

## Parts Per Trillion Gold in Groundwater: Can We Believe It, What's Anomalous, and How Do We Use It?

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### ABSTRACT

*There is a pressing need for new exploration tools to target and vector towards mineralization in covered terrains. Groundwater provides a valuable and under-utilized geochemical sampling medium, and represents an important and cost-effective tool to expose covered terrains to systematic exploration. For Au exploration, researchers agree the best hydrogeochemistry pathfinder is dissolved Au itself, with additional potential from other pathfinders (albeit non-unique) such as, Ag, W and Mo. Despite Au's relatively low solubility, with rigorous field protocols and appropriate analytical methods, explorers can respond to dissolved Au directly with robust parts per trillion (ppt) level analyses.*

*Even with ppt-level analyses, a practical implication of Au's low solubility is that a deposit's dissolved Au signature is generally weaker than seen in other more mobile pathfinders, producing a smaller detectable footprint, which must be considered when designing exploration programs. Using purpose-drilled groundwater sampling bores, explorers can collect groundwater samples at the density required to respond to dissolved Au where existing bore-hole coverage is otherwise insufficient. In addition to its use at the regional scale, with even tighter sample density, hydrogeochemistry also shows promise at the project scale, allowing for 3D modelling of pathfinder dispersion.*

*For hydrogeochemistry to be widely adopted for Au exploration, explorers need confidence in ppt-level dissolved Au analyses, and the context to understand their significance. This paper aims to address these topics and provide a straightforward starting point for Au explorers interested in applying hydrogeochemistry by: (i) summarizing examples of regional sampling programs and more focused case studies to illustrate how covered Au deposits create measurable dissolved Au footprints distinguishable from background; and (ii) sharing examples of dissolved Au analyses being integrated into exploration at the regional and project scales.*

*As seen in the results, the distributions of dissolved Au in the regional- and project-scale programs show remarkably similar and easy to interpret high-contrast, low-frequency anomalies against relatively low backgrounds. These are desirable attributes of any geochemical pathfinder. When combined with the benefits of hydrogeochemistry versus other geochemical exploration tools (e.g., groundwater can create larger footprints requiring fewer samples to detect, and groundwater can recharge from depth to reflect deeper mineralization), dissolved Au is a powerful pathfinder ideally suited for Au exploration in covered terrains.*

*While this paper focuses on the use of dissolved Au, additional pathfinders can provide valuable information, including indications of lithological changes, hydrothermal alteration, and different styles of mineralization, as well as opportunities to use secondary pathfinders when sample density or local conditions may not result in detectable dissolved Au signatures.*

### INTRODUCTION

Gold explorers have seen a decline in exploration success during the last decade. From 2007 to 2016, while Au exploration expenditures hit all-time highs, Au explorers found fewer and lower quality deposits, creating only \$0.46 of value for every dollar spent (Schodde, 2017). As many surface and near-surface deposits have already been discovered, explorers are having to turn their focus to blind targets, and the challenges of exploring in covered terrains have no doubt been a large factor in the declining success rates. Improving exploration performance under cover is vital to all industry stakeholders. While exploring under cover can be more expensive and difficult, it is important to note that covered terrains remain largely underexplored. These greenfield areas present new search spaces with discovery

potential that is hard to overstate—for example, approximately three-quarters of Australia, currently the world's second largest gold producer, is covered by transported sediments. To confront these challenges and take advantage of the opportunity, explorers need cost-effective tools to identify new prospects under cover.

Groundwater provides a valuable and underutilized geochemical sampling medium for exploring in covered terrains. As groundwater flows through the subsurface, it retains a hydrogeochemistry signature that reflects the lithologies and minerals it encounters. Research has shown that when groundwater interacts with covered areas of mineralization it can produce measurable and recognizable hydrogeochemistry footprints (Leybourne and Cameron, 2007). Because

groundwater mixes and flows, deposits can create larger hydrogeochemistry footprints than seen in other sampling media, which can reduce the required sample density to explore a region, providing evidence of nearby mineralization in otherwise barren drill-holes. Additionally, where groundwater recharges from depth it can provide opportunities to detect mineralization beneath thicker cover. Beyond increasing the size and improving the detection of a deposit's geochemical footprint, groundwater movement can also define a gradient or vector pointing back to its source. With these characteristics, hydrogeochemistry allows explorers to evaluate covered terrains faster and cheaper than relying on traditional techniques alone, opening up covered terrains to systematic exploration.

As explorers become more familiar with hydrogeochemistry, its use is increasing around the world, most notably in Australia, led by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), with considerable collaborative support from academic, government, and industry sponsors. In the review of the use of hydrogeochemistry for Exploration '07, Leybourne and Cameron (2007) summarized the primary hydrogeochemical pathfinders and key related publications for several deposit types, including: porphyry copper, volcanogenic massive sulfide (VMS), uranium, and gold. The most significant change in the application of hydrogeochemistry for exploration since Exploration '07 has been the continued widespread availability and lower cost of analytical methods with lower detection limits, such as High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS), and the ability to review datasets from large sampling programs that have used these lower detection limit methods.

A recent example of how lower detection limits have increased the utility of hydrogeochemistry for exploration is the surface-water sampling program at the largely covered Pebble porphyry Cu-Au-Mo deposit in Alaska. Because the program relied on analyses of surface water samples, the researchers were faced with the need to measure low absolute concentrations of pathfinder elements. Using HR-ICP-MS, Kelley et al. (2010) and Eppinger et al. (2010) demonstrated good quality control down to low parts-per-trillion (ng/l, ppt) levels, and successfully defined hydrogeochemical signatures associated with the covered mineralization not previously detected using less sensitive analytical methods, which most notably included a 10 km<sup>2</sup> dissolved Ag halo centered on the deposit.

In terms of its application for Au exploration, Leybourne and Cameron (2007) and others (e.g., Gray et al., 2014) have concluded that the best hydrogeochemistry pathfinder for Au mineralization is dissolved Au itself (though this can be relatively enhanced with other pathfinders). As a consequence of Au's low solubility, explorers are obvious benefactors of the increased availability of analytical methods with lower detection limits. With these improved tools, the functional detection limit for directly measuring dissolved Au is down to concentrations of 2 ppt (Noble et al., 2011), and perhaps lower. As will be shown in the examples below, at these low ppt levels dissolved Au has become an important pathfinder for Au exploration.

A practical implication of Au's low solubility is that a deposit's dissolved Au signature is generally defined by lower

concentrations relative to other more mobile pathfinders, such as Sb and Ag. Through physical and chemical groundwater processes such as mixing and adsorption, these weaker dissolved Au concentrations often return to below-detectable levels over a shorter distance than other pathfinders, creating smaller dissolved Au footprints. The size of a deposit's measurable dissolved Au footprint needs to be considered when designing a hydrogeochemistry exploration program, though because most programs rely on collecting samples from existing bore-holes, samplers often have little control over sample location or density. To mitigate the limitations inherent in relying on existing bore-holes, considerable research has focused on developing multi-parameter indices that include additional more mobile pathfinders (e.g., Gray et al., 2014) to define targets where sampling density may be too wide to rely on encountering measurable dissolved Au alone.

The team of Nevada Exploration Inc. ("Nevada Exploration"), has been advancing the use of hydrogeochemistry for Au exploration in Nevada since the early 2000s. Like Australia, Nevada is a mature mining jurisdiction, characterized by well-explored exposed regions and underexplored covered areas, with more than half of the state covered by post-mineralization basin fill. Based on the results of its efforts, Nevada Exploration places significant value on the use of hydrogeochemistry for early-stage Au exploration, and has acquired and developed boring equipment to collect groundwater samples without being limited by the distribution of existing bore-holes. With this equipment, Nevada Exploration is using hydrogeochemistry as a basin-scale generative exploration tool to identify new prospects in Nevada's covered basins. Additionally, by increasing sampling density, through reducing bore-hole spacing and taking multiple down-hole samples, Nevada Exploration has begun to incorporate the use of hydrogeochemistry to guide exploration at the project scale, which represents a new scale of application than has otherwise been presented in the literature.

Whereas CSIRO, Nevada Exploration, and others are using hydrogeochemistry to explore in covered terrains around the world, many explorers have not yet become familiar with its application. For hydrogeochemistry to be widely adopted for Au exploration, explorers need confidence in field and laboratory methods to assign weight to ppt-level dissolved Au analyses, and the context to understand their significance. This paper aims to address these topics and provide a straightforward starting point for gold explorers interested in integrating hydrogeochemistry into their exploration workflow, with two objectives:

- (1) Building comfort around the use of ppt-level dissolved Au as a pathfinder by providing examples of how covered Au deposits create measurable dissolved Au footprints distinguishable from background.
- (2) Demonstrating the utility of integrating hydrogeochemistry into an exploration workflow, emphasizing the value of "drilling for water", by sharing examples of how Nevada Exploration is applying hydrogeochemistry at the basin scale to identify new prospects, and at the project scale to focus follow-up exploration efforts.

### MEASURING PPT-LEVEL DISSOLVED AU

Whereas anomalous concentrations of Au in most other geochemical sampling media are regularly measured in parts-per-billion (ug/l), dissolved Au in waters is generally measured in ppt (ng/L). Outside of hydrogeochemistry, ppt is not a frequently used unit of measure for most explorers, and for most other geochemical sampling media, ppt-level concentrations would fall well below the detection limits of the most commonly used analytical methods.

There are two strategies to achieve ppt-level detection of dissolved Au in groundwaters: 1) use lower-detection-limit analytical methods; or 2) pre-concentrate samples and apply conventional analytical methods. As will be shown in the examples below, explorers are using both strategies to achieve meaningful and repeatable dissolved Au analyses at the single-digit ppt level (e.g., Grimes et al., 1995; Noble and Gray, 2010).

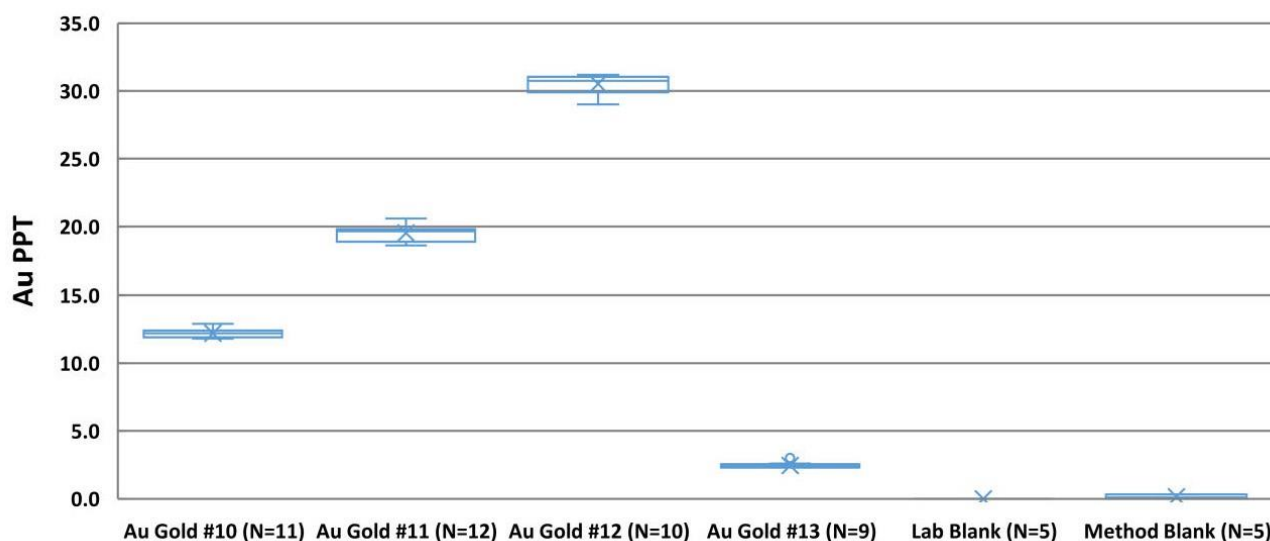
In groundwaters with low salinity (<1,000 ppm Total Dissolved Solids, TDS), samples can be analysed for dissolved Au directly with HR-ICP-MS or low-detection-limit ICP-MS with relative simplicity and accuracy. Other methods, such as atomic absorption spectroscopy (AAS), can also potentially be used for direct Au analysis; however, because explorers need multi-element chemistry to use hydrogeochemistry effectively, ICP-MS methods offer an advantage in providing suitable analyses for ~60 elements with a single method.

In groundwaters with higher salinities (>1,000 ppm TDS), samples must be diluted first to be safely run through an ICP-MS system, which increases the detection limits. In these settings, a pre-concentration step is required to achieve accurate ppt-level dissolved Au analysis. As described in Gray et al. (2014), the most widely used pre-concentration method is to collect a 1 L sample of groundwater and add 1 g of activated carbon enclosed in a nylon mesh along with 10 g of NaCl for ionic balance. To ensure maximum uptake of Au, Ag, Pt and Pd

onto the carbon sachet the sample needs to be agitated for a minimum of 4 days. The sachets are then removed from the sample, rinsed in deionised water, and air dried for 2 days. Once concentrated, the samples are prepared by ashing the sachets, followed by aqua-regia digestion, and analyzed by ICP-MS. Instrumental neutron activation analysis (INAA) of the sachets can also provide robust dissolved Au analyses repeatedly to 2 ng total Au, which equates to 2 ppt in the original solution, though ICP-MS remains the preferred method, because it provides lower detection limits for other important pathfinders: Ag, Pt and Pd.

Compared to Australia, Nevada’s groundwaters have relatively low salinity, and whereas CSIRO (Gray et al., 2016) has adopted a consistent protocol of pre-concentrating samples, Nevada Exploration analyzes groundwater samples for dissolved Au directly. To monitor QA/QC at such ultra-trace, ppt-level concentrations, Nevada Exploration maintains a series of internal dissolved Au standards that are included with sample submittals, along with regular field duplicate, method blank and lab blank samples. As highlighted by the results for the QA/QC standard and blank samples from a 2017 submittal summarized in Figure 1, directly analyzing dissolved Au using HR-ICP-MS provides consistent low variability at these low concentrations, providing the necessary resolution to reliably and reproducibly detect, measure, compare and respond to ppt-level dissolved Au.

While Nevada Exploration has found that HR-ICP-MS offers reliable and consistent low detection limits of <1 ppt for dissolved Au, instrument availability and sample turn around using the method have at times been challenging. To address these challenges, Nevada Exploration has begun to evaluate the suitability of more widely available low-detection-limit ICP-MS methods for direct analysis of dissolved Au at ppt-levels, and early results suggest these methods show promise.



**Figure 1:** Boxplots of dissolved Au HR-ICP-MS analyses for four low-level Au standards and two blanks, each analyzed between 5 and 12 times (N = number of analyses), from a 2017 Nevada Exploration sample batch. Boxes contain 2nd and 3rd quartiles, and whiskers contain 1<sup>st</sup> and 4<sup>th</sup> quartiles.

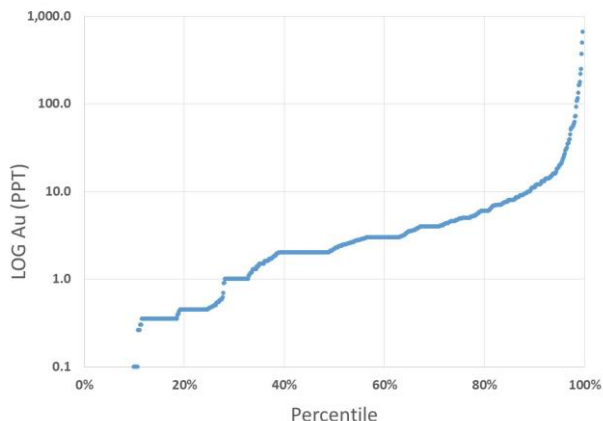
## ESTABLISHING REGIONAL CONTEXT FOR DISSOLVED AU

As with any geochemical pathfinder, the use of dissolved Au for exploration requires a regionally-specific understanding of background concentrations, concentrations surrounding known gold deposits and appropriate sampling density. To examine the importance of regional-scale hydrogeochemistry programs for establishing and characterizing these benchmarks, as well as to provide the context for reviewing the case studies that follow, this section summarizes the results of two large groundwater sampling programs, both from Australia, that have generated two of the largest published datasets reporting analyses for dissolved Au.

### Central Victoria Dataset (CSIRO)

Over a 20-year period, CSIRO collected 1,133 groundwater samples from existing bore-holes in southeastern Australia, primarily focused on central Victoria. The resulting dataset, presented as an appendix to Arne and Giblin (2009), includes 921 dissolved Au analyses. The statistical distribution of dissolved Au (Figure 2) across the entire study area shows that the majority of values cluster near and below the median of 2.2 ppt (73% < 2x median), followed by multiple-order-of-magnitude increases at the upper percentiles. In bore-holes near known Au deposits within the Victorian study area, Arne and Giblin (2009) found dissolved Au showed good correlation with mineralization, including examples in the vicinity of the Stallwall, Ararat, Bendigo, and Tandarra deposits, with enriched dissolved Au in bore-holes near several of the deposits exceeding 50 ppt. Compared to the regional distribution, the dissolved Au near the known areas of mineralization represent clear anomalies (50ppt > 97th percentile and 20x median).

Based on the results of the Victorian sampling program, Arne and Giblin (2009) offered the following conclusions: (a) hydrogeochemistry provides a suitable reconnaissance tool for Au mineralization in covered terrains; (b) in this study area dissolved Au and As provided the most reliable indicators of



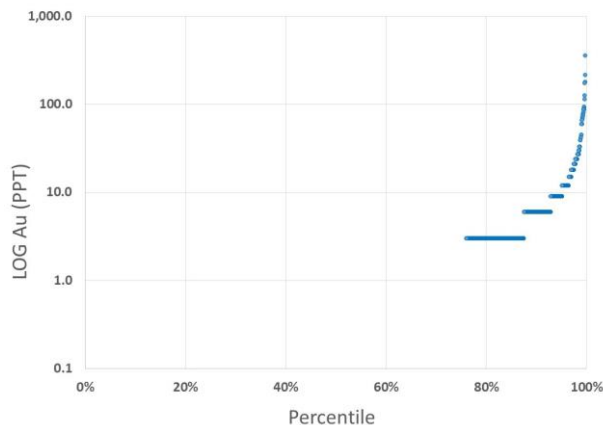
**Figure 3:** Cumulative frequency distribution of dissolved Au from 921 groundwater samples from central Victoria (Data Source: Arne and Giblin, 2009). Y-axis is truncated at 1,000 PPT, and excludes three samples above 1,000 PPT, representing 0.3% of the samples. The highest sample was 5,466 PPT.

bedrock Au mineralization; and (c) the exploration thresholds for dissolved Au in the subregions within the study area range from 5 to 50 ppt. This orientation data provides practical and valuable context to evaluate future sampling in the region.

### Northern Yilgarn Craton Dataset (CSIRO)

Following this research in Victoria, CSIRO focused its hydrogeochemical efforts on the northern Yilgarn Craton, where it has collected more than 2,500 samples from existing wells and bores, at a sampling spacing of approximately 4 to 8 km, using the protocols described in Noble et al. (2011). The resulting dataset is presented as an appendix to Gray et al. (2014), with further analysis and commentary provided in Gray et al. (2009) and Gray et al. (2016), which together present multiple geochemical parameters, as well as geological and lithological indices, to demonstrate the utility of hydrogeochemistry for mapping major geological units and evaluating mineral prospectivity under cover for several commodities of interest.

With respect to Au exploration, based on targeted sampling around known Au deposits, Gray et al. (2009) concluded that while the best pathfinder for Au deposits in the study area was dissolved Au, using dissolved Au alone with the 4 to 8 km sample spacing did not identify all the known deposits. To improve the detection of Au mineralization with this sample spacing, the researchers combined multiple pathfinders to create two mineral indices, which significantly improved the detection rate. Out of 18 active Au mines in the study area, only three were not recognized, two of which were characterized by limited sample coverage and one of which contained lower grade mineralization (Gray et al., 2009). Gray et al. (2014) added that by using dissolved Au together with the “AuMin” index (Au + Ag + As), groundwater sampling reliably identified the larger 4 to 8 km<sup>2</sup> scale mineralized camps. The results of this large sampling program support the previous research in central Victoria and elsewhere (e.g., Giblin and Mazzucchelli, 1997) in highlighting the utility of hydrogeochemistry as a tool to enhance prospectivity, improve exploration success, and allow



**Figure 2:** Cumulative frequency distribution of dissolved Au from 2,830 groundwater samples from the northern Yilgarn Craton (Data Source: Gray et al., 2014). Y-axis is truncated at 1,000 PPT, and excludes five samples above 1,000 PPT representing 0.2% of the samples. The highest sample was 25,128 PPT.

explorers to move into covered terrains to search for economically viable targets (Gray et al., 2009, Gray et al., 2014, and Gray et al., 2016).

The CSIRO northern Yilgarn Craton dataset provides valuable information about the distribution of dissolved Au and other pathfinders for continued exploration in the region. As shown in Figure 3, most of the dissolved Au samples show low to no detectable Au (87.5% showed  $\leq 3$  ppt), followed by multiple-order-of-magnitude increases in the upper percentiles. The distribution of dissolved Au in the northern Yilgarn Craton closely matches that in central Victoria (Figure 2), characterized by similar orders of magnitude at the major percentile breaks (Table 1). With low background concentrations and high contrast between background and anomalous values, both datasets provide clear information to orient future hydrogeochemistry sampling efforts in each region.

### ORIENTATION CASE STUDIES

**Table 1:** Major percentile breaks for dissolved Au for the CSIRO central Victoria and northern Yilgarn Craton datasets.

Percentile Breaks	Central Victoria Dataset	Northern Yilgarn Craton
50%	2.2	LTD
80%	6.0	3.0
90%	11.2	6.0
95%	20.1	9.0
99%	175.1	45.0
MAX	5,466.0	25,128.0
N	921	2,830

Building from the context provided by the two regional-scale programs above, this section summarizes a selection of project-scale hydrogeochemical orientation studies. These studies provide examples of the size of the measurable dissolved Au footprints surrounding known areas of mineralization, and importantly, the variability in the absolute dissolved Au values that define these footprints.

#### Case Study 1: St. Ives Area, Western Australia

Source: Carey et al. (2003)

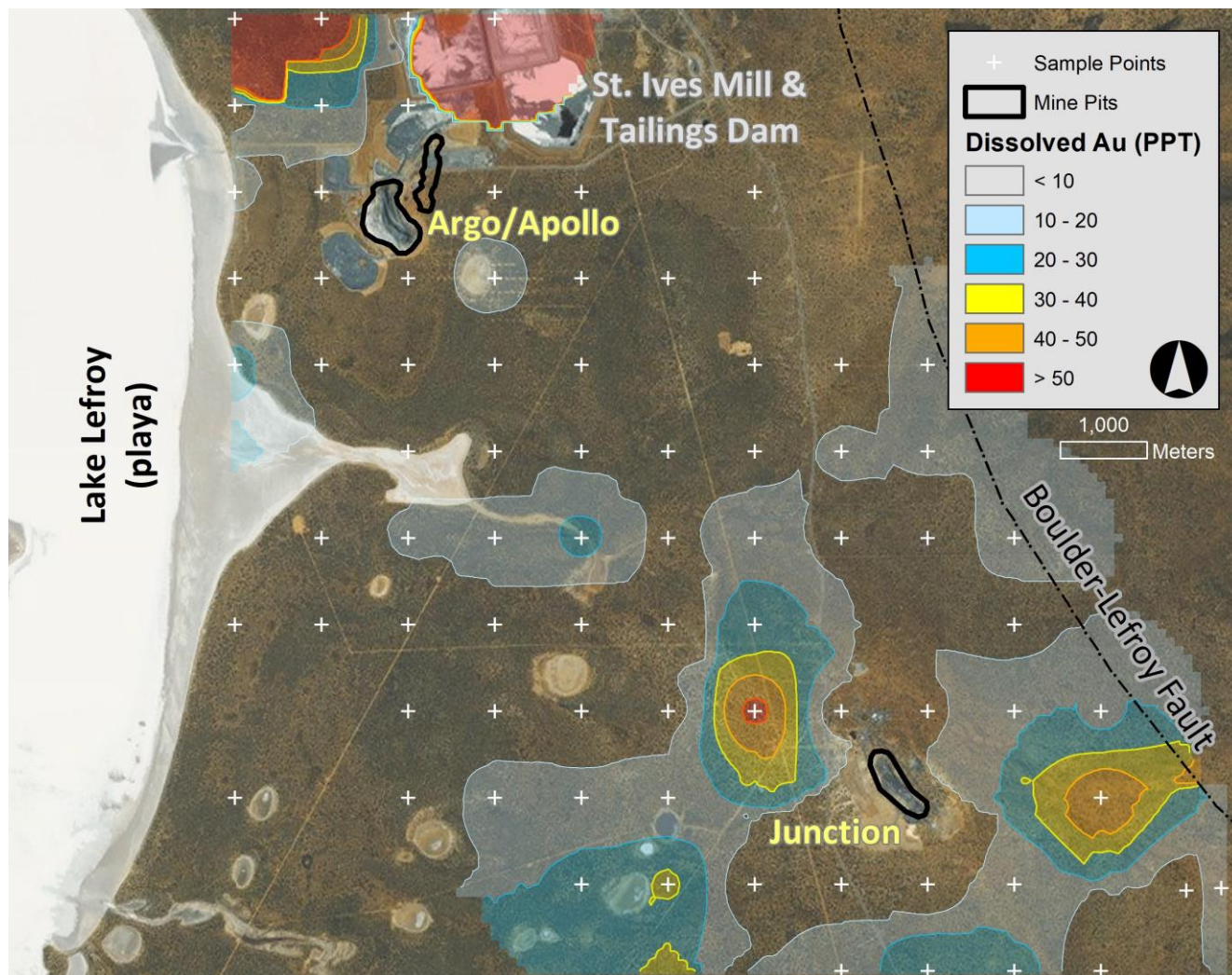
One of the most thorough hydrogeochemistry orientation programs for Au exploration was completed in a study area referred to as St. Ives that includes the Junction (2.3 Moz. Au) and Argo/Apollo (0.8 Moz. Au) Au deposits, located in the Eastern Goldfields of the Yilgarn Craton. Whereas the rest of the case studies mentioned below, as well as elsewhere in the literature, have relied predominantly on collecting groundwater samples from existing bore-holes, the St. Ives study is unique and significant in that it collected groundwater samples from 80 purpose-drilled bore-holes on a regularized 1 km by 1 km grid. At the same time as collecting groundwater samples, the

researchers also collected water level measurements at each bore-hole to establish the regional gradient and direction of groundwater flow, which they determined to be east to west.

Based on the dense and regularized sample distribution, the results of the St. Ives study clearly defined the size and shape of the dissolved Au footprint associated with the Junction deposit (Figure 4). Using a 10 ppt contour, which is now known to be a regionally-significant threshold based on the more recent 2,830-sample CSIRO northern Yilgarn Craton dataset (10 ppt  $> 95^{\text{th}}$  percentile – see Table 1), the data define a horseshoe-shaped dissolved Au footprint extending up to 5 km west (downstream) of the Junction deposit. Dissolved Au increases closer to the deposit, reaching a maximum of 52 ppt in the sample bore immediately downstream of the deposit. At 52 ppt, the dissolved Au in this bore-hole is not only locally significant, but also regionally-significant based on the CSIRO northern Yilgarn Craton dataset, falling within the 99th percentile of all samples collected in the region. In this case, from an exploration perspective, it is reasonable to expect that a hydrogeochemistry sampling program with a similar sampling density would have identified the dissolved Au footprint downstream of the Junction deposit as a significant anomaly to investigate further.

Other than coincident with and downstream of the St. Ives Mill and tailings dam complex, the relatively deep (generally  $>40$  m) groundwater samples from the 1 km x 1 km sampling near the Argo/Apollo deposit did not identify enriched concentrations of dissolved Au or other pathfinders. Carey et al. (2003) attributed the lack of elevated dissolved Au in these samples to the local influence of groundwater recharge from the nearby Lake Lefroy, speculating that the groundwater in the horizons sampled had not been sourced from the areas of mineralization. Nevertheless, Carey et al. (2003) also noted that earlier, shallower ( $<15$  m) groundwater sampling across the Argo/Apollo area had, defined a 4 km x 2 km, 10 ppt, dissolved Au footprint above and downstream of the mineralization, including several samples exceeding 40 ppt with a high value of 2,560 ppt. These findings certainly constitute a regionally-significant anomaly associated with the deposit, though because Carey et al. (2003) did not believe that these shallow groundwaters had directly encountered the Argo/Apollo mineralization, they were left to speculate as to the mechanism of transport.

Overall, the results of the St. Ives program provide a comprehensive example of the value of hydrogeochemistry for Au exploration in covered terrains. In summary, the program concluded: (i) that where groundwater had interacted with mineralized zones, the resulting dissolved Au footprints were larger than seen in the regolith cover; (ii) that the 1 km x 1 km sample spacing was sufficient to detect these dissolved Au footprints; and (iii) that coarser sampling would likely still have been effective. These are significant observations because drilling holes for hydrogeochemical sampling allows for a much broader drill pattern than required for conventional regolith and bedrock sampling, thus providing a considerably less expensive sampling tool for evaluating covered areas. The results also highlight the important fact that for groundwater to be an effective sampling medium, the water needs to have an opportunity to interact with mineralization.



**Figure 4:** Dissolved Au distribution of the St. Ives study area based on IDW of Carey et al. (2003) sampling program.

In addition to providing insight into appropriate sample spacing, Carey et al. (2003) also identified anomalous dissolved Au upstream from the Junction deposit, along the southeastern portion of the study area, following the Boulder–Lefroy Fault, an important structural control for Au mineralization in the region. With both anomalous dissolved Au and a favourable geological setting, this area presents a compelling target for follow-up investigation, and also highlights how hydrogeochemistry can be integrated into a generative exploration program.

### Case Study 2: Carosue Dam, Western Australia

Source: Gray et al. (2007)

The Carosue Dam Au deposit (0.5 Moz.) is also located in the Eastern Goldfields of the Yilgarn Craton, and is covered by more than 80 m of regolith, including up to 20 m of transported material. As part of a study to characterize the Au dispersion halo in the regolith at Carosue Dam, Gray et al. (2007) analyzed

dissolved Au in samples collected from several drill-holes near the deposit. The samples were spaced irregularly in a small study area measuring approximately 1,000 m long by 600 m wide. Out of 21 samples collected, 18 were deemed uncontaminated and suitable for analysis.

With the presence of both acidic and oxidising conditions in the groundwater at Carosue Dam, Gray et al. (2007) expected relatively higher dissolved Au than at other Yilgarn sites, such as St. Ives, and this was certainly the case. Eight samples contained dissolved Au greater than or equal to 640 ppt, including two samples greater than 2,000 ppt. At this local <1 km<sup>2</sup> scale, Gray et al. (2007) concluded that dissolved Au provided the best correlation with the mineralization. This correlation was variable though, likely due to the small area of investigation with a lack of background samples further from the deposit. At the regional scale, however, based on the distribution seen in the more recent CSIRO northern Yilgarn Craton dataset, the dissolved Au concentrations proximal to the mineralization correspond with some of the highest

concentrations anywhere in the region (640 ppt > 99.7<sup>th</sup> percentile). From the standpoint of conducting regional-scale exploration to identify geochemical footprints associated with covered deposits, the dissolved Au surrounding the Carosue Dam deposit defines a clear anomaly and an obvious target for follow-up exploration.

In addition to demonstrating the utility of dissolved Au as a pathfinder for regional exploration, the results from the Carosue Dam also point to the influence that local conditions can have on a deposit's hydrogeochemistry footprint. In this case, acidic and oxidizing groundwater conditions likely contributed to dissolved Au enrichment measurable on the order of 1,000s of ppt.

### Case Study 3: Harmony Gold Deposit, Western Australia

Source: Noble et al. (2010)

Noble et al. (2010) presented several hydrogeochemistry case studies for mineral exploration in Western Australia, including an Au-related study from the covered Harmony deposit (250 Koz. Au; Robertson and Gray, 2003). The Harmony study was based on groundwater samples collected from approximately 40 drill-holes covering 6 km<sup>2</sup>.

The results at Harmony defined a hydrogeochemical footprint characterized by enriched dissolved Au, as well as Mo, W and Rb (Noble et al., 2010). Compared to local background concentrations of 2–3 ppt, the deposit's hydrogeochemical footprint included 10 samples with dissolved Au greater than or equal to 5 ppt, with 3 samples greater than or equal to 7 ppt clustered close to the deposit.

While the absolute dissolved Au concentrations near the Harmony deposit are considerably lower than those seen in other case studies, such as the Carosue Dam, it is important to recognize that these concentrations are still regionally significant based on the CSIRO northern Yilgarn Craton dataset—5 and 7 ppt correspond to approximately the 88<sup>th</sup> and 93<sup>rd</sup> percentiles, respectively. Locally, dissolved Au quickly returned to lower concentrations away from the mineralization marking the deposit as a hydrogeochemical anomaly. With this regional context and local contrast, it is reasonable to expect that a hydrogeochemical exploration program would have identified the covered Harmony deposit as a target for follow-up exploration. Noble et al. (2010) concluded the same, and that dissolved Au is a good pathfinder for Au mineralization in the region. Based on further review of the results, Noble et al. (2011) later added that dissolved As in the study area closely correlated with areas of major hydrothermal alteration. This correlation points to the complementary utility of other pathfinder elements in regional Au exploration.

### Getchell District, Nevada

Source: Grimes et al. (1995)

The significant and ongoing government-led support for hydrogeochemical exploration in Australia is unique, and accordingly most recent case studies and published regional-

scale sampling programs are Australian; though in the mid-1990s, the U.S. Geological Survey conducted several important groundwater sampling programs surrounding known Au deposits in Nevada. As part of these efforts, Grimes et al. (1995) completed a hydrogeochemical study along the Getchell district in the Kelly Creek Basin to determine if hydrogeochemistry could reveal the presence of otherwise concealed Au deposits. The researchers collected between 2–5 down-hole samples from active and recent drill-holes near what is now known as the Twin Creeks mine (Chimney Creek + Rabbit Creek), the Summer Camp deposit, and an unnamed low-grade deposit 1.5 km northwest of the Preble mine. The samples were analyzed for major pathfinders, including dissolved Au, which was analyzed by graphite-furnace atomic-absorption spectrometry after pre-concentration using anion-exchange resins.

At Twin Creeks, the dataset included 14 groundwater samples collected from 4 drill-holes, 3 of which were located close to the mine, and 1 of which was located 800 m downstream from the mine. Of the 3 drill-holes closest to the mineralization, the dissolved Au values ranged from 1–23 ppt, with each drill-hole having at least one sample greater than 10 ppt, together defining a measurable dissolved Au footprint at Twin Creeks. The 2 samples from the fourth drill-hole, located 800 m downstream from the mineralization contained dissolved Au values of 11 ppt and 26 ppt, confirming that this enriched Au footprint extended beyond the limits of the mineralization.

At Summer Camp, the dataset included 9 groundwater samples collected from 2 drill-holes, 1 located on top of the deposit, penetrating the mineralized bedrock, and 1 located 380 m downstream from the deposit. Dissolved Au in the samples collected from the drill-hole penetrating mineralization ranged widely, from 370–4,700 ppt—the highest concentration came from a sample collected from an upper, oxidized bedrock unit, and the lower concentrations came from the samples collected from a deeper, unoxidized bedrock unit, which demonstrates how local conditions influence the enrichment of dissolved Au. As seen at Twin Creeks, the down-gradient samples at Summer Camp also contained higher dissolved Au levels, ranging from 10 - 140 ppt, confirming the size of the measurable dissolved Au footprint was larger than the deposit. These downstream samples also provide an indication of the rate of dispersion for dissolved Au at this site, with concentrations falling more than an order of magnitude over 380 metres.

At the unnamed deposit near Preble, the dataset included 7 groundwater samples collected from 2 drill-holes, 1 located 450 m upstream from the deposit, and 1 penetrating the low-grade, unoxidized deposit. The groundwater samples collected from the upstream drill-hole showed low to no detectable dissolved Au ( $\leq 1$  ppt), as well as relatively low concentrations of other regionally-important pathfinders: As, Sb and W. These samples likely provide an approximation of the local background. In comparison, the samples collected from the drill-hole that penetrated the mineralized bedrock showed 10–50x enrichment of As, Sb and W, although no significant dissolved Au (Max = 1 ppt). Grimes et al. (1995) speculated that the low dissolved Au levels were likely due to the reducing groundwater conditions surrounding the unoxidized, low-grade mineralization, which

provides another example of how site-specific variables can influence a deposit's hydrogeochemical signature.

Based on results of the Getchell sampling program, Grimes et al. (1995) summarized: (i) that the background dissolved Au concentration in the study area was likely less than 1 ppt; (ii) that the dissolved Au near the deposits ranged from 1–140 ppt; and (iii) that the dissolved Au in the drill-holes that penetrated mineralized bedrock reached as high as 4,700 ppt. Grimes et al. (1995) suggested that the results indicate measurable dissolved Au is being mobilized from concealed Au deposits and actively dispersed into the surrounding groundwater, and concluded that hydrogeochemistry can provide valuable information to explore for covered Au deposits in Nevada and elsewhere.

While the sample coverage is too focused to be considered representative of the larger region, these findings are significant for Nevada's Au explorers. It is interesting and useful to note that the dissolved Au found upstream of, downstream of, and in contact with the known mineralization in the Getchell study closely match the distributions seen in the regional datasets (Table 1) and case studies from Australia, with high contrast anomalies, defined by similar orders of magnitude, against similarly low background values.

Because the Getchell dataset only includes samples from 2–4 drill-holes at each deposit, it does not provide much information to characterize the spatial extent of their measurable dissolved Au footprints. As a complement to Grimes et al. (1995), for some regionally-specific insight into the lateral extent of hydrogeochemical footprints surrounding covered Au deposits in Nevada, readers are encouraged to review Muntean and Taufen (2011), which included hydrogeochemistry as part of a series of orientation surveys over covered Au deposits in the Cortez area to evaluate their utility. While the published data did not include analysis for dissolved Au, based on samples from monitoring wells surrounding the Pipeline deposit, Muntean and Taufen (2011) defined an approximately 5 km<sup>2</sup> hydrogeochemical footprint associated with the deposit characterized by enriched secondary pathfinders: As, Tl, K and F. The spatial extent of the Pipeline footprint provides some indication of appropriate sample spacing for groundwater sampling in this part of Nevada. In terms of evaluating its suitability for Au exploration in Nevada, Muntean and Taufen (2011) echoed Grimes et al. (1995) in concluding that hydrogeochemistry is an effective and underutilized sampling medium for reconnaissance-scale exploration.

## CONCLUSIONS FROM REGIONAL AND PROJECT-SCALE PROGRAMS

The sampling programs summarized above illustrate that in many settings dissolved Au deposit footprints are measurable, recognizable, readily distinguishable from background and larger than the deposits themselves. The resulting datasets provide useful examples of the distributions of dissolved Au at regional and project scales, the variability in both the enrichment and extent of dissolved Au footprints, and ultimately, the significance and utility of ppt-level analysis for Au exploration.

Even with ppt-level detection limits, one of the biggest challenges in using hydrogeochemistry for Au exploration remains the relatively low solubility of Au. As seen in the deposit case studies, the enrichment and dispersion of Au is influenced by many site-specific factors, such as the degree and nature of groundwater interaction with mineralization and the presence of oxidizing or reducing conditions, all of which together determine the detectable extent of a deposit's dissolved Au footprint, and accordingly, the appropriate sample spacing for exploration. Gray et al. (2009) found that analyzing dissolved Au at the 4 to 8 km scale did not identify all deposits in the northern Yilgarn study area, whereas Carey et al. (2003) concluded that spacing coarser than the 1 km x 1 km sample grid used in the St. Ives study area would likely have still been effective, which together provide two important points for this discussion. In practice, however, sample spacing is often limited by the distribution of existing bore-holes, and given the lower solubility of Au compared to other target commodities, the lack of available sampling bores presents a considerable challenge.

On the whole, despite significant differences in geological settings, hydrogeological conditions, sampling protocols, and analytical methods, that the dissolved Au results of the studies above are so remarkably similar in terms of their: (a) relatively low background concentrations, (b) high-contrast anomalies, and (c) major percentile breaks, speaks to the robustness of the dissolved Au method, and define it as a reliable pathfinder for gold exploration around the world.

With so many site-specific and sampling-related sources of variability, it is important to note that the objective of using dissolved Au as a pathfinder for regional-scale exploration is not to compare or rank exploration targets based on absolute dissolved Au concentrations. Rather, the objective of using dissolved Au at this scale is to provide a cost-effective tool to evaluate large areas and identify discrete exploration targets. The results from the programs above illustrate that the entire range of dissolved Au associated with the known areas of Au mineralization, whether 7 ppt or 700 ppt, represent at least multiple-times, and in most cases orders-of-magnitude, enrichment relative to the local background concentrations, as well as corresponding to the upper few percentiles of the regional distributions. With such high-contrast and low-frequency anomalies, dissolved Au represents a model geochemical pathfinder to reduce large covered areas and focus exploration efforts on targets defined by significantly enriched Au.

While the focus of this paper is on the practical application of dissolved Au as a primary pathfinder for Au exploration, Leybourne and Cameron (2007) and others have highlighted the additional value of other hydrogeochemical pathfinders in the search for Au. In addition to Noble et al. (2011), who identified a relationship between As and areas of major hydrothermal alteration, Giblin and Mazzucchelli (1997) observed that enriched As helped distinguish between bedrock-hosted Au deposits versus palaeochannel deposits. As noted above, Gray et al. (2009) used a multi-element index based on Au, Ag and As to improve the detection of Au mineralization where sample spacing was too coarse to rely on dissolved Au alone. Using the same dataset, with implications beyond just Au exploration,



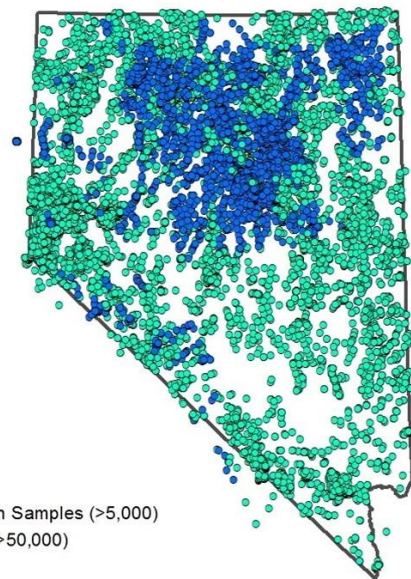
Gray et al. (2014, 2016) demonstrated the broader value of multi-parameter hydrogeochemistry in defining lithological changes, hydrothermal alteration and other types of mineralization. These studies illustrate that the value of hydrogeochemistry for Au exploration is enhanced with the support of additional pathfinders.

### INCORPORATING DISSOLVED AU INTO AN EXPLORATION WORKFLOW

Faced with the now familiar challenges of exploring in a mature district, where over half of the bedrock is hidden by post-mineralization cover, Nevada Exploration is integrating hydrogeochemistry into its exploration workflow to explore for covered Au deposits in Nevada. The foundation of Nevada Exploration's hydrogeochemical efforts is a groundwater sampling program centred on north-central Nevada, primarily within the basins near the Battle Mountain-Eureka and Carlin Trends. Having collected more than 5,500 samples (Figure 5), including focused sampling near more than 30 known Au deposits, Nevada Exploration uses the resulting dataset to provide the context to define regionally-specific background concentrations, anomalies and exploration thresholds. To augment the results of its own sampling, Nevada Exploration has also aggregated the results from approximately 50,000 historic samples that include analyses for many important secondary pathfinders, which provided additional regional context and indications of prospectivity in areas that have not yet been sampled and analyzed for dissolved Au.

To overcome the compounding challenges of Au's relatively low solubility and the limited distribution of existing sampling bores, Nevada Exploration uses boring equipment to "drill for water", with purpose-drilled groundwater sampling bores, at a suitable density to respond to dissolved Au directly, rather than relying on more mobile secondary pathfinders. The ability to control sample density has been a key factor in Nevada Exploration extending its regional generative exploration program into areas with few to no existing bore-holes, and most recently, in broadening the scope of its application of hydrogeochemistry to include focusing exploration efforts at the project scale.

Based on a significant sample size, the distribution of dissolved Au across Nevada closely mimics that of the CSIRO Central Victoria and northern Yilgarn Craton datasets, with widespread low background concentrations, and relatively few anomalies characterized by significant enrichment (80<sup>th</sup> percentile = 3x median, and 98<sup>th</sup> percentile > 100x median). In terms of dissolved Au in samples collected in areas surrounding known Au mineralization, the concentrations seen upstream of (background), near to, and right at mineralization in the Nevada Exploration samples also closely match those seen in the Getchell district sampling program, which suggests that exploration thresholds based on the benchmarks summarized by Grimes et al. (1995) are appropriate starting points for sampling elsewhere in north-central Nevada. With this context, the following two examples illustrate how Nevada Exploration is using hydrogeochemistry, and dissolved Au specifically, at the regional and project scales.



**Figure 5:** Nevada Exploration groundwater samples and historic groundwater analyses.

### Hydrogeochemistry at the Regional Scale – Grass Valley, Nevada

Grass Valley is located 90 km southwest of Carlin in north-central Nevada, immediately south of Barrick Gold Corp.'s Cortez complex along the Battle Mountain-Eureka Trend, well-known for its large Carlin-type Au deposits. Its location and proximity to significant known mineralization make the Grass Valley Basin an important prospective search space, and with 10s to 100s of metres of post-mineralization cover, a logical setting to incorporate the use of hydrogeochemistry.

Nevada Exploration has completed a groundwater sampling program across Grass Valley, collecting samples in the Basin dominantly from purpose-drilled groundwater sampling bores, as well as from range-front springs along the basin margin to confirm the local background. Based on the results of 366 Basin samples, the distribution of dissolved Au in Grass Valley parallels that of Nevada Exploration's larger dataset, as well as that of Grimes et al. (1995), with a handful of high-contrast anomalies against a lower background. By focusing on multi-sample anomalies anchored by at least one > 50 ppt sample (50 ppt > 98<sup>th</sup> percentile of Grass Valley samples), the sampling program identified two exploration targets in Grass Valley characterized by regionally-significant enriched Au, successfully satisfying the objective of this stage of Nevada Exploration's exploration in the Basin (Figure 6). Today, Nevada Exploration is advancing both targets, which are now referred to as its Grass Valley and South Grass Valley projects.

At a cost of approximately US\$500,000, collecting 366 groundwater samples from mostly purpose-drilled groundwater sample bores represents an expensive program on a cost-per-sample basis. On the more important cost-per-area basis, however, Nevada Exploration believes evaluating an

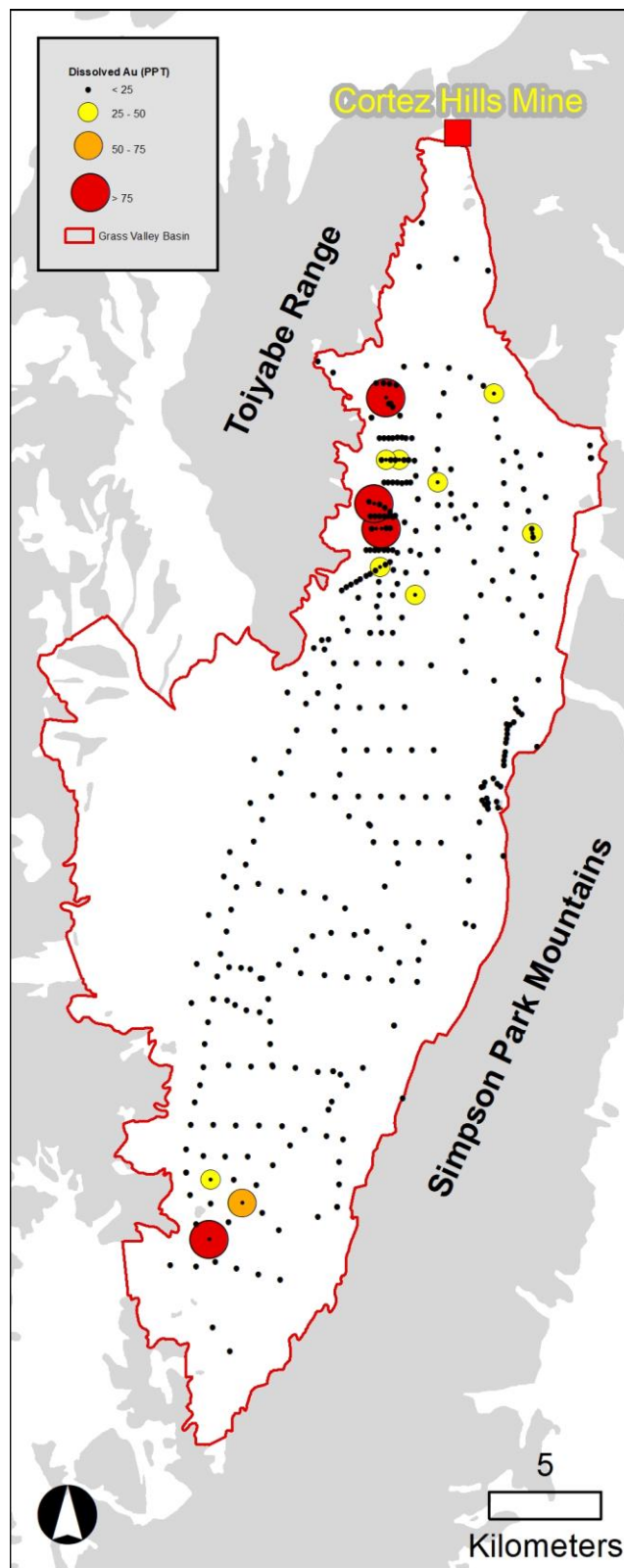
approximately 500 km<sup>2</sup> portion of Grass Valley—an underexplored, covered search space located within a world-class Au-producing district, and reducing the area down to two discrete follow-up targets at a cost of US\$500,000 represents significant value. Encouraged by the results of its sampling programs in Grass Valley and other basins, Nevada Exploration continues to use purpose-drilled bore-holes to conduct basin-scale hydrogeochemical exploration programs to identify new Au targets in Nevada’s covered basins.

### Hydrogeochemistry at the Project Scale – Kelly Creek Basin, Nevada

The Kelly Creek Basin is located north of Battle Mountain, Nevada, along the Battle Mountain-Eureka Trend. Significant Au mineralization is known to exist at the periphery of the Basin at Twin Creeks, Getchell and Turquoise Ridge to the north, and at Lone Tree and Marigold to the south. The interior of the Basin is covered by syn- to post-mineralization volcanic units and post-mineralization alluvium, with combined depths of 10s to 100s of metres. Located between major camps along an important regional trend of Au mineralization, and with more than 1,000 km<sup>2</sup> of covered bedrock, Kelly Creek provides another logical search space to incorporate hydrogeochemistry as an exploration tool.

Nevada Exploration’s Kelly Creek program began with basin-scale groundwater sampling from existing sample bores, and based on encouraging results, continued with denser sampling using purpose-drilled sample bores. The program defined an exploration target characterized by significantly enriched dissolved Au over more than 10 km<sup>2</sup> near the centre of the Basin, similar in size and dissolved Au enrichment to the Grass Valley targets described above. To improve the geological context for this covered target, Nevada Exploration and its partners have completed approximately 30 orientation drill-holes, and several geophysical surveys, including gravity, seismic, airborne magnetic and CSMAT (controlled-source audio-frequency magnetotellurics). This work has confirmed the presence of coincident Au anomalies in regolith and bedrock, shallow hydrothermally-altered bedrock and major high-angle structural zones, which together provide additional support for the geologic significance of the project.

While the combined datasets have helped reduce Nevada Exploration’s Kelly Creek Project down to several smaller focus areas, each approximately 1 km<sup>2</sup>, these focus areas remain too large to transition to conventional regolith and bedrock drill sampling. With improved boring equipment, better suited to collecting multiple groundwater samples down hole, Nevada Exploration has begun to use significantly tighter sample spacing to develop a detailed hydrogeochemical model at the project scale, with the objectives of further constraining the focus areas, and vectoring closer to the source of the dissolved Au. Compared to regional-scale hydrogeochemical programs, where site-specific and sampling-related sources of variability make it difficult to assign relative weights to dissolved Au concentrations, project-scale programs face fewer sources of



**Figure 6:** Dissolved Au concentrations in Grass Valley from Nevada Exploration groundwater sampling program.

variability. With control over sample density, project-scale hydrogeochemistry allows for meaningful interpretation of relative changes in dissolved Au to significantly reduce search spaces.

Nevada Exploration’s current detailed hydrogeochemistry program at Kelly Creek consists of sampling from purpose-drilled bore-holes, spaced generally from 200–400 m apart, at approximately 10 m down-hole intervals, to depths of up to 140 m. Nevada Exploration has now completed more than 50 multi-sample bore-holes, collecting approximately 490 groundwater samples over 7 km<sup>2</sup>.

The most important additional information provided by the increased sampling density is the vertical dimension needed to characterize the hydrogeochemistry between sampling horizons. At the bore-hole scale, the results illustrate significant down-hole variability in pathfinder concentrations, likely reflecting relative differences in hydraulic conductivity between different strata in the alluvium, typical of hydrologic environments (i.e., clay vs. sand). At the project scale, however, the variability resolves into constrained targets, considerably smaller than identified by the shallower sampling.

Compared to programs where a single sample is collected from each bore-hole, effectively producing a two-dimensional dataset (e.g., the St. Ives study), collecting multiple down-hole samples allows for modelling the dispersion of dissolved Au and other pathfinders in three dimensions. Figure 7 shows an example of the distribution of dissolved Au from a cluster of four bore-holes designed to follow up on a target characterized by >50 ppt dissolved Au identified by earlier, wider-spaced, basin-scale, 2D sampling (one sample per bore-hole). In this cluster, the detailed 3D hydrogeochemistry defined an upper zone of dissolved Au enrichment across all four holes (130–168 ppt), perched above a more focused zone of dissolved Au enrichment (410–482 ppt) intersected by one of the bore-holes (KCBS046) located at the bedrock contact. Coincident with this focused zone of enriched dissolved Au, the geochemistry samples (alluvium and bedrock) collected from the same bore-hole

included an 11 m interval that spanned the bedrock contact averaging 0.095 ppm Au, which included two 3 m intervals averaging 0.149 ppm Au and 0.120 ppm Au, respectively. These Au concentrations at the bedrock-alluvium contact represent the most consistent volume of mineralized material seen at the project to date, and present a compelling target now suitable for the focused application of conventional regolith and bedrock drilling.

Nevada Exploration’s Kelly Creek exploration program is ongoing, though the results to date already emphasize the suitability of different scales of hydrogeochemistry sampling at different stages of exploration. While the first stage of wide-spaced, regional-scale, 2D groundwater sampling at Kelly Creek provided a suitable scale of information to reduce the search space from 100s of km<sup>2</sup> to a handful of small focus areas, these areas were still too large to transition to conventional drilling. By increasing the sample density to provide the resolution to use hydrogeochemistry in 3D at the project scale, Nevada Exploration has significantly constrained the targets at Kelly Creek and identified new, previously undiscovered mineralized targets of a size now suitable to transition to conventional regolith and bedrock drilling. By providing this otherwise missing scale of information to direct the application of conventional drilling tools in large, otherwise blind search spaces, Nevada Exploration considers the Kelly Creek program a success, and expects to utilize this proven workflow in similar programs at its other projects in Grass Valley and elsewhere.

### CONCLUSIONS

There is a pressing need for innovative exploration tools to target and vector towards mineralization in covered terrains. As summarized by Leybourne and Cameron (2007), and highlighted in the presented case studies, covered deposits create distinct hydrogeochemical footprints providing an important and under-utilized exploration sampling medium. Researchers agree the best hydrogeochemical pathfinder for Au mineralization is dissolved Au, and despite its relatively low solubility, with appropriate field protocols and analytical methods, explorers can

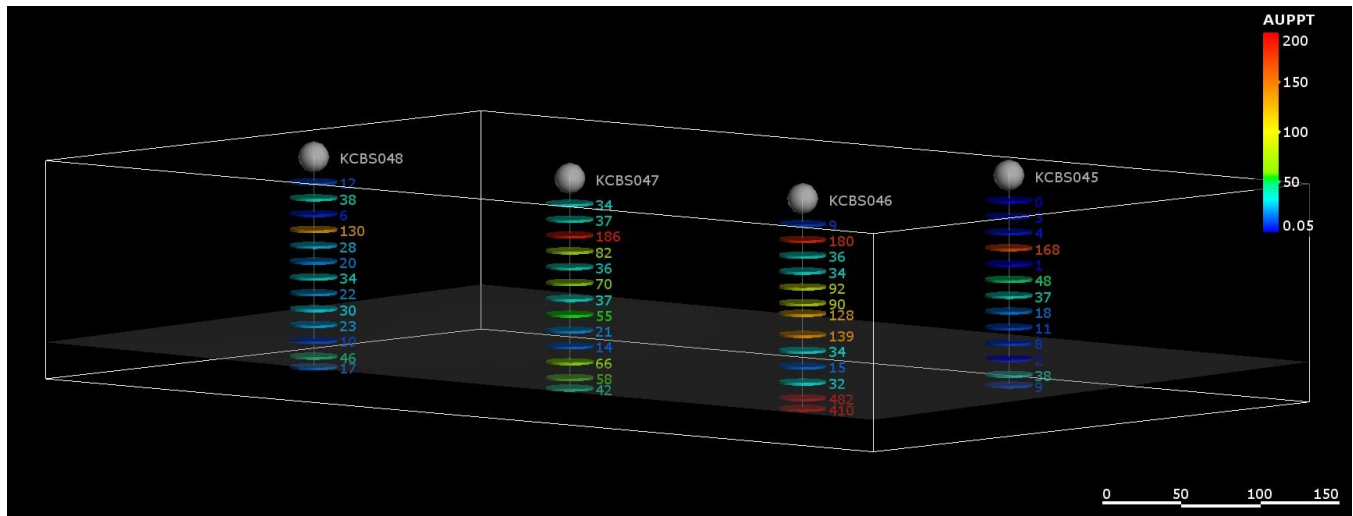


Figure 7: Dissolved Au concentrations in sampling bore-holes at the Kelly Creek project. Bore-hole spacing is 200 metres.

achieve the ppt-level analysis required to detect and respond to dissolved Au anomalies directly.

The dissolved Au distributions from large sampling programs in Australia and Nevada show remarkably similar and easy to interpret high-contrast, low-frequency anomalies against relatively low background values. These are desirable attributes of any geochemical pathfinder, and when combined with the benefits of hydrogeochemistry versus other geochemical exploration tools (e.g., produces larger footprints requiring fewer samples to detect, and groundwater can recharge from depth to reflect deeper mineralization) make dissolved Au a powerful pathfinder ideally suited for Au exploration in covered terrains.

In terms of its application, to effectively incorporate dissolved Au analyses into an exploration workflow, explorers need large orientation datasets to establish meaningful regionally-specific background values and exploration threshold—good examples of which are the 2,803-sample CSIRO Northern Yilgarn and >5,500-sample Nevada Exploration datasets. Even with comprehensive regional context, it is important, however, not to place undue weight on absolute dissolved Au concentrations to compare or rank targets, because dissolved Au is influenced by many local and sampling-related sources of variability (such as pH and salinity). Rather, the significance of dissolved Au as a pathfinder is that it allows for relatively wide sample spacing, compared to other geochemical sample media, with a high degree of selectivity, to provide a cost-effective tool to evaluate large covered areas.

One of the biggest challenges in conducting groundwater sampling programs is the availability of sampling bore-holes. Using purpose-drilled groundwater sampling bores, explorers can complete sampling programs at the density required to respond directly to dissolved Au where existing bore-hole coverage is otherwise insufficient. While the cost-per-sample from purpose-drilled bores is high, the value of the information on a cost-per-area basis offers the potential to open up new covered search spaces for exploration.

To date, the adoption of hydrogeochemistry for exploration has been focused on regional-scale exploration. With increased sample density allowing for 3D modelling of the dispersion of dissolved Au and other pathfinders, project-scale hydrogeochemistry offers an important new scale of information to constrain targets and direct more focused application of high-cost conventional regolith and bedrock drilling.

Lastly, while this paper focuses on the use of dissolved Au, it is important to note that other pathfinders can provide valuable and complementary information for gold explorers, including indications of lithological changes, hydrothermal alteration and different styles of mineralization, as well as the opportunity to use more mobile secondary pathfinders when the sample spacing or local conditions may not result in detectable dissolved Au signatures.

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