

Reproducibility of Gold Analyses in Stream Sediment Samples from the White Gold District and Dawson Range, Yukon Territory, Canada.

Introduction

A number of significant bedrock Au discoveries have been made in the western Yukon Territory, Canada in recent years (Fig. 1).

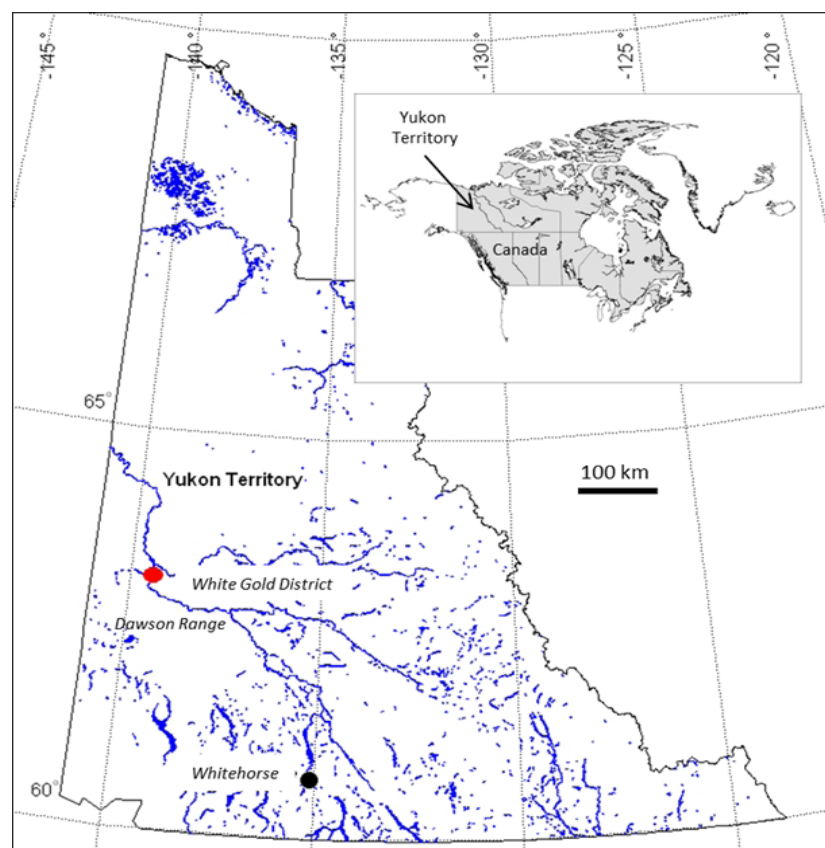


Figure 1. Location of the White Gold District and Dawson Range in the Yukon Territory, Canada. Rivers and lakes are shown in blue.

Underworld Resources announced the discovery of the Golden Saddle deposit in 2008 in what has subsequently become known as the White Gold District (MacKenzie et al. 2010), which is named after the White River where it enters the Yukon River in the vicinity of the Golden Saddle deposit. A resource of 1.0 M oz of indicated Au mineralization at 3.2 g/t with a total resource of 1.5 M oz at 2.7 g/t was delineated by Underworld Resources prior to purchase of the company by Kinross Gold Corporation in 2010 (Underworld Resources press release, January 19, 2010). There are also a number of other known bedrock Au occurrences on the property. Kaminak Gold Corporation announced the

discovery of the Coffee Au deposit in 2010 to the south of the White Gold District in the Dawson Range. This deposit currently has a defined resource of 3.4 M oz inferred at 1.36 g/t and 0.7 M oz indicated at 1.56 g/t, comprised mainly of oxide mineralisation (Sim & Kappes 2014). Comstock Metals Ltd. announced the discovery of significant Au mineralisation on their QV project approximately 10 km north of the Golden Saddle deposit in 2012 and recently announced an inferred resource of 0.23 M oz at 1.65 g/t (<http://www.comstock-metals.com>). Taken together, these discoveries have defined a new metallogenic province in the west-central Yukon Territory (Allan et al. 2013)

All three discoveries were the result of reconnaissance and follow-up soil sampling of C-horizon material developed on residual bedrock. The region is characterized by preglacial soils that were largely unaffected by the major glaciations in North America that spanned the last 2 million years, although they have been disturbed by periglacial processes and internal mixing of loess related to the most recent glacial advance in the region (McKillop et al. 2013). The collection of stream sediments and the interpretation of new and/or existing government survey data appear to have played little or no role in these discoveries, in spite of the fact that the terrain is favourable for such surveys and an extensive Regional Geochemical Sample (RGS) government database exists for the region (Héon 2003). One possible reason for the apparent lack of stream sediment sampling in exploration programs in the area may lie in the poor quality of the Au data from the Yukon RGS programs. The samples from central and

western Yukon Territory generally consisted of a maximum of 10 g of -80 mesh (<0.177 mm) material, some of which contained particulate Au. Sampling theory suggests that such material will produce inherently imprecise results (e.g. Abzalov 2008).

Of a total of 1609 duplicate Au fire assay analyses from the 2003 Yukon regional geochemical stream sediment database, a subset of 898 sample pairs with average Au contents greater than 10 ppb (i.e. more than 10 x the lower limit of detection for most analyses) has a global root mean square coefficient of variation of $\pm 94\%$, which indicates very poor repeatability (Fig. 2). In extreme cases, an original sample contained no detectable Au at a lower limit of

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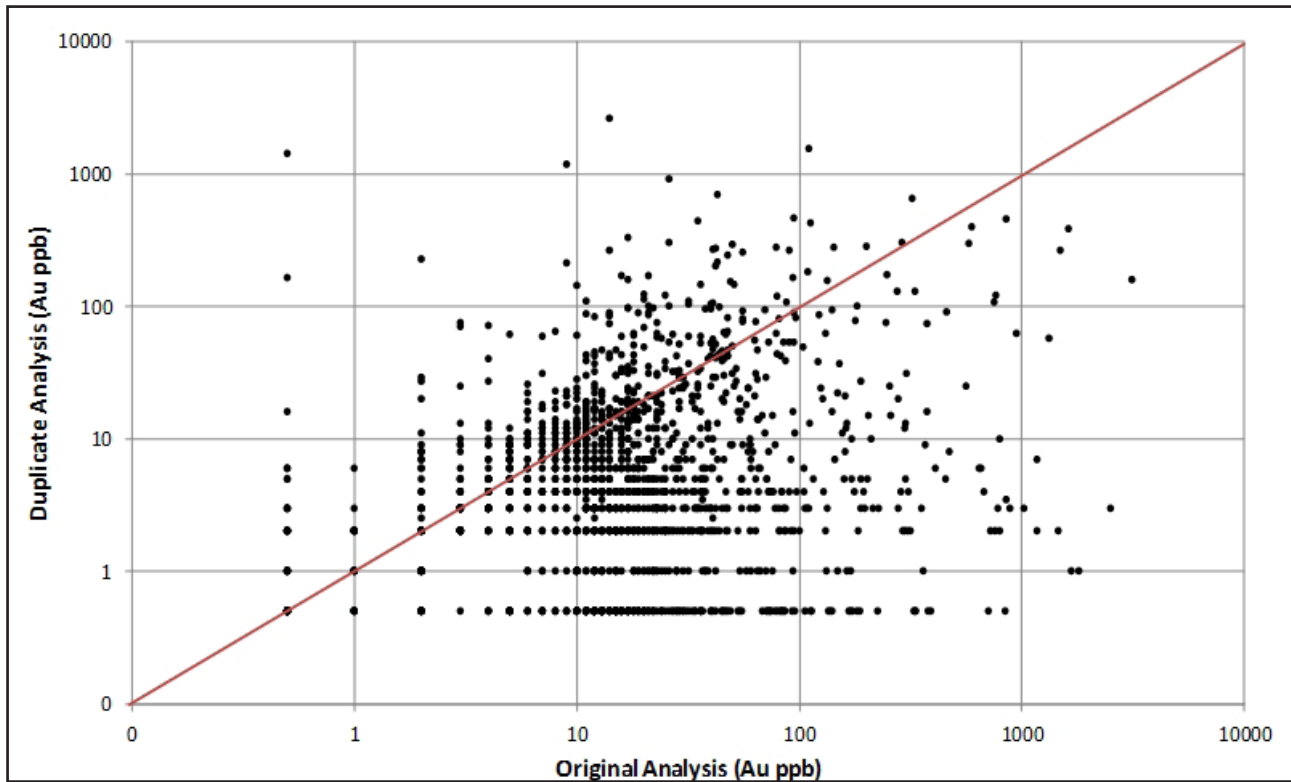
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Figure 2. Gold data from 1609 duplicate pairs from the 2003 Yukon Territory RGS (Héon 2003) data set.

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detection of 1 ppb, whereas the repeat contained over 1,000 ppb! In a specific example from the White Gold District, the original Au value in a stream sediment sample collected downstream of the Golden Saddle deposit was 10 ppb, slightly less than the anomalous threshold value of 15 ppb determined from 951 RGS samples in the area. The repeat Au analysis for this sample is 42 ppb, but normally only the original analyses would be plotted in thematic maps and so a subtle Au anomaly might be missed. The poor quality of

the publicly available Au data appears to have resulted in a loss of confidence in the use of stream sediment sampling in parts of the Yukon Territory, leading to a preference for a more costly, albeit effective, approach involving ridge and spur soil sampling followed by extensive gridded soil sample collection.

The Au data from near the Golden Saddle deposit produce only a subtle anomaly in the Yukon (RGS) dataset (Fig. 3). However, As and Sb contents in stream sediments

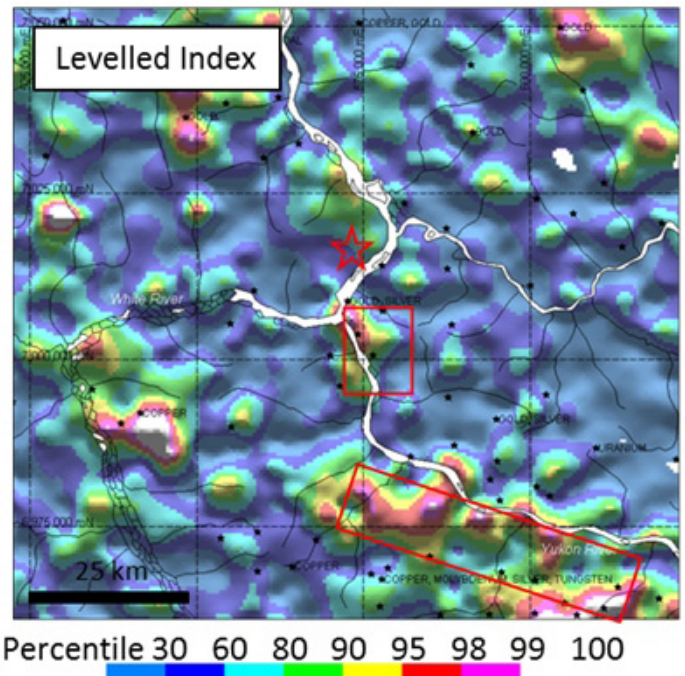
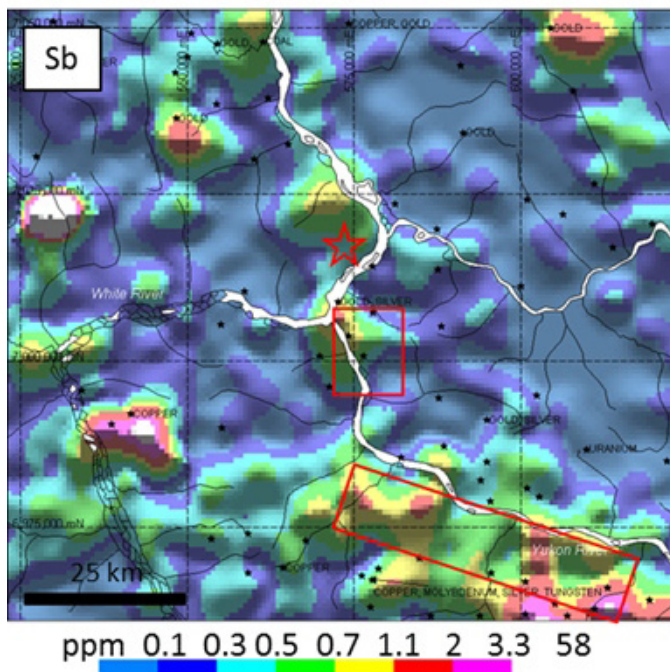
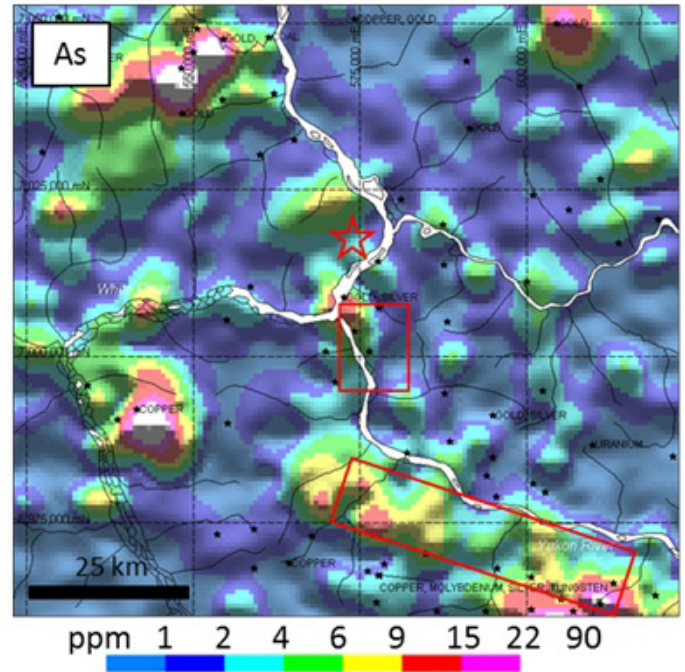
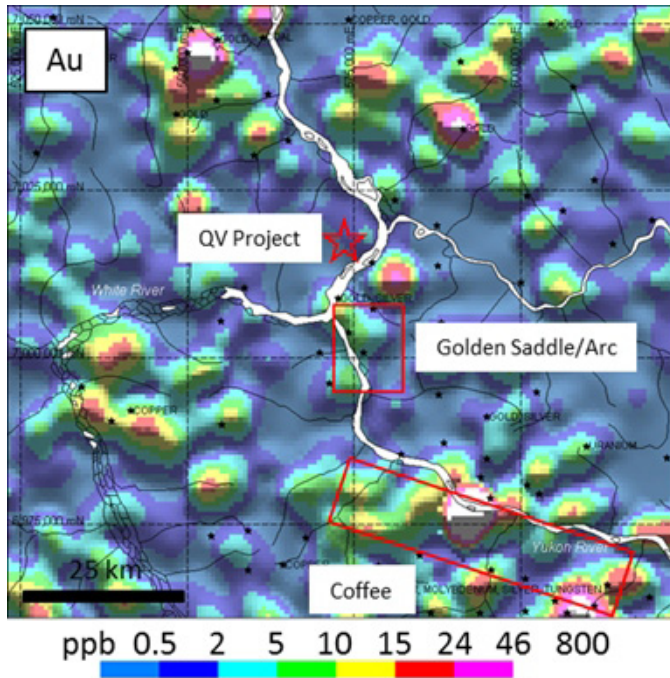


Figure 3. Percentile gridded images of Au, As, Sb and an additive levelled index for the three elements using the <0.177 mm fraction of stream sediment sample data of Héon (2003) from the White Gold District, Yukon Territory. The approximate locations of the main discovery areas are outlined by red polygons.

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do provide a positive response using raw data presented in the form of gridded percentile images, and the presence of the Golden Saddle deposit, along with associated mineralisation in the adjacent Arc deposit, is clearly evident using an additive index of Au plus As and Sb levelled for dominant catchment lithology (see Arne & Bluemel 2011 for a recent discussion of catchment analysis applied to regional stream sediment data). The presence of the Coffee deposit is also evident in the raw As and Sb data, as well as from a single Au analysis, but the extent of the anomaly associated with this mineralised system is best illustrated by the levelled additive index. The Comstock discovery is not evident at all in the data because the catchment this deposit lies in was not sampled during the Yukon RGS program. Therefore, while we would argue that clear evidence for Au mineralization in the White Gold District and Dawson Range lies within the historical RGS data (provided the streams draining the mineralised catchments were sampled), the interpretation of those data requires examination of the distribution of suitable pathfinder elements and less reliance on the Au data. Unfortunately, most explorers tend to focus on the element for which the data are least precise (i.e. Au).

The issues associated with sampling particulate Au in stream sediments are widely known and have been discussed exhaustively elsewhere. It is not our intention to review sampling theory other than to point out that there are only two practical ways to increase the precision of Au data in stream sediment samples containing particulate Au. The first and most common approach is to increase the sample size, either through the use of bulk leach-extractable gold (BLEG) methods or by concentrating heavy minerals by panning in the field or heavy liquid separation in the laboratory. These methods generally involve the collection of large samples of up to 10 kg of relatively coarse-grained material up to 1 or 2 mm in diameter. The BLEG samples are then treated with a cyanide solution in order to dissolve the particulate Au which is then concentrated onto a collector (an organic solvent) or precipitated using zinc sulphide. Alternatively, Au grains can be physically concentrated and the heavy mineral fraction either assayed or the actual Au grains sized and counted. Such an approach also effectively reduces the detection limit of the overall analysis.

The problem with both approaches involving a larger sample is that the benefit generated by a greater sample mass is offset by the use of a coarser grain size that allows incorporation of larger Au particles and thus exacerbates the nugget effect in analysis of the material, particularly if the cyanide extraction is too aggressive. Furthermore, given the size of the sample used for the traditional BLEG approach, the use of laboratory duplicates is seldom undertaken and generally only field duplicates are available to assess total variability in the data. Bulk methods also introduce extra logistical costs in the collection and transport of large samples from remote locations.

The second approach involves either the use of finer grained material, where the possibility of aeolian dilution can be discounted (e.g. Bugrov 1974), or the use of very weak cyanide digestions on smaller BLEG samples to ensure that only the smallest Au grains are dissolved (i.e. a “chemical sieve”). Traditionally, this approach has been incorporated into stream sediment programs either through sieving in the field or in the laboratory, typically using 80 or 100 mesh screens (<0.177 or <0.150 mm), or decanting sediment-laden stream water in the field with or without the use of a flocculant to settle clays out of suspension. An alternative to these approaches is now available at commercial laboratories that involves the use of a centrifuge to isolate a clay-sized fraction <2 µm in diameter from the sample. Use of this fraction allows a smaller aliquot size to be used for analysis but does require careful sampling in the field to ensure the collection of sufficient volume of fine grained material. The use of the clay-sized fraction has been previously reported for till samples (e.g. Shilts 1977 and many others at the Geological Survey of Canada since the 1970s) but its use in analysis of stream sediment samples is rare, as is its use in this particular medium for Au determination. Another advantage of using the clay-sized fraction is that a representative aliquot size of 0.5 g is small enough to allow routine use of analytical duplicates that can be used to assess preparation and analytical variances, and thus allow estimation of sampling variances from field duplicates.

Extraction of clay-sized material from soils and sediments is also often undertaken to isolate clay minerals that are excellent secondary traps for mobile pathfinder elements due to the high cation exchange capacities of some clay minerals (Rose et al. 1979). Elimination of signal dilution from barren silicates and the consistent matrix presented to the leaching procedure also produces better anomaly to background contrast and fewer analyses that are too close to the method lower detection limit to provide reproducible results. The reduction in nugget effect can often be as significant as the improvement in pathfinder anomaly to background contrast in the case of Au-focused projects.

In this article we present data from six sample sites in the White Gold district and Dawson Range to test the reproducibility of three approaches to the analysis of particulate Au in stream sediment samples. Catchments that included portions of the Golden Saddle, Arc, and Coffee deposits were sampled. The data are compared to arithmetic means calculated from three background samples. Although this is a small number of samples to define background, proprietary data collected elsewhere in the region but not presented here for reasons of confidentiality suggest the values are reasonable. In addition, the effects of concentrating various pathfinder elements (As, Sb, Mo) in the clay-sized fraction are also discussed.

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Methodology

Samples collected in the field consisted of ~5 kg of -20 mesh (<0.84 mm) material obtained from a number of trap locations within the creek over a stream length of about 10 m. The samples were initially collected in a 10 L plastic bucket and then decanted into large polypropylene bags purchased from Legend Inc. in the USA. These bags were specifically chosen because of their tight fabric and double stitching of the seams which limits the amount of clay-sized material lost from the bag when the water is squeezed out. They also allow drying of the sample in the field prior to transport. Separate field duplicate samples were collected at each site.

The samples were processed by three separate methods in most instances:

- Acid digestion of the <0.177 mm fraction
- Acid digestion of the <2 μm fraction
- BLEG of the <0.177 mm fraction

After drying, a -80 mesh fraction (<0.177 mm) was prepared at the laboratory and a 30 g aliquot digested using modified aqua regia consisting of a 1:1:1 mixture of $\text{H}_2\text{O}:\text{HNO}_3:\text{HCl}$, followed by ICP-MS analysis for 37 elements, including Au, at AcmeLabs in Vancouver. This method is similar to that employed for some of the historical Yukon RGS data, albeit with a larger aliquot weight, and so would be expected to yield more representative Au data than obtained historically. One kg of the -80 mesh material was shipped to the AcmeLabs facility in Santiago, Chile for BLEG analysis for Au only using gentle agitation for 12 hours. A reduction in the grain size used for the BLEG analysis would be expected to produce more precise results than a standard BLEG done on a coarser grain size fraction. In addition, 300 g of the -80 mesh material was suspended in water and centrifuged to isolate the <2 μm clay fraction and 0.5 g of this material was analyzed by ICP-MS for 31 elements at AcmeLabs in Vancouver, also following a modified aqua regia digestion.

Problems were encountered with the routine use of BLEG analysis on some samples from the region, presumably due to interferences caused by the presence of charcoal in stream sediments derived from catchments affected by recent forest fires. The organic solvent (DIBK) used to collect the Au in solution was adsorbed by some of the samples, although this is not considered to have affected the orientation data presented here. No BLEG determinations were made on the background samples for this reason, as they were collected in an area recently burnt by forest fires. The possibility of charcoal from bush fires in Western Australia preferentially attracting Au in solution (“preg-robbing”) has previously been assessed and found not to be an issue, although zinc sulphide was used as a collector in those trials (S. Harrison, pers. comm., 2013). In general, samples should be roasted prior to treatment with cyanide where charcoal from forest fires could potentially be an issue.

To extract the clay-sized fraction, 300 g of -80 mesh material was suspended in deionised water using ultrasonic agitation and the addition of an anti-flocculant. After a brief settling period the solution was decanted and centrifuged, first at low speed to remove coarse material, and then again at high speed to remove the clay-sized fraction from the water column for collection. It should be noted that for many samples, the resulting fraction consists dominantly of clay minerals, but the separation process is not phase-specific meaning that any clay-sized mineral grain will be captured. This can have important implications for the relative abundances of trace elements from sample to sample, but for Au determinations this is not of concern. In samples containing coarse Au, clay separation effectively removes the larger particles responsible for poor precision allowing more reliable determination of the ultra-fine Au content. Since anomalous sites should contain elevated Au across all particle sizes, targeting the ultra-fine fraction should yield full contrast with background data, while eliminating noise associated with the analysis of large Au particles in more traditional test methods.

Quality of the sample preparation and analytical data was monitored using both external (blind) and internal (laboratory) certified (Ore Research & Exploration OREAS 45p) and standard (Acme DS8) reference materials (CRM & SRM), the use of both field and pulp duplicate analyses, and analysis of both field (Au-only) and instrumental blanks. Packets of OREAS 45p were diluted by physically mixing it with sufficient certified blank pulp (CDN Resource Laboratories BL8) in a large plastic bag to make 1 kg standards for BLEG analysis. OREAS 45p was manufactured using oxide material only, and is therefore suitable for this purpose.

The stream sediment analyses were part of a geochemical program predominantly comprising soil samples described by Arne et al. (2014) and data quality can be evaluated within the context of the broader QA/QC program implemented during the overall sampling program. For example, the Au data from OREAS 45p submitted as external controls are illustrated in Figure 4 from the portion of the field program that overlapped with analysis of the stream sediment samples. The results generally lie within one standard deviation (SD – as calculated from the certification round-robin data) of the expected value. The number of analyses lying outside of two SD from the certified value is consistent with the expected spread in data for a normal distribution of the results. Overall, the coefficient of variation (CV) for the analysis of Au in OREAS 45p is $\pm 8.0\%$, similar to the CV for Au in this CRM of 8.2%, and providing a benchmark by which to evaluate the Au data from the orientation samples. Overall, the Au analyses provided by the laboratory are considered to be excellent.

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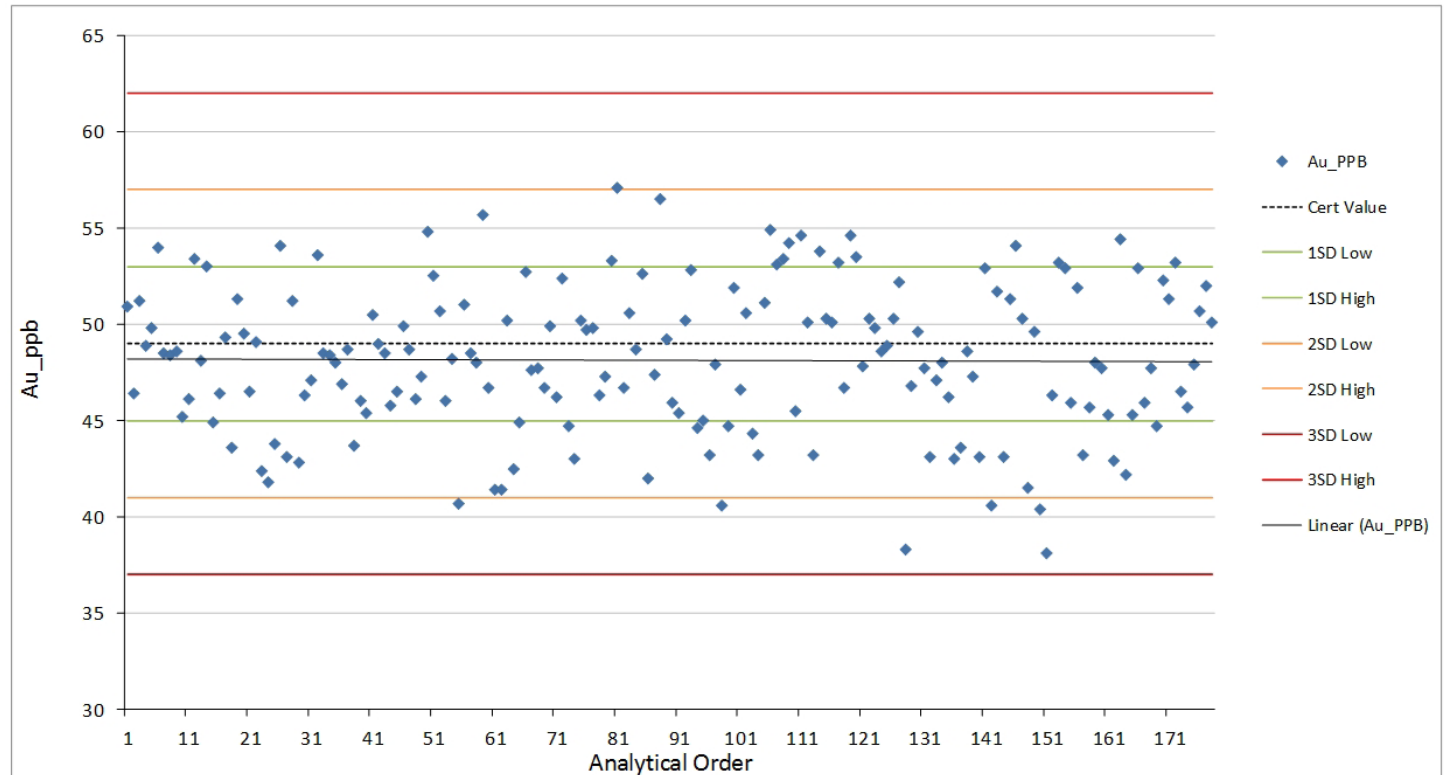


Figure 4. Gold analyses of Ore Research & Exploration CRM 45p by ICP-MS following a modified aqua regia digestion at Acme Labs from May until August, 2011. A linear regression fit to the data is also shown.

Results

Summaries of the Au results and data for selected pathfinder elements are presented in Table 1. Field duplicate pairs are presented in sequential order, with -80 mesh data, Au data from BLEG, and data from a clay-fraction separate. Only data for Au and a few important regional pathfinder elements are presented. Note also that the

presence of clay-sized material was not recognized in all samples at the time of collection as they were dominated by silt and sand-sized material. In spite of this, sufficient clay-sized material (a minimum of 0.5 g) was separated from all samples to allow digestion and analysis by ICP-MS.

Table 1. Summary of selected analytical results for stream sediment samples in this study

Sample	Clay%	Silt%	Sand%	Organics%	Color	Au_ppb*	BLEG_Au	Au_ppb**	Mo_ppm*	Mo_ppm**	As_ppm*	As_ppm**	Sb_ppm*	Sb_ppm**
5125	10	80	10	0	gray brown	2.5	4.5	10.8	0.51	2.56	4.8	34.5	0.31	0.7
5125Dup	10	80	10	0	gray brown	2.7	11.3	10.3	0.46	2.75	5.1	35.9	0.30	0.69
5133	5	60	30	5	gray brown	12.5	6.4	70.3	0.75	3.96	15.5	117.6	0.67	1.63
5133Dup	5	60	30	5	gray brown	6.7	6.6	70.3	0.79	3.71	16.1	112.1	0.75	1.47
5135	5	70	20	5	gray brown	7.2	20.3	69.1	0.62	4.43	47.8	530.9	1.63	4.53
5135Dup	5	70	20	5	gray brown	101.1	86.3	65.5	0.64	4.38	48.0	498.6	1.66	4.64
5127	0	40	60	0	brown	17.0	2.5	7.9	0.95	5.69	10.7	77.9	0.56	1.18
5127Dup	0	40	60	0	brown	1.9	28.9	7.3	0.92	6.01	9.8	77	0.56	1.14
5129	0	60	30	10	brown	77.6	9.3	47.8	0.62	2.61	16.6	84.1	0.98	1.72
5129Dup	0	60	30	10	brown	9.9	3.9	42.5	0.64	2.7	16.5	87.9	0.96	1.68
5129Dup	Laboratory pulp duplicate							42.5	2.67	85.9	1.63			
5131	5	50	45	0	gray brown	4.5	<0.1	14.8	0.84	3.63	13.5	65	0.68	1.01
5131Dup	5	50	45	0	gray brown	3.5	22.6	15.7	0.96	3.36	14.3	58.3	0.65	1.02
Bkgd	7	82	7	5		2.5	n/a	9.2	0.38	1.34	3.73	23.9	0.23	0.33

* < 177 µm grain size fraction; ** < 2 µm grain size fraction; n/a not applicable. Field duplicates are in order and pairs are shaded consistently. Background (Bkgd) values are estimated from an arithmetic average of three samples.

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What is immediately clear in the Au data for the -80 mesh 30 g aliquot and the BLEG analyses is that the results for the field duplicate samples are inconsistent (Fig. 5). The

silicates. The anomaly/background ratios are also slightly improved in the clay-sized separates.

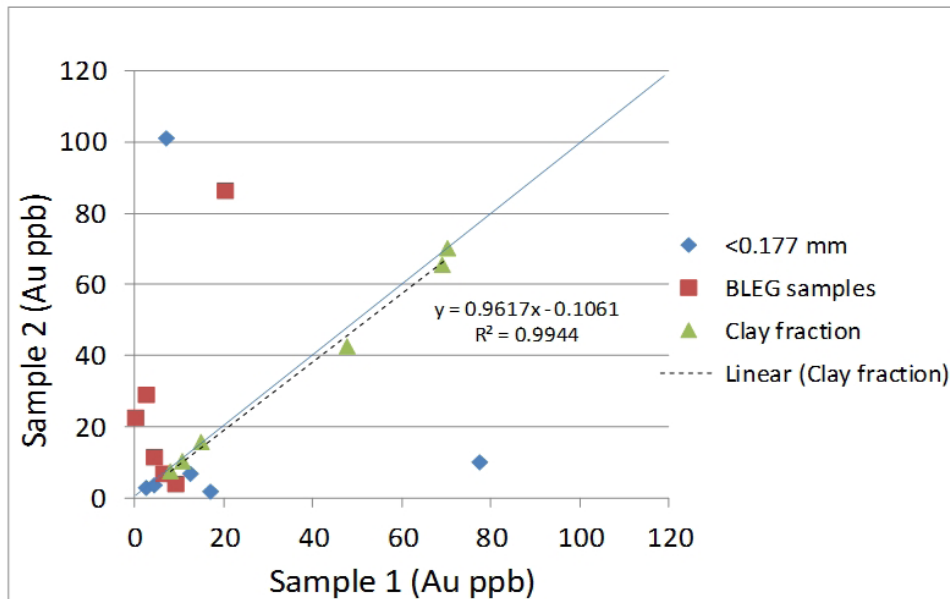


Figure 5. Comparison of Au data from field duplicate stream sediment samples analyzed by three different methods. A linear regression fit to the clay fraction is also shown.

differences are so significant that if the 15 ppb threshold from the RGS data set were applied to the data, several anomalous streams would potentially be overlooked depending on which sample was analyzed. There are also inconsistencies in which samples are higher from the two methods. In some cases the 30 g aqua regia analysis gives the higher result for one of the field duplicates, but the order is reversed for the BLEG results (Table 1). Clearly, both types of analyses suffer from poor precision.

By contrast, the field duplicates for the clay separates give Au results that show a relative difference of less than $\pm 5\%$, which is a reproducibility seldom found in field duplicate analyses for Au, and well within the overall precision of the Au data produced by the laboratory for this method over the relevant time period (Fig. 5). A single analytical repeat of the clay separates gave an identical Au value. Four of the six sites gave Au values that are significantly above background, which is estimated from data for three samples not considered to carry a mineralized signature. In a large orientation survey, these samples should also give a more realistic estimate of background levels for Au since erroneously high values produced by any nugget effect are removed from the population.

The base metals and potential Au pathfinder elements, Mo, As, and Sb also show good reproducibility in both the -80 mesh and clay fraction data, as do most other analyzed elements that are not discussed here. An additional advantage of clay separate data is that the base metals and potential pathfinder elements report higher concentrations due to adsorption onto clay minerals and significantly less dilution from barren and coarse grained non-reactive

Conclusions

Poor data precision for Au in historical, publicly available stream sediment data sets from the Yukon Territory has led to a loss of confidence in this medium for Au exploration in some instances and an underutilisation in exploration programs where the geochemical focus has been solely on Au. The traditional approach of taking large samples for bulk analytical treatment or heavy mineral concentration has issues related to reproducibility from field duplicates due to the generally coarse-grained Au collected in the field, particularly where aggressive cyanide digestions are employed. Bulk cyanide leach methods using an organic solvent for Au collection are also potentially subject to the interfering effects of charcoal in the samples from forest fires. In contrast, an alternative approach to obtaining representative Au data in samples described here involves the analysis of the clay-sized fraction to provide more reproducible data for Au than conventional aqua regia digestion and analysis of the <0.177 mm fraction, as well as providing data for other potential pathfinder elements. This approach appears to be successful even in samples that are not found to be particularly clay-rich in the field, as only 0.5 g of clay-sized material is sufficient for analysis. However, 1 g is preferable and allows for a laboratory duplicate analysis. Special care must be taken in the field to ensure the collection of sufficient volume of the finest-grained material available. The approach may not be applicable in areas where contamination/dilution by aeolian dust has occurred. The evaluation of reliable Au data for stream sediment samples, coupled with low-level multi-element analysis for potential pathfinder elements, is a cost-effective way to undertake regional exploration over large areas and should not be discarded simply because of issues with the reproducibility of historical Au analyses.

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