.9	0.8	75.2	21.2	22	–28.44	121.15
Bentley	NE Yilgarn	Zn	5YR 5/6	0.4	0.4	1.7	491	5.13	3.4	1.2	80.9	14.5	24	–28.44	121.15
Bentley	NE Yilgarn	Zn	5YR 5/6	0.5	0.4	1.56	387	5.13	4.7	3.5	63.3	28.5	6	–28.44	121.15
Boddington	SW Yilgarn	Au	10YR 5/4	12.7	5.1	1.27	933	4.77	2.5	2.3	27.3	67.9	15	–32.77	116.38
Boddington	SW Yilgarn	Au	10YR 5/4	13.8	5.2	10.79	641	6.4	1.0	5.6	40.7	52.7	56	–32.77	116.38
DeGrussa	Bryah Basin	Cu	5YR 5/6	0.5	0.4	1.36	575	4.93	1.6	4.4	58.3	35.8	38	–25.53	119.32
Kintore	Kalgoorlie	Au	7.5YR 6/4	3.4	0.5	22.5	27 020	8.36	3.5	6.5	43.2	46.7	28	–30.59	121.01
Kintore	Kalgoorlie	Au	5YR 6/6	1.8	0.5	60.44	45 660	8.14	2.9	4.2	66.9	25.9	42	–30.59	121.01
Kopai	Kalgoorlie	Au	5YR 5/4	2.8	0.4	16.17	5370	9.34	1.4	7.4	59.9	31.3	28	–30.80	121.25
Kopai	Kalgoorlie	Au	5YR 4/4	2.7	0.3	16.04	5951	9.16	1.9	7.1	68.3	22.6	41	–30.80	121.25
Moolart Well	NE Yilgarn	Au		1.1	0.6	1.42	937	4.89	4.3	3.8	80.8	11.1	58	–27.62	122.35
Area 7	Yandal	Au	5YR 5/6	0.4	0.4	3.72	26 800	6.55	4.2	3.9	80.6	11.4	20	–26.47	120.69
Area 7	Yandal	Au	5YR 5/6	0.3	0.4	2.52	7503	5.78	2.1	5.9	76.7	15.4	20	–26.47	120.69
Tropicana	Albany–Fraser	Au	7.5YR 3/2	1.6	1.4	3.89	889	6.74	1.3	1.4	95.1	2.1	54	–29.24	124.54
Tropicana	Albany–Fraser	Au	7.5YR 3/2	1.7	1.1	3.68	1353	7.12	1.5	1.5	95.1	1.9	26	–29.18	124.52

n, number of samples that were combined to represent that site.

*A single sample collected as a 10 kg composite from an area of c. 1 m².

Note: clay and silt % is underestimated, refer to the main text.

Table 2. Various tests performed and referenced in this paper with the adjusted variables

Test	Experiment	Variables tested
1	Soil weight	0.1, 0.2, 0.5, 1 and 4 g
2	Ultrafine size	2, 0.75 and 0.2 μm
3	Solubility of ultrafine particles	Supernatant of 2, 0.75 and 0.2 μm fractions
4	Extraction	Four acid, microwave aqua regia, aqua regia, dilute aqua regia and hydroxylamine
5	Dispersants	3 \times Na-hexametaphosphate, ammonia and Na-carbonate
6	Separation	Dispersant only ('none'), dispersant + ultrasonics ('ultrasonics') and dispersant + 2 DI water rinses ('rinsed')
7	Alternative laboratories	ALS clay separation compared to UltraFine+™ at LabWest
8	Spectral reflectance response	Reflectance of bulk and ultrafine sizes using visible to shortwave infrared spectrometer and shortwave to thermal infrared Fourier transform infrared (FTIR) spectrometer

extraction has lower detection limits than those stronger acid extractions with 0.1 ppb Au.

Weak (cold) hydroxylamine hydrochloride leach (LabWest PL04)

Soil samples (0.2 g) were weighed into a 50 ml polypropylene centrifuge tube with 45 ml of 0.01 M hydroxylamine hydrochloride. Each sample was then shaken for 24 h at room temperature, centrifuged for 10 min (4500 rev/min), and the supernatant was decanted into test tubes for analysis. This extraction is interpreted to selectively digest elements bound in amorphous Mn oxide and, to a lesser extent, amorphous Fe oxide fractions of soil samples (Chao 1984; Gray *et al.* 1999).

Microwave-assisted four-acid digestion (LabWest MMA-04)

Soil samples (0.2 g) were subjected to a HF/multi-acid regia digestion and heated to 180°C in a closed Teflon tube in a microwave (Anton Paar Multiwave PRO Microwave Reaction System). The detection limits are slightly higher than other extractions and, importantly, the Au detection limit is 5 ppb.

Spectral analysis

Visible and near-infrared (VNIR) to shortwave-infrared (SWIR) reflectance measurements were acquired on the bulk and separate samples using a Malvern Panalytical Analytical Spectral Devices (ASD) FieldSpec4 standard-resolution spectroradiometer. The ASD FieldSpec4 collects in the 350–2500 nm wavelength region. For the initial testing of the bulk and separated samples, reflectance data were obtained using a muglight accessory and black anodized aluminium sample cups with 25 mm sapphire glass windows. A reference measurement was made on a plug of sintered polytetrafluoroethylene (PTFE, aka Spectralon™) sitting inside the cup which was ratioed with the sample measurement to obtain a relative reflectance. The relative reflectance was converted to absolute reflectance in post-processing by a reflectance correction factor for the Spectralon™ plug.

Testing of the separates of the <2 μm separations in the main workflow were performed using a bifurcated optical-fibre probe supplied by Malvern Panalytical ASD. A calibrated piece of PTFE was used as the reflectance standard and measured before each set of soil measurements. The samples were measured in their plastic vials after being gently crushed with a glass stirring rod. After each

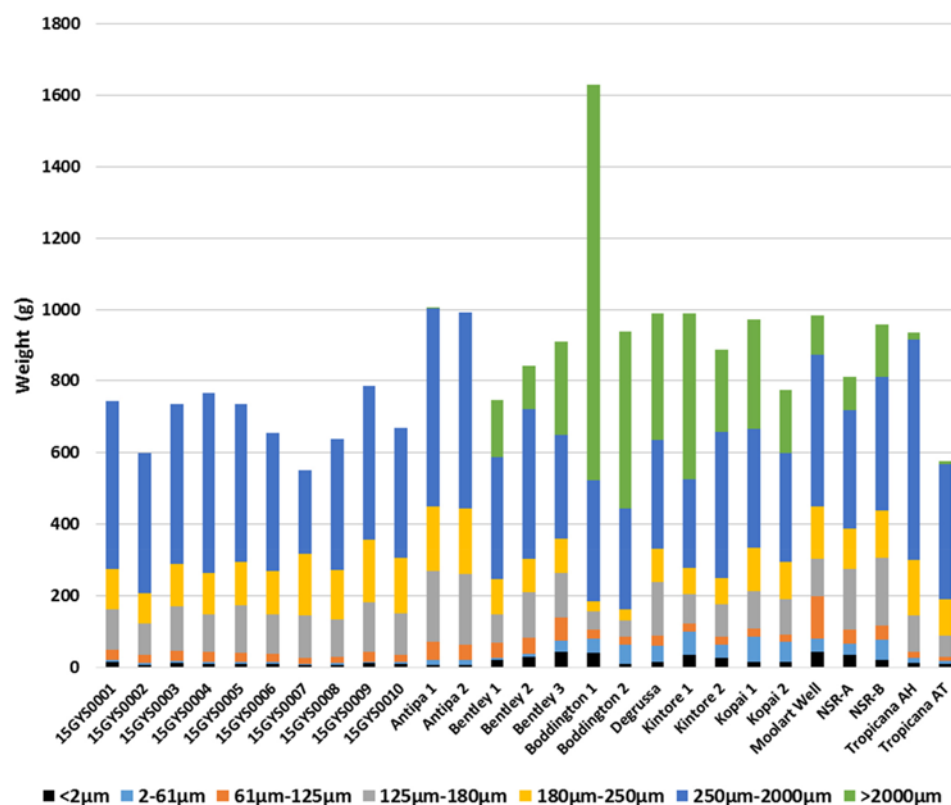


Fig. 2. Bulk reference samples particle-size fractions by weight. Weight was determined by dry sieving and then by calculation using a proportion of the laser-scatter particles size to ratio the remaining <61 μm material. GY samples are Gruyere, NSR are Area 7 from Northern Star Resources.

measurement, the probe was cleaned with a Kimwipe and jet of compressed air. A total of 40 scans were averaged into a single measurement. Each measurement took *c.* 10 s.

Mid- to longwave infrared diffuse reflectance measurements were acquired on the bulk and clay-separate samples using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer with a Bruker A562 Au integrating sphere attachment. A glow bar internal source and KBr beam splitter were used in the fore-optics of the Bruker Vertex, with a 2 × 2 mm MCT (mercury–cadmium–telluride) detector attached to the baffled exit port of the integrating sphere. The samples were placed in a black anodized aluminium 25 × 3 mm sample cup and the surface gently smoothed with a glass slide. The sample cup was placed in the bottom port of the integrating sphere and a background reference measurement of the sphere wall was collected before the internal mirror in the sphere was manually switched to point the incoming beam down towards the lower port containing the sample. The diffuse reflectance between 7000 and 500 wavenumbers (cm⁻¹) was acquired and converted into *c.* 1428–16 667 nm (due to the data being noisy below 600 cm⁻¹).

Additional analysis

Total carbon was measured using an Elementar CS cube combustion method, with organic carbon measured using the same device, but samples were pre-treated with HCl to destroy any carbonate carbon.

Prior to settling or separation methods, the pH (TPS 900-P) and electrical conductivity (TPS *k* = 1 sensor) of 1:10 w/w soil/water ratio slurries were measured at the CSIRO laboratories, Kensington, Western Australia for all reference samples collected in this study. Using the UltraFine+™ developed workflow, similar measurements were made at LabWest using a TPS AQUA-CP/A waterproof conductivity/total dissolved solids (TDS)/salinity/pH/temperature meter.

Particle-size analysis was measured using a Malvern Mastersizer 3000 in both dry mode using the AeroS attachment and in suspension using the HydroMV unit. Both techniques assumed

non-spherical particles and kaolinite as the dominant mineral with a refractive index of 1.45 (this is not dissimilar to the value for quartz or Fe oxides which are also common minerals with 1.51 and 1.456, respectively).

Quality control and data treatment

A certified reference soil (OREAS 250) was incorporated into all analyses as a geochemical standard. Laboratory duplicates were analysed at a rate of one per 20 samples (*n* = 5 per extraction test). The per cent half absolute relative difference (HARD) was determined on the standard soil to be acceptable if it was <10% for the aqua regia, multi-acid and hydroxylamine hydrochloride extractions. The HARD (Stanley & Lawie 2007) was calculated as a percentage for all compounds using method and field duplicate samples:

$$\text{HARD} = \left(\frac{\text{assay 1} - \text{assay 2}}{\text{assay 1} + \text{assay 2}} \right) \times 100$$

Quality control on the spectral reflectance measurements involved the measurement of an internal sand standard of quartz (from Lucky Bay, Western Australia) and on KGa-1b (Clay Mineral Society well crystalline kaolinite from Georgia, USA) at the start, middle and end of daily measurements.

Results

Bulk reference soil-particle size and chemistry

The bulk reference samples were dominated by sand-size fractions. Figure 2 shows the particle-size distribution by weight, with the fine, medium and coarse sand (>100 μm) dominating most of the soil mass, as is common in many Western Australian soils. This distribution was determined by dry sieving, and so some clay coatings contribute to the weight of the larger particles. Dry sieving only gets to the silt fraction (*c.* <61 μm in this study). To calculate the proportion of silt and clay, the proportions between these two fractions in the laser-scatter analysis was used and applied to split

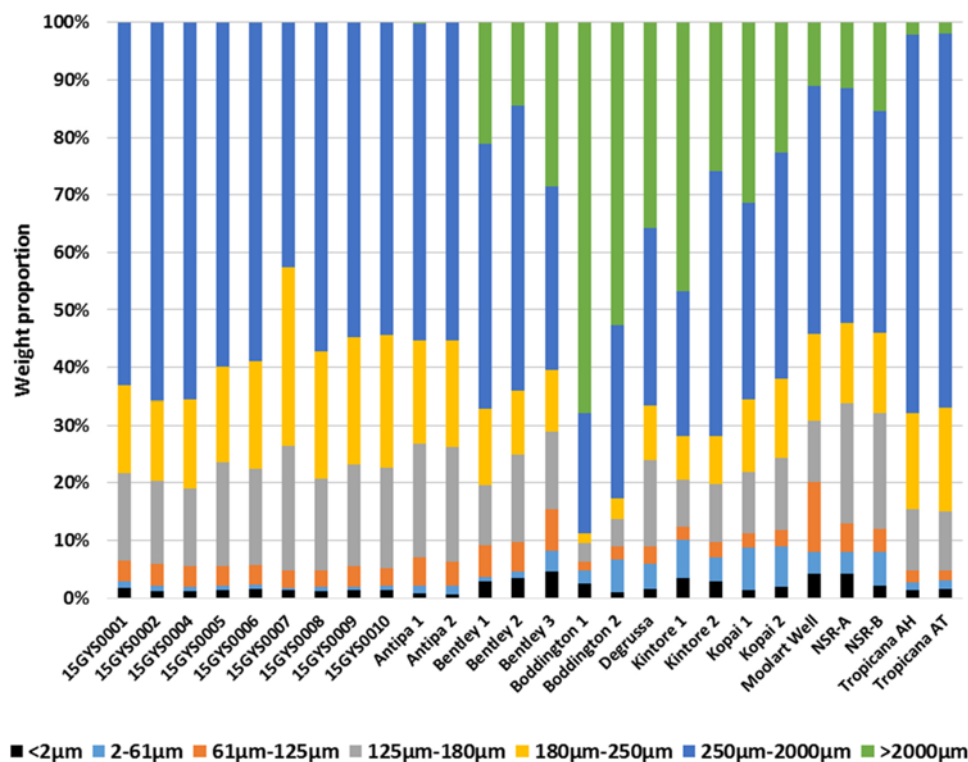


Fig. 3. Bulk reference samples percentage fractions of particle size by weight. Weight was determined by dry sieving and then by calculation using a proportion of the laser-scatter particles' size to ratio the remaining <61 μm material. GY samples are Gruyere; NSR are Area 7 from Northern Star Resources. As expected the finer fraction comprises <10% of the soil.

the dry weight recovered. This slightly underestimates the fine materials. The results of the Au analysis for the reference sites and the other size fractions show that Au and Cu is commonly higher in the $<2\ \mu\text{m}$ fraction (see [Supplementary material](#)).

Scaling the various weights of the size fractions to 100% provides a more even comparison of the bulk reference soils. For many samples, the fine to medium sand is quite similar (yellow and grey coloured bars in [Fig. 3](#)), with the biggest differences highlighting those soils with a significant coarse soil component (green colour in [Fig. 3](#)) such as Boddington which has abundant pisolith gravels in the surface environment. The Boddington site was also unusual in not having the sand fraction that most other sites had and in its large organic component ([Table 1](#)). All of the samples used in this study as reference samples had $<5\%$ clays and a similar proportion of silts ($2\text{--}61\ \mu\text{m}$: black and light blue in [Fig. 3](#)). These minor components by weight were determined to have a similar or greater concentration of trace elements of interest.

Adjusting the Au and Cu concentration by assuming that all the soil-size fractions were equally proportioned highlights the dominance of Au ([Fig. 4](#)) and Cu ([Fig. 5](#)) in the fine fractions and those size fractions that have the most exchange sites ([Table 1](#)).

Test 1. Sample weight required for analysis

The results from six replicates of seven reference samples using five different weights were tested using the MAR04 (microwave-assisted aqua regia extraction) analytical method from LabWest. The weights investigated were 0.1, 0.2, 0.5, 1.0 and 4.0 g. A multiple analysis of variance (MANOVA) test showed no significant differences in the results for all weights tested for Au ([Table 3](#); [Fig. 6](#)), and minor differences for Cu ([Fig. 7](#)) and Zn (not shown).

[Figure 7](#) shows that even when significant differences are observed between the weights used, the differences are not extreme and do not greatly influence the interpretation of the data in practice (e.g. orientation surveys: [Noble *et al.* 2019a, b](#)). Not surprisingly, the MANOVA also showed significant differences between all sites and nearly all elements – since the samples are from distinct regions,

this is to be expected and any similarities are coincidental. Based on these findings, the use of very small weights for the analysis is suitable and preferred as it requires less starting material, and lower energy and consumption of acids to complete the digestion. From this finding, the following experimental comparisons (extractions, settling chemicals and method variations) used the 0.2 g sample weights.

Test 2. Ultrafine sample-size fraction

Results show that there is no additional benefit to analysing fractions smaller than $2\ \mu\text{m}$ clay (submicron), with the 0.2 and $0.75\ \mu\text{m}$ fractions showing very little difference to the larger and more easily extracted $<2\ \mu\text{m}$ fraction at most sites (e.g. [Table 4](#)). Combining all six sites, there was no significant differences between the 0.75 and $2\ \mu\text{m}$ fractions, although both of these were different to the very small $0.2\ \mu\text{m}$ fraction. These differences tended to be more pronounced at the sites that were more challenging from a separation aspect: Boddington with a much greater organic content ([Table 1](#)), and Kopai which had a higher salt content and very little easily separated clay fraction. These sites also had the highest Au concentrations (tens of ppb of Au). The $2\ \mu\text{m}$ fraction, on average, tended to have slightly greater Au ([Fig. 8](#)), although this is not always the case; as is evident at Boddington. The extraction results were consistent, especially at the Boddington site ([Fig. 9](#)). None of the fractions shows evidence of nugget effects, although reproducibility of Au varied by 100% at the lower concentrations (e.g. 4 and 8 ppb replicates for Au; less than 10 times the detection limit (DL)), but none of the samples varied from near detection to many tens or hundreds of ppb of Au, as had been observed with nugget effects in other samples and analytical techniques. Other elements are much more stable, with Cu being very consistent in all of the size fractions tested ([Fig. 9](#)).

Test 3. Solubility of ultrafine particles into supernatant

As an additional check on the effectiveness of the separation and analysis, the supernatant fluid was also analysed. No Au was

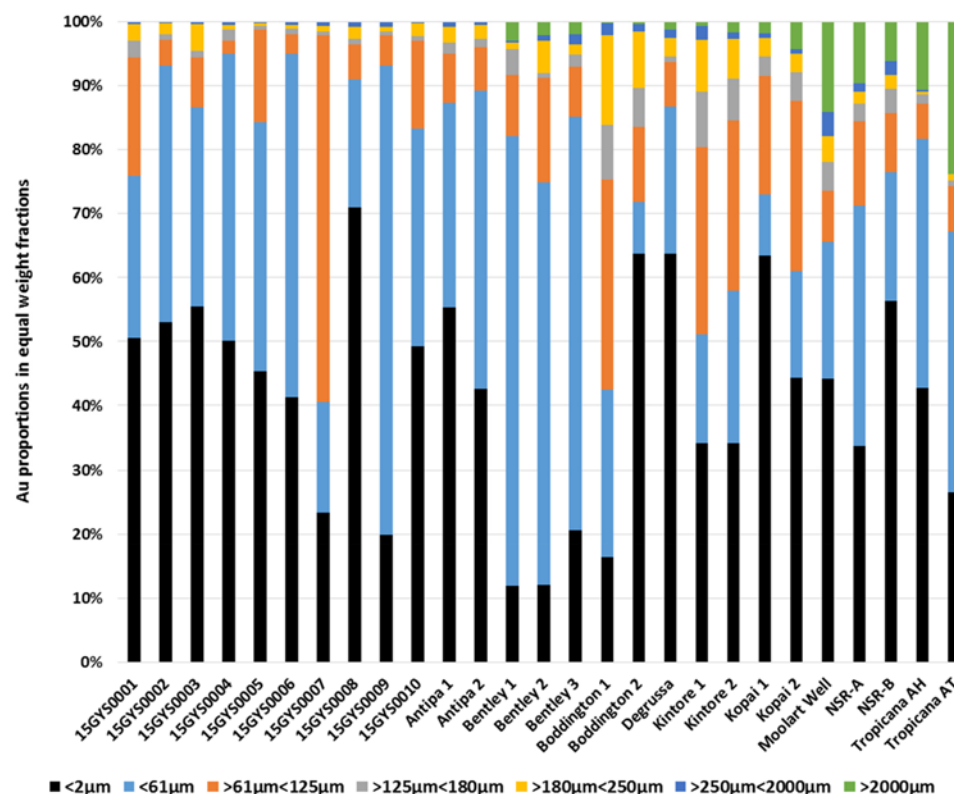


Fig. 4. Bulk reference sample distribution of Au extracted with MAR-04 in each fraction of larger particle sizes adjusted for the proportional weight of each fraction (i.e. if particle sizes were in equal proportions). The finer fractions ($<125\ \mu\text{m}$) commonly hosts more Au than most other fractions. GY samples are Gruyere; NSR are Area 7 from Northern Star Resources.

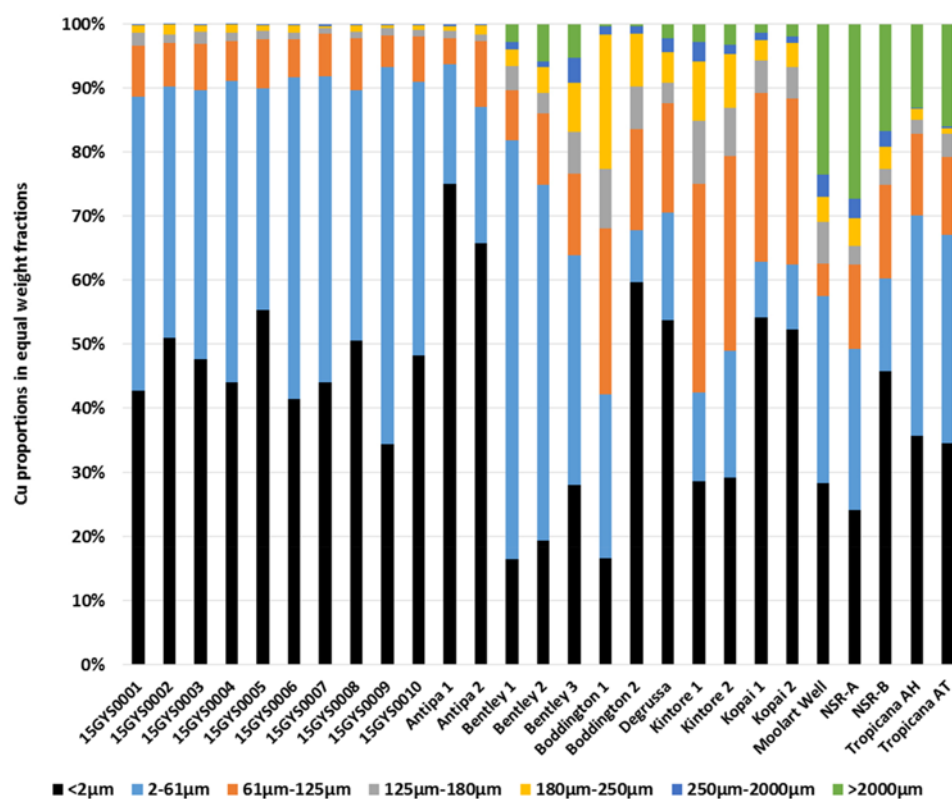


Fig. 5. Bulk reference sample distribution of Cu extracted with MAR-04 in each fractions of larger particle sizes adjusted for the proportional weight of each fraction (i.e. if particle sizes were in equal proportions). The finer fractions (<125 µm) commonly host more Cu than most other fractions. GY samples are Gruyere' NSR are Area 7 from Northern Star Resources. Results were similar for Zn.

detected in the discarded supernatant solutions in these tests and only trace amounts of Cu were in the solution. The trace soluble Cu was equivalent to 0.2% of the total extracted in the solid phase and did not influence the interpretation of the data. The difference in the mean values between the different size fractions separated and the concentrations in the remaining supernatant is not significant to exclude the possibility that the difference is just due to random sampling variability after allowing for the effects of differences at the sites. There is not a statistically significant difference ($P=0.120$) and the individual comparison tests are shown in Table 5.

Test 4. Extraction comparison of soil chemistry

Five replicates of five bulk reference soils, including a standard reference soil, were subject to extraction from five different solutions to provide an indication of the best method to partner with the 2 µm particle size extraction. All extractions and analyses were conducted by LabWest. The results showed that aqua-regia-related extractions are effective for Au solubilization, with microwave-assisted aqua regia multi-element analysis by ICP-MS/

Table 3. MANOVA comparisons of sample weights for Au

Comparison (g)	Difference of means	<i>t</i>	<i>P</i>	<i>P</i> < 0.050
0.100 v. 4.000	3.286	1.52	0.753	No
0.100 v. 1.000	2.964	1.371	0.817	No
0.200 v. 4.000	2.526	1.168	0.894	No
0.100 v. 0.500	2.493	1.153	0.867	No
0.200 v. 1.000	2.205	1.02	0.891	No
0.200 v. 0.500	1.733	0.802	0.937	No
0.500 v. 4.000	0.793	0.367	0.993	No
0.100 v. 0.200	0.76	0.351	0.979	No
0.500 v. 1.000	0.471	0.218	0.97	No
1.000 v. 4.000	0.321	0.149	0.882	No

All pairwise multiple comparison procedures (Holm–Sidak method). Overall significance level = 0.05.

ICP-OES the preferred method (MAR-04 in the LabWest scheme). Testing the known standard OREAS 250 (Fig. 10) shows that all the strong acid digests were effective. The microwave-assisted extraction reports greater concentrations than any other method (Fig. 10). The 100% aqua regia does not extract all the Au, although both the 100% and 10% aqua regia extractions are effective (Fig. 10a). The four-acid digestion is probably the most accurate at this concentration range. However, it should be evident in Figure 11 that many sites have much lower Au concentrations in soil. In samples that are low in Au concentration, the four-acid digest is limited as the detection limit of 5 ppb may cause samples to report below detection. This 5 ppb detection limit would prove problematic in other regional studies (Noble *et al.* 2018, 2019a)

The hydroxylamine hydrochloride (HA) extraction is not effective (Figs 10 and 11). In the ultrafine fractions separation, there are no significant concentrations of Mn oxides that would be reduced and, in turn, liberate metals in this phase. Reducing Au solid particles (0 valence state) is also not effective in solubilizing Au that ideally is mobile in a +1 or +3 state. As a result, HA is not a viable extraction method for these soils and this workflow.

Although strongly focused on Au to avoid the nugget effect and the variants of aqua regia extraction that are known to be most effective at Au solubilization, the extraction of Cu is also effective using the microwave aqua regia and strong Cu recovery is achieved (Fig. 12).

Test 5. Comparison of dispersants

Initial testing had indicated that a dispersant was valuable to ensure adequate recovery of the fine particles for Western Australian soils. A number of dispersants are viable and this experiment compared three different grades of Na hexametaphosphate, with Na carbonate and ammonia. Two bulk reference soils (DeGrussa and Kopai) were used and each separation was done with five replicates. A MANOVA test showed that the main effects of the dispersants cannot be properly interpreted collectively using both sites. This is because the size of the dispersant's effect depends upon the site: that

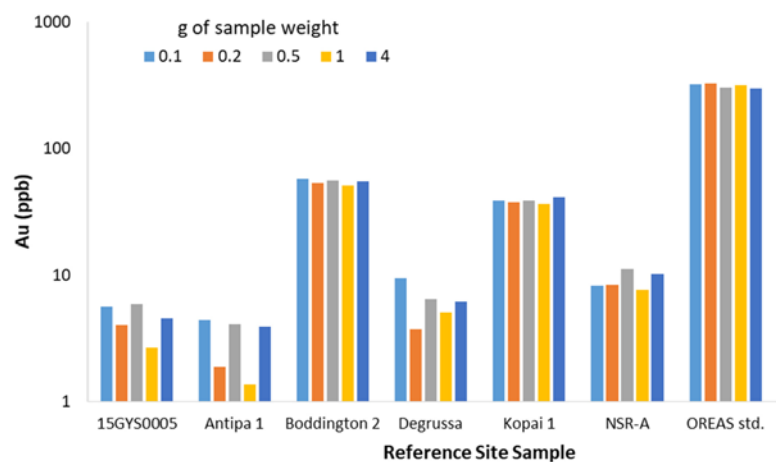


Fig. 6. Comparing weight of the <2 μm fine fraction sample used in the analysis of Au extracted with MAR-04 at six reference sites and using the OREAS 250 standard. No significant differences occur between any of the weight classes. GY samples are Gruyere; NSR are Area 7 from Northern Star Resources.

is, the sites (and the soil type) respond very differently and variably to the dispersants. These soils are distinctly different, and there is a statistically significant interaction between site and dispersant ($P < 0.001$). Table 6 shows that the dispersants are significantly different, except for the bulk and laboratory-grade Na-hexametaphosphate. The results of the DeGrussa soils only show that there is little difference between the dispersants except for ammonia (Table 6). Ammonia extracted slightly more Au than the other dispersants for both reference soil types (Fig. 13). The biggest contrast in treatments was the Na-carbonate that was reasonably effective at DeGrussa, but performed poorly for Au and Cu at Kopai. The Kopai site is the most alkaline soil tested ($\text{pH} = 9.3$; Table 1) and adding a carbonate solution did not disrupt the standard conditions of that soil (Fig. 13).

Another test of the dispersants looked at the effectiveness of disaggregating the clays and fine particles, and the % recovery. This is a percentage of the total bulk soil for comparison of the dispersants and not the total percentage of the fine fraction that is recovered. Table 7 indicated that the Na-hexametaphosphate was a much better dispersant, even if the ammonia solution had extracted more Au in this separation. With the laboratory-grade reagent significantly more expensive, using the lesser-quality Na-hexametaphosphate could be beneficial (Table 7), but the amount used in the technique is small, so the better-grade material is preferred. Another consideration is that the better-quality reagents (laboratory and technical grades) were much easier to dissolve to make up the

bulk solutions due to a decrease in impurities compared to the bulk commercial-grade material.

Test 6. Separation comparison

The process of separation requires Na-hexametaphosphate to maximize the fine-fraction recovery in the soils used in this study. Ultrasonics alone was not effective in consistently separating the fine materials (not shown). The testing of ultrasonics, in addition to dispersants, and the rinsing of dispersants was completed. Rinsing (twice with DI H_2O and drying: Table 2) did show some slight variation to the other two treatments (none and ultrasonics) for some elements, but it was minor: for example, for Au a mean of 14.0 ppb compared to 15.7 ppb and for Cu 53.4 ppb compared to 50.6 ppb, rinsed compared to other treatments, respectively. The Boddington site, with greater amounts of organics, was strongly influential in the statistical tests. Four replicates of five reference samples using three treatments (dispersant-only labelled 'none'; dispersant + ultrasonics labelled 'ultrasonics'; and dispersant + two DI water rinses labelled 'rinsed') were tested using the MAR04 analytical method from LabWest. A MANOVA test showed no significant differences in the results for all treatments tested for Au if the Boddington samples were excluded (Table 8). The difference in the mean values between the different treatments is not significant enough to exclude the possibility that the difference is just due to random sampling variability after allowing

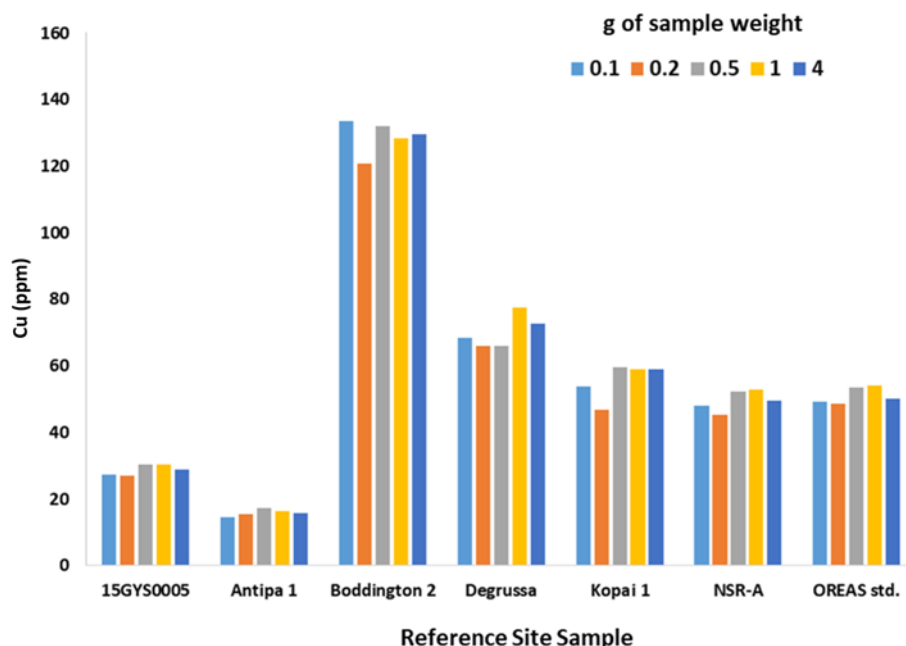


Fig. 7. Comparing weight of the fine fraction sample used in the analysis of Cu extracted with MAR-04 at six reference sites and using the OREAS 250 standard. Some differences occur between most of the weight classes, but any differences observed are small. GY samples are Gruyere; NSR are Area 7 from Northern Star Resources.

Table 4. MANOVA comparisons of size fractions for Au at all sites combined and then some of the individual sites

Sites	Comparison	Difference of means	<i>t</i>	<i>P</i>	<i>P</i> < 0.050
All	0.200 v. 0.750	5.042	10.073	<0.001	Yes
All	0.200 v. 2.000	4.961	9.912	<0.001	Yes
All	2.000 v. 0.750	0.0806	0.161	0.872	No
Calibre	2.000 v. 0.750	1.35	1.101	0.617	No
Calibre	0.200 v. 0.750	0.983	0.802	0.669	No
Calibre	2.000 v. 0.200	0.367	0.299	0.766	No
DeGrussa	2.000 v. 0.200	1.633	1.332	0.461	No
DeGrussa	2.000 v. 0.750	1.267	1.033	0.516	No
DeGrussa	0.750 v. 0.200	0.367	0.299	0.766	No
Gruyere	2.000 v. 0.750	2.683	2.189	0.091	No
Gruyere	2.000 v. 0.200	1.4	1.142	0.447	No
Gruyere	0.200 v. 0.750	1.283	1.047	0.298	No

All pairwise multiple comparison procedures (Holm–Sidak method). Overall significance level = 0.05.

for the effects of differences in sample sites. There is not a statistically significant difference for Au ($P = 0.765$). The effect of different sites does not depend on what level of treatment is present. There is not a statistically significant interaction between site and the treatment ($P = 0.928$).

Only minor differences for most metals and metalloids including Cu were observed (Table 9). Consistently, there was no significant difference between ‘none’ and ‘ultrasonics’, indicating that the use of ultrasonics in the UltraFine+™ workflow adds unnecessary time to the separation method (Tables 8 and 9). Not surprisingly, the results showed significant differences between all sites and nearly all elements – since the samples are from distinct regions this is to be expected and any similarities are purely coincidental.

Test 7. Comparison of UltraFine+™ to other commercial separation techniques

Both Bureau Veritas and ALS commercial laboratories provide a clay separation and analysis service (in their Vancouver laboratories). To better understand the results obtained from our study, the same reference samples were sent to ALS to compare results. The ALS method used was ME-MS41L which is an aqua regia digestion with ‘super trace’ best detection limits available using ICP-MS. This method is comparable to the technique employed for the rest of the analysis in this project (MAR-04 from LabWest). The ALS results did not use the OREAS 250 standard as it was not a sufficient amount and the ME-MS41L technique

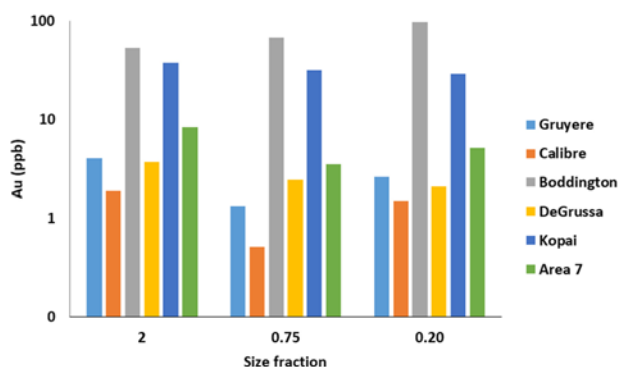


Fig. 8. Comparing sizes of the fine fractions and the average concentration of Au extracted with MAR-04. Results are the average of six replicates at six reference sites. Few significant differences occur between any of the size classes.

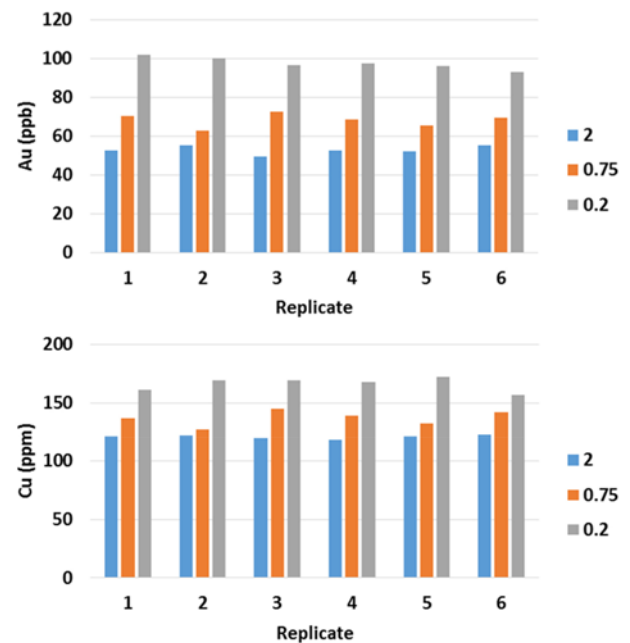


Fig. 9. Comparing sizes of the fine fractions and the concentration of Au (top) and Cu (bottom) extracted with MAR-04. Results show the consistency of the analysis of six replicates at the Boddington site. The results were uncharacteristic of most sites in that it that showed greater concentrations in the <0.2 μm fraction and not the <2 μm.

has a caveat that Au determinations are semi-quantitative due to the small sample weight used (0.5 g). Regardless of the caveat, the duplicate data were excellent, with an average %HARD of 3 and most elements <2% among our blind duplicates ($n = 3$). One initial observation with the ALS extraction is that the initial sample size is much larger (*c.* 300 g), yet the average percentage of material recovered for analysis was 1.1%, which is much less than the 3.75% obtained using the methods described in this paper (data not shown).

Gold (Fig. 14) and Cu correlate very closely between the two laboratories, and the trace elements are similar. Differences are evident in a few of the major elements and this is likely to be a product of the dispersants used in the separation process (e.g. for Al a mean of 8.6% compared to 2.8%, Lab West compared to ALS, respectively). The difference in the mean Au concentrations from the different laboratory methods is not great enough to exclude the possibility that the difference is just due to random sampling variability after allowing for the effects of differences in sites. There is not a statistically significant difference ($P = 0.455$) for Au analysis between the laboratories. This is not the case for Cu, with the UltraFine+™ method reporting an average 24% more Cu. The linear relationship between the Cu results from the two methods is consistent, even if the data are not truly the ‘same’ as they were for Au. Correlation analysis for Cu was strong ($R^2 = 0.95$). These closely aligned results are expected as the initial

Table 5. MANOVA comparisons of size fractions and the remaining solution for Au at all sites combined

Comparison	Difference of means	<i>t</i>	<i>P</i>	<i>P</i> < 0.050
0.200 v. 2.000	0.0061	2.082	0.123	No
0.750 v. 2.000	0.00417	1.433	0.292	No
0.200 v. 0.750	0.00193	0.5	0.619	No

All pairwise multiple comparison procedures (Holm–Sidak method). Overall significance level = 0.05.

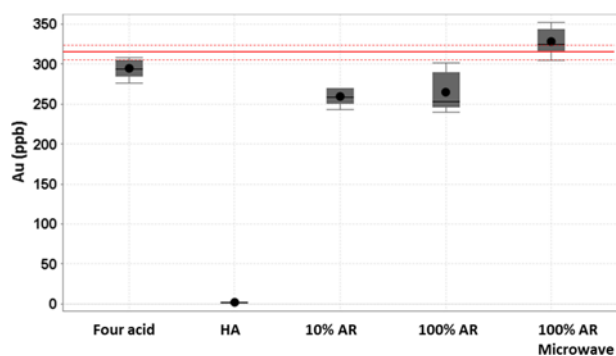


Fig. 10. Comparison of the Au extracted from the OREAS 250 standard using the five different extractions tested. The reported value in concentrated aqua regia is 303 ppb (solid red line) \pm 13 ppb or 1 SD (red dashed lines).

separation method is similar and quite standard practice, with the exception of the dispersants used which may influence some elements.

Test 8. Variation in spectral reflectance from fine fraction materials

Testing was conducted to optimize the spectral mineralogy. Using the Bentley 3 $<$ 2 μ m sample, 0.2, 0.3, 0.45, 0.55 and 1.0 g were weighed out and measured with the ASD between each cumulative addition of more material. Each sample measurement was replicated six times. Although the 0.2 g sample (the preferred amount of material for chemical digestion analysis) was only a very thin layer of sample in the sample holder and light was visible from underneath when placed on the vertical upwards-shining light of the muglight apparatus, the spectral reflectance results were highly comparable to the 1.0 g amount of sample (Fig. 15). The standard deviation varied with the different sample weights; with the 0.2 g sample having the most variance (Fig. 16) between measurements (due to not filling the complete field of view measured by the FieldSpec4 when using the muglight). Overall, there was confidence that 0.2–0.5 g of sample could be measured consistently with the ASD FieldSpec4 using the muglight and sapphire glass spectral sampling cups. However, it is noted that removal of the sample from the tubes and placing it in the spectral sampling cups added additional time. Thus, a new method for spectral measurement was proposed for the UltraFine+™ method.

A new fibre-optic dip probe was tested to improve the analysis time. A small (*c.* 0.5 g) amount of $<$ 2 μ m DeGrussa sample was placed in a conical centrifuge flask and was tested in comparison to a large (3 g) amount of sample using the normal ASD muglight sample cups. The spectra of the small sample had slightly more noise in the longer wavelength regions ($>$ 2400 nm), where the energy is starting to get weak (Fig. 17). However, this region is not used much for clay mineralogy and is unlikely to be influential in identifying the presence of the dominant regolith minerals reported in the samples.

Spectral measurements using the ASD and FTIR were collected on the various sieved size fractions ($>$ 2000, 2000–250, 250–180, 180–125, 125–61 and $<$ 61 μ m), as well as the $<$ 2 μ m separation. The spectral results found the $>$ 2000 μ m fraction to typically contain the most variation within a site due to the presence of large rock fragments, whereas the spectra of the size fractions from 2000–250 to $<$ 61 μ m were largely similar. The $<$ 2 μ m spectra were noticeably different from that of the $<$ 61 μ m fraction. Pulverization of the $<$ 2 μ m separation samples caused the spectral features to become less distinct and more rounded in shape, making identification of the mineral phases more difficult.

The mineralogy of the bulk samples comprises hematite, goethite (VNIR), kaolinite, montmorillonite (SWIR) and quartz (FTIR). Minor carbonate and feldspar were seen in some samples using the FTIR. Gibbsite was the dominant SWIR mineral in the Boddington samples (data available in [Supplementary material](#)). On first glance of the spectra of the bulk samples, besides the Boddington samples, there appears to be little difference in the spectral features. However, the use of scalars to calculate the depth and wavelength position of absorption features identifies the samples containing stronger iron oxide and kaolinite features, as well as those with a higher water content.

The relative proportions of hematite to goethite were spectrally estimated using the wavelength of the ferric oxide absorption feature around 850–950 nm, with shorter wavelengths representing a greater proportion of hematite and longer wavelengths more goethite. The relative abundance of these iron oxide/oxyhydroxides (FeOx) was estimated based on the depth of this feature. Although the X-ray diffraction (XRD) results for Boddington show a large amount of hematite (31.2%), the VNIR spectra show almost no FeOx absorption, which could be due to the FeOx minerals being present inside the cemented matrix of the weathered material (pisoliths), rather than present as coatings on quartz grains, which is the typical form for soils (data available in [Supplementary material](#)). In the bauxitic Boddington samples, the grains could be coated in gibbsite. The $<$ 2 mm bulk samples from Kintore, Moolart Well,

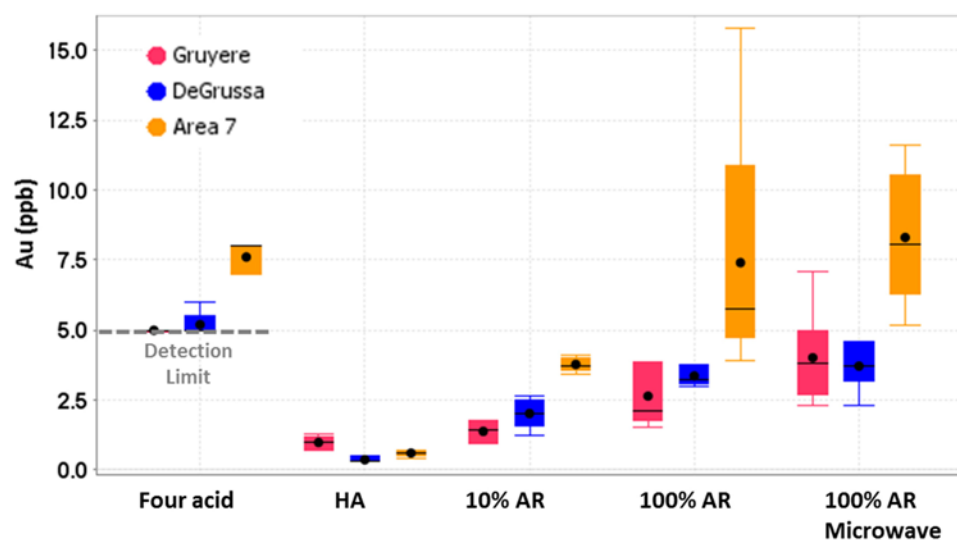


Fig. 11. Comparison of the Au extracted from the bulk reference samples from DeGrussa, Gruyere and Area 7 using the five different extractions tested. Refer to [Table 1](#) and [Noble *et al.* \(2019a\)](#) for more details on the reference samples and sites.

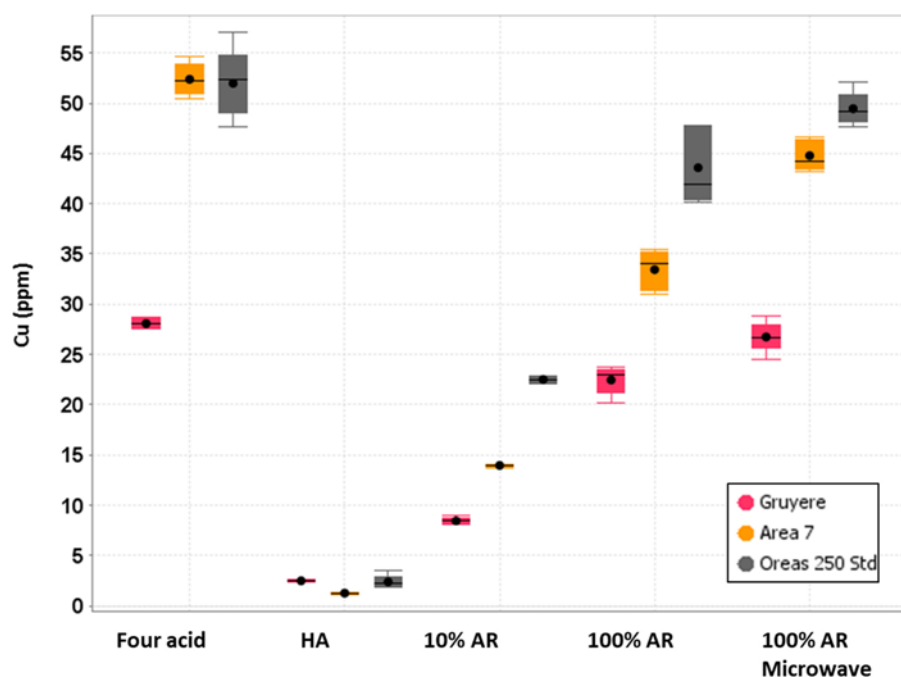


Fig. 12. Comparison of the Cu extracted from the OREAS 250 standard, and reference samples from Gruyere and Area 7 in the eastern Yilgarn Craton using the five different extractions tested. The reported value for the OREAS 250 standard in concentrated aqua regia is 44.7 ± 1.3 or 1 SD.

Bentley, DeGrussa, Kopai and NSR all displayed iron oxide XRD concentrations of >4%, and typically exhibit absorptions in the reflectance spectra in the iron oxide region. The samples where XRD identified a greater content of goethite (i.e. Kintore, DeGrussa and Bentley) also correspond to samples with longer wavelength features for FeOx (i.e. >895 nm), indicating that the wavelength position of the iron oxide is a good indicator of the proportions of goethite to hematite.

All <2 mm bulk samples displayed kaolinite absorption features (asymmetrical 2207 nm absorption with inflection at c. 2170 nm), with the Kintore and Kopai samples displaying deep 1900 nm and asymmetrical 1400 nm absorptions corresponding to the presence of water. This may be due to the presence of an aluminium-bearing clay mineral (montmorillonite).

The FTIR measurements of the bulk <2 mm samples found the presence of an absorption at c. 2550 nm (just outside the wavelength region of the ASD) which is related to the presence of carbonate for the Kintore and Kopai samples. These samples display a strong asymmetrical absorption due to carbonate at 3970 nm and a peak at c. 6400 nm, which has been used to identify the presence of calcite. All samples display prominent quartz absorptions at c. 4465 nm and 8640 nm except for the Boddington, Kopai and Kintore samples, which have only small absorptions. These samples were found to have lower amounts of quartz in the XRD analysis. All samples have an absorption feature at 9000 nm, which could either be attributed to kaolinite or feldspar; however, all but the Boddington and Kopai samples have a 10 960 nm peak, which would indicate the presence of kaolinite.

Table 6. MANOVA comparisons of dispersant types and grades with respect to Au concentration using two reference soils and five replicates of each treatment

Comparison	Difference of means	<i>t</i>	<i>P</i>	<i>P</i> < 0.050
Degrussa and Kopai soils <i>n</i> = 10				
Ammonia solution v. Na-carbonate	9.28	15.787	<0.001	Yes
Ammonia solution v. laboratory-grade Na-hexametaphosphate	6.19	10.53	<0.001	Yes
Bulk commercial-grade Na-hexametaphosphate v. Na-carbonate	5.64	9.594	<0.001	Yes
Technical-grade Na-hexametaphosphate v. Na-carbonate	4.95	8.421	<0.001	Yes
Ammonia solution v. technical-grade Na-hexametaphosphate	4.33	7.366	<0.001	Yes
Ammonia solution v. bulk commercial-grade Na-hexametaphosphate	3.64	6.192	<0.001	Yes
Laboratory-grade Na-hexametaphosphate v. Na-carbonate	3.09	5.257	<0.001	Yes
Bulk commercial-grade Na-hexametaphosphate v. laboratory-grade Na-hexametaphosphate	2.55	4.338	<0.001	Yes
Technical-grade Na-hexametaphosphate v. laboratory-grade Na-hexametaphosphate	1.86	3.164	0.006	Yes
Bulk commercial-grade Na-hexametaphosphate v. technical-grade Na-hexametaphosphate	0.69	1.174	0.247	No
DeGrussa soils only <i>n</i> = 5				
Ammonia solution v. laboratory-grade Na-hexametaphosphate	3.1	3.729	0.006	Yes
Ammonia solution v. bulk commercial-grade Na-hexametaphosphate	2.82	3.392	0.014	Yes
Ammonia solution v. technical-grade Na-hexametaphosphate	2.72	3.272	0.018	Yes
Ammonia solution v. Na-carbonate	1.68	2.021	0.302	No
Laboratory-grade Na-hexametaphosphate v. Na-carbonate	1.42	1.708	0.452	No
Bulk commercial-grade Na-hexametaphosphate v. Na-carbonate	1.14	1.371	0.625	No
Technical-grade Na-hexametaphosphate v. Na-carbonate	1.04	1.251	0.626	No
Technical-grade Na-hexametaphosphate v. laboratory-grade Na-hexametaphosphate	0.38	0.457	0.957	No
Bulk commercial-grade Na-hexametaphosphate v. laboratory-grade Na-hexametaphosphate	0.28	0.337	0.931	No
Bulk commercial-grade Na-hexametaphosphate v. technical-grade Na-hexametaphosphate	0.1	0.12	0.905	No

All pairwise multiple comparison procedures (Holm–Sidak method). Overall significance level = 0.05.

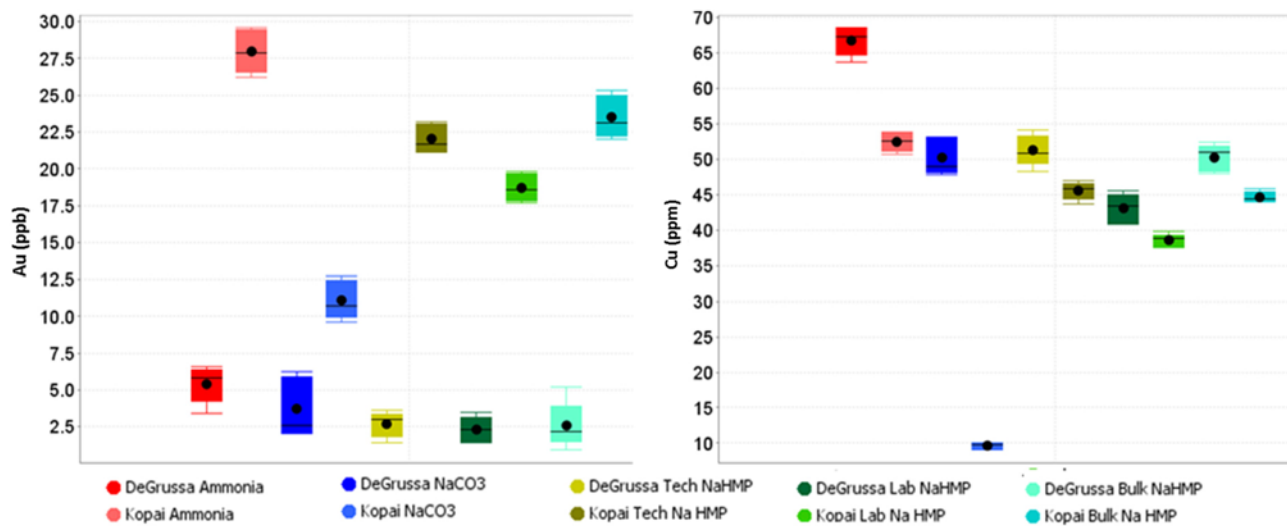


Fig. 13. Box plots comparing the five different dispersants and two soil types compared to the concentration of Au and Cu assayed and extracted with MAR-04 in the fine separates. $n = 5$.

Table 7. Comparison of dispersants for weight of material dispersed and the approximate economic costs

Dispersant	Average μm weight (g)	SD	% Recovered	Cost (\$ per equivalent unit)
Laboratory-grade Na-hexametaphosphate	2.5	0.39	12.5	0.84
Technical-grade Na-hexametaphosphate	2.1	0.54	10.5	0.5
Bulk commercial-grade Na-hexametaphosphate	2	0.33	10	0.07
Ammonia solution	1.2	0.4	6	nd
Sodium carbonate	0.8	0.48	4	nd

nd, not determined.

Table 8. MANOVA comparisons of fine-fraction separation treatments for Au (Boddington excluded)

Comparison	Difference of means	t	P	$P < 0.050$
'Ultrasonics' v. 'Rinsed'	0.47	0.684	0.873	No
'None' v. 'Rinsed'	0.395	0.575	0.814	No
'Ultrasonics' v. 'None'	0.075	0.109	0.914	No

All pairwise multiple comparison procedures (Holm–Sidak method). Overall significance level = 0.05.

Table 9. MANOVA comparisons of fine-fraction separation treatments for Cu (Boddington excluded)

Comparison	Difference of means	t	P	$P < 0.050$
'Rinsed' v. 'None'	1.455	2.918	0.016	Yes
'Rinsed' v. 'Ultrasonics'	0.805	1.614	0.214	No
'Ultrasonics' v. 'None'	0.65	1.304	0.199	No

All pairwise multiple comparison procedures (Holm–Sidak method). Overall significance level = 0.05.

The ASD spectra for the $<2 \mu\text{m}$ samples displayed variations in the iron oxide, kaolinite and water absorptions. The Kintore sample was very different in appearance and possessed deep-water features, with absorptions similar to a sulphate mineral, possibly gypsum. The XRD results for the Kintore samples found sodium chloride and thenardite (sodium sulphate).

Similarly to the bulk measurements, the samples with a longer hematite–goethite wavelength index corresponded to the higher XRD goethite abundances. The spectra for Kopai and Boddington are different in their appearance to the other samples, which are kaolinite dominated. The Boddington $<2 \mu\text{m}$ samples display

gibbsite absorptions and minor kaolinite, whereas the Kopai has a spectrum more like an aluminium smectite.

The FTIR spectra for the $<2 \mu\text{m}$ samples do not contain any quartz or feldspar features and are dominated by kaolinite. The exceptions are the Boddington, Kintore and Kopai samples. The Kintore spectra have an unusual 4735 nm absorption feature, which could be a sulphate, whereas the Kopai samples have a 3970 nm carbonate absorption. Owing to the fine grain size of the carbonate in the $<2 \mu\text{m}$ samples for Kopai, the carbonate spectrum is dominated by volume scattering in the $>6500 \text{ nm}$ region. The Boddington spectra are weak and display numerous broad absorptions and peaks, but do not display diagnostic kaolinite, goethite or gibbsite in the TIR wavelength region.

Discussion

The study in the East Wongatha region of Western Australia showed that the Au was hosted in different size fractions (Noble *et al.* 2013). Depending on which size fraction was viewed spatially, a number of different targets were identified: that is, the exploration priorities changed based on the size fraction analysed. The results of this research demonstrate the value of concentrating and analysing the fine fractions (or any fraction) separately – it provides a more level comparison. This effect is most strongly evident in the finest fractions. For example, if the coarse fractions have minimal Au, a sample may have 10 ppb Au but only have 2% of this fine ($<2 \mu\text{m}$) clay material. If another sample in the same survey contains 10% clay and is 20 ppb Au, the likely scenario is that the explorer is drawn to the greater number. However, if we adjust for the assumed clay proportion hosting that Au, the first sample had an equivalent 100 ppb Au compared to the second sample, and potentially it is a five times stronger anomaly that is overlooked. This adjustment needs to be carefully considered in future exploration. The same

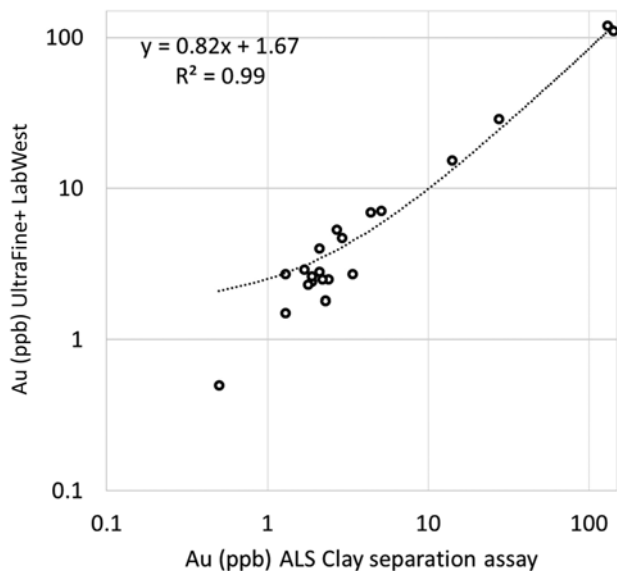


Fig. 14. Scatterplot of the Au concentration extracted from the UltraFine+™ method at LabWest and the clay separation at ALS that correlate well and show a little more variation at the low end.

could be said for a stronger integration of physicochemical parameters and mineralogy that greatly influence the soil, regolith and sediment chemistry. The UltraFine+™ workflow developed and tested with these key reference samples is a starting point to develop this application into future exploration. To better evaluate this approach in the field, Noble *et al.* (2019a, b) have applied this method to a range of prospects and (re-)assaying regional surveys samples from the Geological Survey of Western Australia.

This approach has been promoted by others, but the combination of separation and chemical analysis with a range of other data in the same workflow is an advancement. The separation of finer materials has been used in different exploration environments (Robertson 1999; van Geffen *et al.* 2012; Carlson 2016; Stewart *et al.* 2017;

Sader *et al.* 2018) and all have had some degree of success. More routinely, geochemists are investigating the <63 μm fraction that is easily dry sieved: for example, Anand *et al.* (2014) showed that the <53 μm fraction had much greater concentrations of Au over the arid Moolart Well deposit whereas the commonly used <250 μm soils were ineffective. Others have shown the benefit of using the <63 μm fraction in till settings for base-metal, uranium and REE exploration (Hashmi *et al.* 2018; McClenaghan & Paulen 2018).

The results of our study support the application of this fine separation for base metals and Au, with a significant enrichment in both. The average percentage increase in Au and Cu using the <2 μm fraction is 188 and 195%, respectively, in the bulk reference samples compared to the other fractions. The East Wongatha study by Noble *et al.* (2013) showed that samples are predominantly coarse materials, and initially reported Au concentrations of less than detection (0.5 ppb) up to about 30 ppb. This was very much aligned with the bulk reference samples studied in this paper. When the fine fraction is concentrated the detection limits become obsolete, as the concentrations are commonly well above this limit. The results for the new testing support the increase in concentrations, but not to the extent shown in the earlier study of Noble *et al.* (2013), where Au concentrations were in some cases an order of magnitude or more greater in the <2 μm fractions.

The enrichment of Au and Cu is certainly valuable, the benefit for Au is greatly supported in the <2 μm fraction with the removal of nugget effects. Micro- and nanoparticulate 'invisible' Au has been problematic to study (Hough *et al.* 2008). One particular observation was that nanoparticulate populations seem to increase in number and decrease in size as the detection/visualization technology improves (Hough *et al.* 2008, 2011). The populations appear almost fractal in nature and no research has evaluated what this means for exploration. For both resource definition and mineral exploration, Au is notoriously difficult to analyse due to its 'nuggety nature' (Stanley 2006). The results of our study show no 'nuggety' results using the <2 μm fraction and this is supported by other results published by Arne & MacFarlane (2014), who removed nugget effects in stream sediment samples by separating and analysing the <4 μm material. The results of our study potentially contradict or at

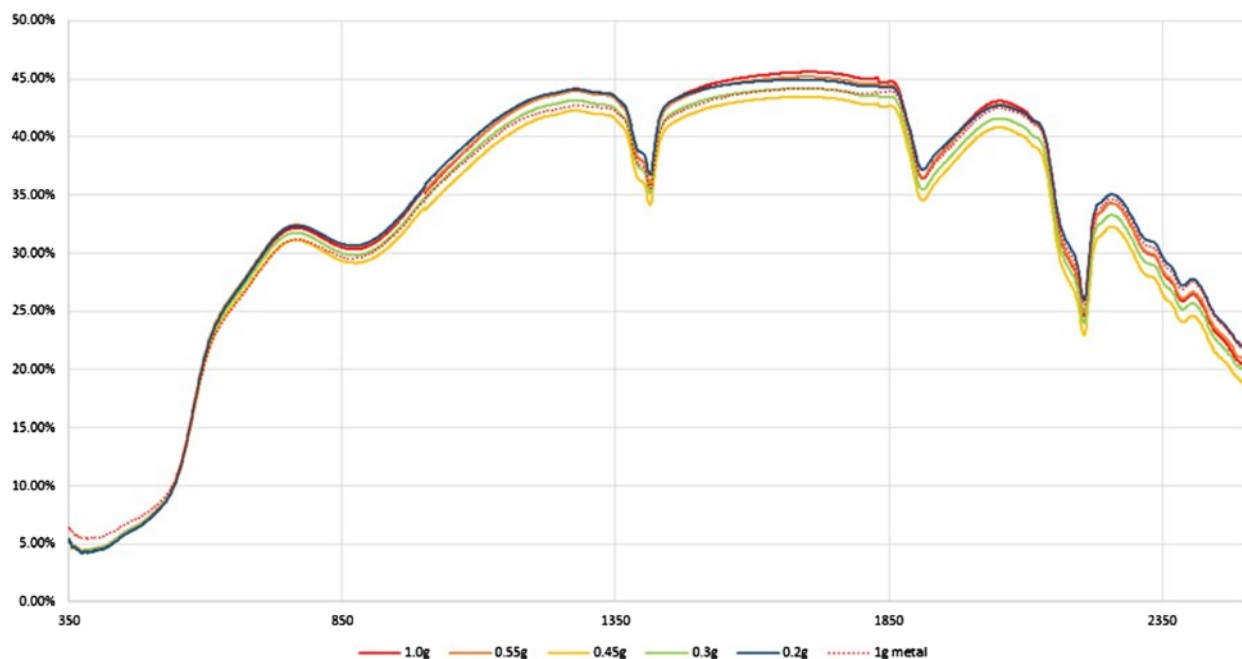


Fig. 15. Mean reflectance with increased sample amount. The Bentley 3 sample <2 μm measured with an ASD FieldSpec4 using different sample weights of 0.2, 0.3, 0.45, 0.55 and 1 g with a muglight and sampling cups. Each sample measurement was replicated six times. The 1g metal line shows the change related to a metal spacer used in the sample holder to reduce variance.

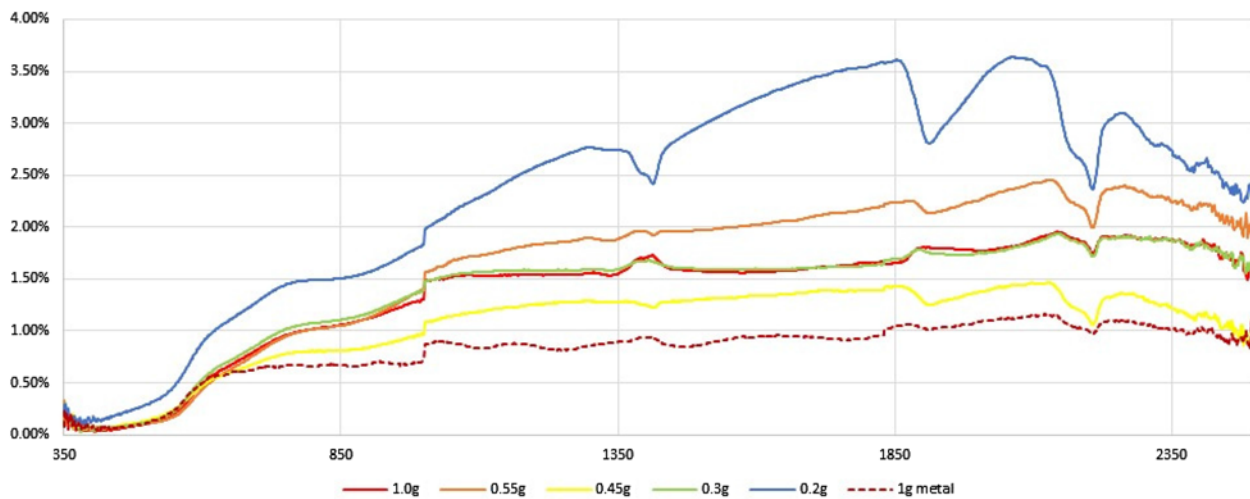


Fig. 16. The standard deviation of the measurements performed in Figure 15 at the different spectral wavelengths. The 1g metal line shows the change related to a metal spacer used in the sample holder to reduce variance.

least put a limit on the push to smaller size fractions. We did not observe a marked benefit from separating to the submicron level, even though Hough *et al.* (2008, 2011) show more Au in these morphologies. Our results indicate that the $<2\ \mu\text{m}$ fraction captures all of the data effectively, and the complications associated with separating to smaller fractions ($0.75\ \mu\text{m}$ and $0.2\ \mu\text{m}$) are avoided.

Sader *et al.* (2018) found that the $<2\ \mu\text{m}$ fraction has significantly better anomaly to background contrast ratios for Au and Ag (37 and 16%, respectively) compared to the $<180\ \mu\text{m}$ fraction, and that the reproducibility was better, supporting the growing examples where nugget effects have been reduced or removed by using smaller particle sizes.

Dispersants were important for the disaggregation of Western Australia soils and not all performed the same. Sodium hexametaphosphate was preferred, and this was also shown in fine-fraction separation and testing comparing Acumer™ and Calgon® (commercial-grade Na-hexametaphosphate) for sediments related

to uranium exploration (Kyser 2015). The results showed that the Acumer™ extraction did not successfully disaggregate particles with similar centrifuge times to the Calgon® treated soils, and this resulted in more coarse material being included in the final digestion. Other evidence suggests that in till soils, or other heavy clay materials, dispersants are not necessary and may provide further complications based on work by the commercial laboratory, Bureau Veritas (J. Sader 2018 pers. comm.). This seems plausible for high clay soils, but is definitely not the case for the soils used in this study or those representative of many semi-arid climate soils. The salinity of soils was problematic for dispersion in this study and, as with other exploration regions of interest hosting saline soils, this may require increased amounts of dispersants or multiple separation steps. Some soils of the Atacama Desert in South America have required up to eight times the common amount of dispersant when used in other clay separation procedures (J. Sader 2018 pers. comm.). Results of this study found that doubling the amount of soil

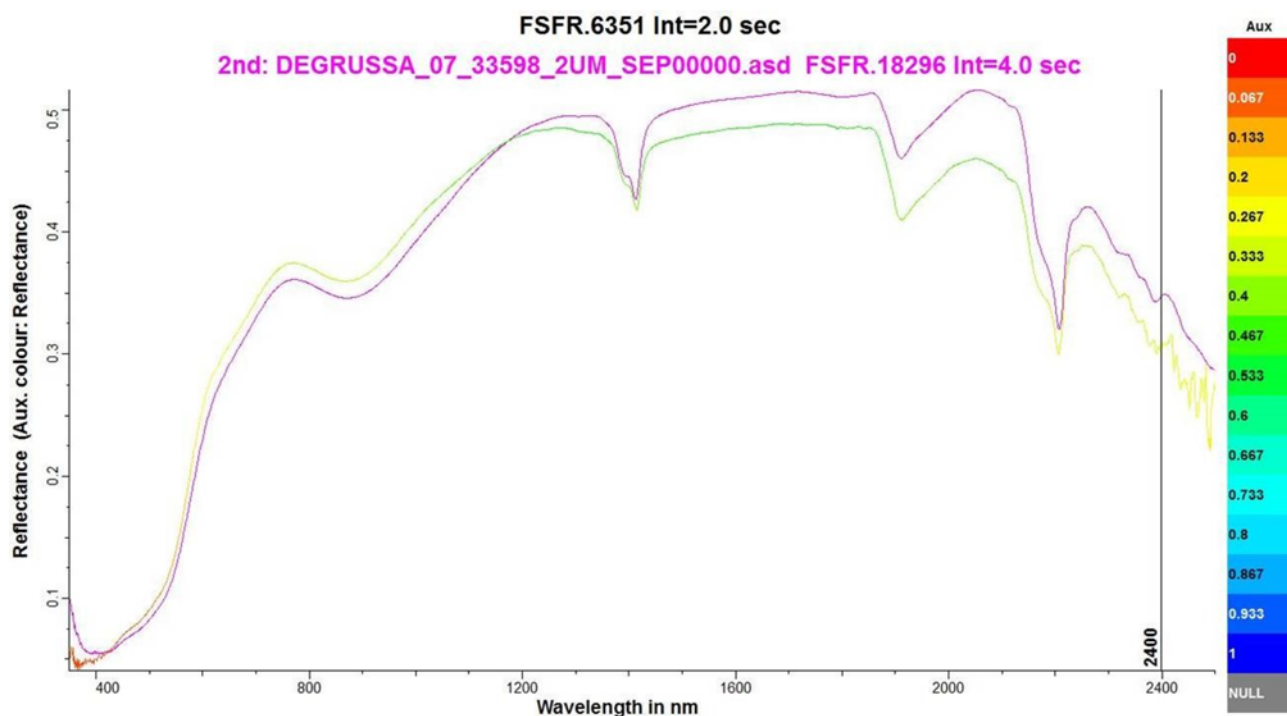


Fig. 17. The standard set-up and spectral analysis using the ASD (pink line) with a lot of sample in a muglight sample cup compared with the new test probe method (rainbow coloured line).

and dispersant was enough to recover the required sample for the UltraFine+™ analyses.

Another difference observed in this study compared to the other commercial offerings was the use and recovery of fine material from a small initial bulk sample. Typically, 20–40 g was used for the UltraFine+™ workflow, with recovery of 0.5–2 g in many of these soils. The UltraFine+™ method uses nearly an order of magnitude less starting material compared to the 300 g required by ALS for their clay separation and analysis.

Conclusions

This study into fine soil separation (<2 µm) for mineral exploration refined analytical methods and should enhance surface exploration success. By analysing fine fractions (<2 µm), we produced reproducible, reliable results with bigger concentrations. Key benefits were the removal of nugget effects (in Au) and the challenges with detection limits in materials that are dominantly quartz sand. Testing submicron fractions showed that, although the <0.2 µm fraction was slightly different to the 0.75 µm and <2 µm fractions, there was no significant additional value in going to this extra effort, so the <2 µm is favoured as the best fine-fraction separate. The overall method development showed that ultrasonics was not required, a dispersant was critical for solid recovery and that Na-hexametaphosphate (technical or laboratory grade) was the most effective. The developed method proved that the use of a small weight for analysis was effective (0.2 g) and microwave-assisted aqua regia was the best analytical method for Au. This research shows obvious benefits in using fine fractions for Au. However, there is no loss of benefit to using this fraction to analyse for base metals and other pathfinder elements. Copper and Zn were consistently and abundantly extracted from the fine particle-size fraction. The new workflow (UltraFine+™) developed in this study provides c. 40 elements, spectral mineralogy, particle-size distribution, pH, electrical conductivity (EC) and specific surface area, offering more quality data that should improve future mineral exploration using soil and regolith samples.

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Correction notice: The copyright has been updated to Open Access.

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