



Determination of Gold in Soils and Sediments by Fire Assay or Aqua Regia Digestion: Choosing the Optimal Method

INTRODUCTION

Although there are a number of analytical techniques that are used to measure the content of Au in soils, sediments and rocks, it is not always obvious to the exploration geochemist which is the optimal method to use. Some methods are designed to extract all of the Au present within the sample, whereas other methods only provide, at best, 'near-total' abundance, and some methods are specifically designed to extract only Au associated with specific mineral phases. Advances in analytical techniques, instrumental sensitivities and demands of the exploration and industrial processing industries have meant that Au detection limits are continuously being lowered (e.g., Mladenova *et al.* 2012). Low detection limits are particularly important for geochemical exploration in deeply covered terrain, where Au contents of soils, till, and sediments may be governed by poorly understood transport mechanisms, with consequent uncertainties in where Au is sequestered (Cameron *et al.* 2004).

There are a variety of methods that are used in analysis for Au, including inductively coupled plasma emission spectroscopy (ICP-ES), ICP mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), graphite furnace AAS, and neutron activation analysis (NAA). There is also an increase in the use of hyphenated techniques, in particular laser ablation ICP-MS, e.g., femtosecond laser ablation analysis for Au in fire assay buttons (Vanhaecke *et al.* 2010). Several methods for extracting Au from geological matrices in addition to fire assay and aqua regia also exist, including more traditional techniques such as cyanide leach (Leduc & Itard 2003), and newer methods such as activated carbon microextraction (Hassan *et al.* 2011) and cloud point extraction (Tong *et al.* 2011; Hartmann & Schuster 2012). For a recent review see Mladenova *et al.* (2012). Many of the newer techniques are capable of reaching Au detection limits at the low ppt level,

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but these require time-consuming and complicated extraction and pre-concentration steps not suited to a production laboratory, and so will not be discussed further.

In this paper we discuss the benefits and limitations of two of the major Au analytical methodologies (fire assay and aqua regia digestion)

used on soils, till and surficial media and provide insights into how to determine the optimal method to use based on the type of exploration or analytical program. To illustrate the utility of both methods, we also present a case study where we have analyzed more than 2000 soil samples by both fire assay and aqua regia digestion.

GOLD BY FIRE ASSAY

Fire assay (FA) is a fusion technique that results in full sample decomposition, followed by a separation step to preconcentrate the Au contained within the sample. There are two major sub-types of fire assay: Pb and NiS. The NiS-FA method is particularly useful where all of the platinum group metals (PGM) are required in addition to Au (Hall & Oates 2003; Savard *et al.* 2010; LeFort *et al.* 2011). However, where Au is the primary metal of interest, the NiS-FA technique is less widely used, owing to the increased complexity of the method, and because some studies have shown that the method has lower Au recoveries compared to the Pb-FA method (e.g., Juvonen *et al.* 2004). Thus,

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the NiS-FA will not be discussed further.

The Pb-FA technique involves mixing of a sample with a flux, which includes PbO, Na₂CO₃, Na₂B₄O₇•10H₂O, silica and flour. The precise amounts of these ingredients commonly need to be adjusted depending on the sample matrix, in particular the sulfide content. A small amount of Au-free Ag is added and the sample mixture is then fused under reducing conditions at high temperature (~1000 °C); the Au, Ag and precious metals form a dense button with the Pb. The Pb button is recovered and fused again under oxidizing conditions to separate the Pb from the Au (see for example, Hall & Oates 2003).

Advantages of the Pb-FA method are that it is a: 1) complete digestion of the sample, so that Au encapsulated within resistive minerals is measured; 2) process that results in a preconcentrated sample that is relatively free of the sample and fusion matrix, so that minimal sample dilution or matrix-associated interferences are encountered during analysis; and 3) historically standardized method generally performed in the same manner by different laboratories such that data from different sources are reliably comparable.

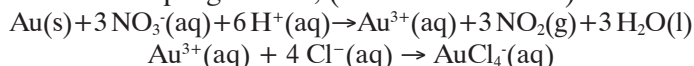
By contrast, the limitations of the method include: 1) the detection limit for Au by Pb-FA is controlled mainly by the impurities in the flux, rather than instrumentation; 2) flux ingredients commonly need to be modified depending on the nature of the sample (e.g., high sulfide), requiring more highly skilled laboratory technicians than is the case for aqua regia digestion; 3) the total dissociation of Au-bearing minerals negates information on how much Au is available in native form or in sulfide phases versus encapsulated phases; and 4) large sample aliquot required (15 or 30 g), although this can also be an advantage as it reduces the nugget effect.

GOLD BY AQUA REGIA DIGESTION

In aqua regia digestion, the sample is subjected to attack by a mixture of concentrated HCl and HNO₃ acids. Aqua regia is a widely used in soil, sediment and rock analysis as a partial digestion. Aqua regia is the term used to typically describe a 1:3 mixture of concentrated nitric (HNO₃) and hydrochloric (HCl) acids. Note, however, that this usage is not consistent, with ratios between the two acids being variable between different laboratories and research groups. Because aqua regia is not a total digestion technique, other factors in addition to the nitric/hydrochloric acid concentrations and ratio influence metal recoveries. One of the most critical factors is

temperature; higher temperatures generally result in higher metal recoveries, and more consistent results in the experience of ALS Geochemistry.

Aqua regia is particularly useful for Au dissolution; neither nitric acid nor hydrochloric acid alone will keep Au in solution. The two acids, combined, perform the required steps to dissolve Au and keep it in solution. Nitric acid and reaction products in combination with HCl (e.g., nitrosyl chloride, NOCl) are strong oxidizers, forming gold ions (Au³⁺) in solution following dissolution of Au-bearing minerals. The hydrochloric acid provides the source of Cl⁻ ions, which form strong aqueous chloroaurate (AuCl₄⁻) complexes, removing Au from solution and allowing Au dissolution and oxidation reactions to progress i.e., (Renner *et al.* 2000):



The advantages of the aqua regia Au method compared to Pb-FA include the following: 1) lower detection limits compared to Pb-FA are achieved in many laboratories, owing to the ready production of ultraclean HCl and HNO₃ via distillation and the advances made in ICP-MS instrumentation in recent years; 2) this relatively simple digestion method means that less technical training and experience for laboratory personnel is required than is the case for Pb-FA; and 3) small sample sizes (< 1 g) can be analyzed for Au when analyzing the clay size (< 2 μ) fraction.

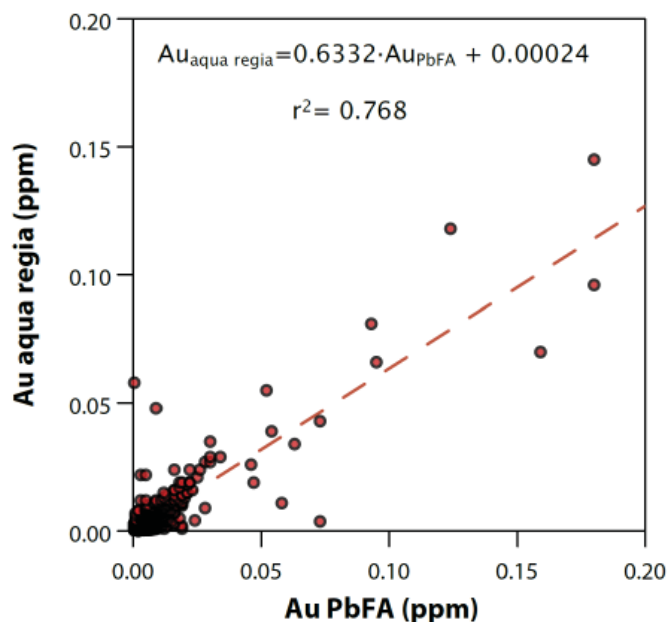


Figure 1. Plot of Au content determined by Pb-FA versus Au by aqua regia.

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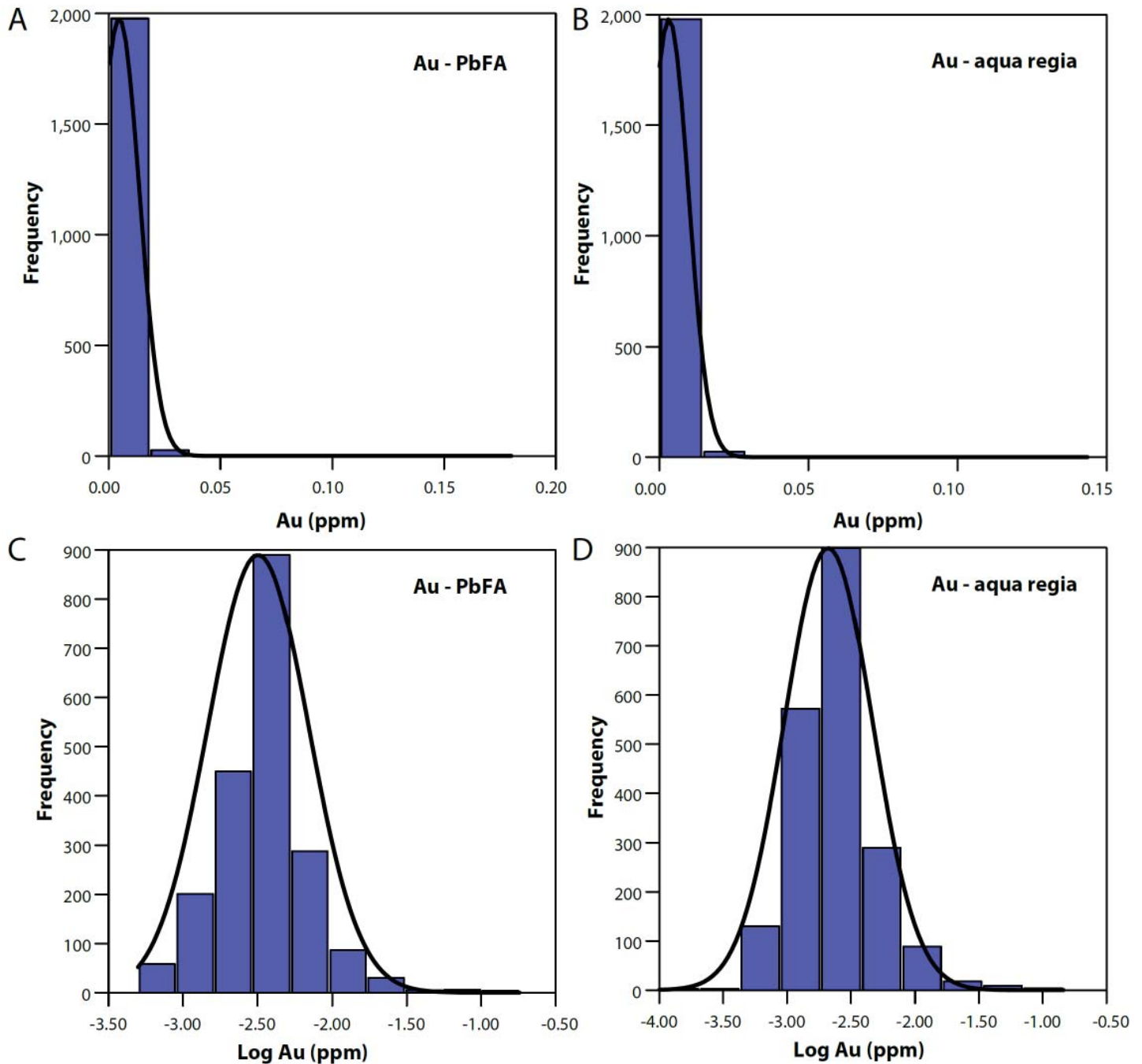


Figure 2. Frequency distribution plots for Au content determined by Pb-FA and aqua regia. The Au data are in ppm and show the highly skewed (i.e., non-normal) nature of Au in geological materials. However, the data for both methods are approximately log normal (C and D).

By contrast, the limitations of the method include: 1) for most samples, an aqua regia digest will not recover 100% of the Au, in particular, Au occluded within most (aluminous) silicate minerals; 2) large sample sizes (25-50 g) for representative analysis for Au require special laboratory setup to maintain consistent heating and mixing across the digestion solution; 3) depending on the mineralogy of the

sample, the total dissolved solids content can be high, as this method does not involve preconcentration and separation in the same way as the Pb-FA method.

CASE STUDY

In order to evaluate the differences between Pb-FA and aqua regia analyses of soil, till and sediment

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for Au, we analyzed 2016 samples of soils from northwestern Canada, using both methods, with a nominal weight of 25 g for aqua regia and 30 g for Pb-FA in most cases (except where sample volumes were too low, in which case the nominal weights were around 15 g, and 10 g in rare cases). Soil samples were dry screened to -80 mesh (< 0.177 mm) prior to analysis. For this dataset, 123 samples were determined to contain less than detection amounts of Au for one of the two methods (Pb-FA detection limit = 0.001 ppm; aqua regia detection limit = 0.0001 ppm for most samples, 0.001 ppm for a small subset).

Because the number of samples reported as below detection was small relative to the total number of samples, in the figures and for the statistics presented below, we have reassigned the below detection samples Au values to half the respective method detection limit.

For the 2016 samples, Au values by Pb-FA ranged from the detection limit of 0.0005 ppm to 0.18 ppm (mean = 0.0047 ppm, median = 0.0030 ppm, standard deviation = 0.0090 ppm, skewness = 12.8), whereas aqua regia Au values ranged from 0.0001 to

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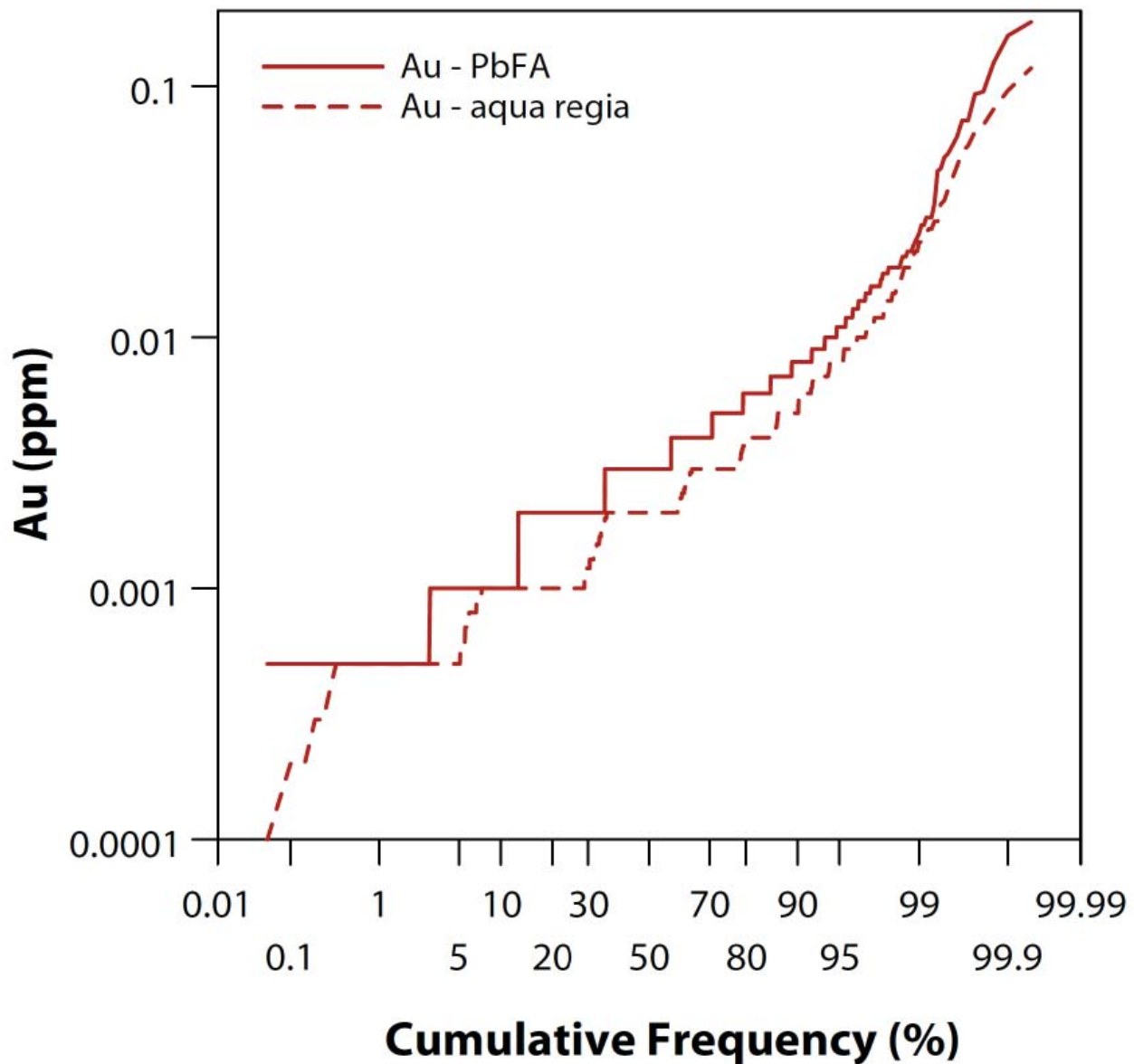


Figure 3. Cumulative frequency plot for Au by Pb-FA and aqua regia. Both datasets show similar distribution patterns, with a shift to lower abundance overall for the aqua regia Au.

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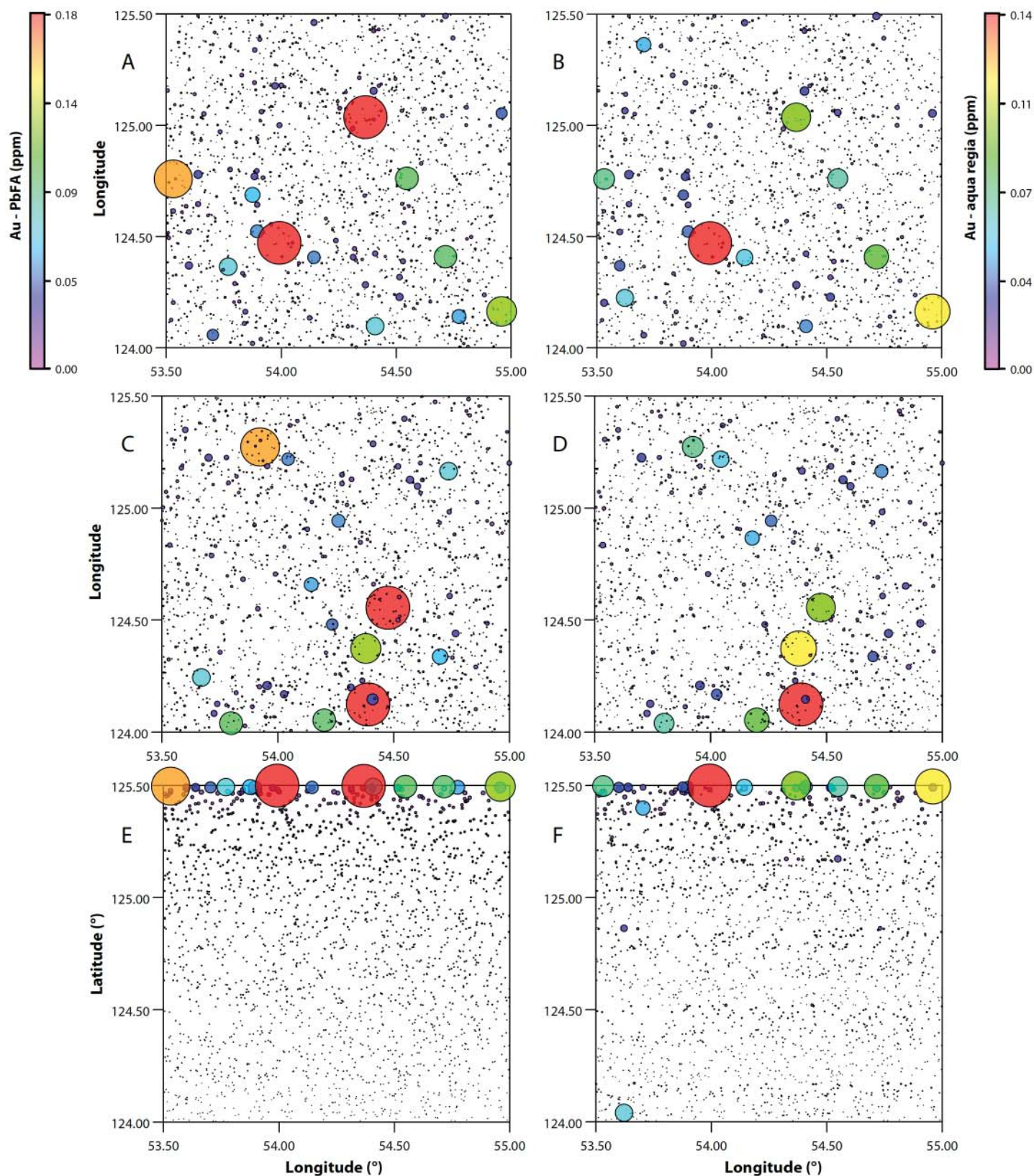


Figure 4. Proportional dot plots of Au by Pb-FA (A, C, E) and aqua regia (B, D, F). The locations were generated randomly within a randomly selected region of space measuring 1.5° by 1.5° in latitude and longitude, to mimic a typical regional geochemical survey.

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0.145 ppm (mean = 0.0032 ppm, median = 0.0020 ppm, standard deviation = 0.0065 ppm, skewness = 12.3) (Fig. 1A). The means and medians of the two datasets are statistically significantly different at the 99% confidence interval (Students T-test; $p < 0.001$). However, for the log-normalized data, although also statistically significantly different in terms of mean and median, both datasets are approximately log-normally distributed and have similar log-probability distributions (Figs. 2, 3). Overall, the two datasets show a statistically significant correlation at the 99% confidence interval (Fig. 1A; $r^2 = 0.768$). The strong correlation indicates that despite some scatter in the data, both datasets would show similar geochemical anomalies. The parallel shapes but shift to lower Au contents in the aqua regia log-probability distribution compared to the Pb-FA distribution indicates that, on average, about 80% of the Au is recovered by aqua regia digestion.

The difference in Au recovery between the two methods is interpreted to reflect the inability of an aqua regia digestion to extract Au that is occluded

in resistant minerals. Aqua regia will digest all native Au, carbonate, sulfide and Fe, Mn oxide minerals, suggesting that the most likely location of the occluded Au is in quartz and/or silicate minerals (Church et al. 1987). The extent to which an aqua regia digestion will extract Au is therefore dependent primarily on sample type (both in terms of medium sampled and deposit type being targeted) and nature of Au sequestration and the grain size of the material being analyzed; a finer sieve fraction or grind (<0.063 mm vs <0.177 mm) exposes more surface area for an aqua regia leach. The much stronger correlation between the two methods for the ranked data versus the paired data (i.e., Fig. 1B versus 1A) may in part be due to analytical uncertainties, but is probably dominantly a function of the nugget effect for Au, even for sample sizes as large as the 25-30 g nominal weights dominantly used in this study.

To test the robustness of both methods for mineral exploration, we generated a random set of locations within a fictional study area and produced

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proportional dot maps for both Au techniques (Fig. 4). In Figure 4 there are three scenarios plotted. Figures 4A (Pb-FA) and 4B (aqua regia) show the results where the individual samples are assigned random locations (although the same location for both methods). The anomalies produced are therefore randomly distributed, yet both methods show similar the anomaly patterns, although with slight differences in relative intensity (Figs. 4A, 4B). Figures 4C and 4D show the same data, but in this case, the Au data were ranked prior to assigning the random locations. Again, both analytical methods produce essentially identical anomaly patterns. Finally, the data were ranked and the latitude data were ranked (longitude remained randomized; Figs. 4E, 4F). Because of this latitude ranking, all of the Au Pb-FA anomalies lie along the upper limits of the 'study area'. The Au aqua regia anomalies are essentially identical, although the mismatches are more evident where plotted this way, e.g., there is an anomaly in the SW corner of the map area (Fig. 4F). For geochemical exploration in glaciated terrain, previous studies have shown that most of the native Au in till is < 0.177 mm in size (e.g., McClenaghan 2001), indicating that the aqua regia digestion method would be a suitable alternative to Pb-FA, with the advantage of lower detection limits (i.e., 0.0001 with a 25 g aliquot, 0.0002 with a 0.5 g aliquot). Indeed, a recent study by Ward *et al.* (2013 in press) has shown that analysis of the clay sized fraction (<0.002 mm) of till by aqua regia digestion reduces the nugget effect for Au and enhances anomaly to background signals for fine-grained Au. Note that the clay fraction Au would best be analyzed in conjunction with a larger size fraction to account for nugget Au; McClenaghan (2001) noted that the greatest abundance of Au in till was in the 0.01 to 0.05 mm fraction.

SUMMARY

Both the Pb-FA and aqua regia digestion methods are excellent choices for routine geochemical exploration soil surveys. The decision as to which method to choose will rest primarily on the nature of the sample medium and requirements of the exploration program, such as detection limits and sizes of sample available. The costs and analytical turnaround for Pb-FA and aqua regia Au are typically comparable. For soil, till and stream sediment geochemical surveys, aqua regia is an excellent method of choice, owing to relative ease of analysis and ability to achieve low detection limits; the low

detection limits offset the fact that typically < 100% of the Au is recovered. Furthermore, the conditions of the aqua regia digestion can be adjusted (i.e., acid strength, HNO₃/HCl value, temperature) depending on the strength of leach desired. As shown by our case study, it is important to recognize that for many deposit types (and depending on Au transport mechanism), the aqua regia digest will not be total for Au. This is not always critical, as in many soil and till surveys we are interested in the more labile Au in any case (Cameron *et al.* 2004). By contrast, for drill core and rock samples, fire assay is the method of choice because of its ability to liberate essentially all the Au contained within the sample. However, as we have shown here, Au anomalies for the case study are essentially identical, albeit with subtle differences in anomaly strength, as determined by Pb-FA and aqua regia results.

Acknowledgments

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Matthew I. Leybourne and Sarah Rice

matthew.leybourne@alsglobal.com

ALS Geochemistry,

2103 Dollarton Hwy,

North Vancouver, B.C.,

Canada V7H 0A7

