Hydrogeochemistry of porphyry-related solutes in ground and surface waters; an example from the Casino Cu–Au–Mo deposit, Yukon, Canada

J. A. Kidder1*, M. B. McClanaghan1, M. I. Leybourne2,3, M. W. McCurdy1, P. Pelchat1, D. Layton-Matthews2 and A. Voinot2,3

1 Geological Survey of Canada, 601 Booth Street, Ottawa, ON, Canada K1A 0E8
2 Queen’s Facility for Isotope Research, Department of Geological Sciences and Geological Engineering, Queen’s University, 36 Union Street, Kingston, Ontario, Canada K7L 3N6
3 Arthur B. McDonald Canadian Astroparticle Physics Research Institute, Department of Physics, Engineering Physics & Astronomy, Queen’s University, Kingston, Ontario, Canada K7L 3N6

Abstract: The Casino Cu–Au–Mo deposit is one of the largest and highest-grade porphyries of its kind in Canada, residing in an unglaciated region of west-central Yukon. A batch of 22 stream water samples and eight groundwater samples were collected proximal to the deposit for the purpose of identifying the most diagnostic trace element and isotopic pathfinders associated with the hydrothermal mineralization, as well as establishing natural hydrogeochemical baselines for the area. Water chemistry around this deposit was investigated because: (i) the deposit has not yet been disturbed by mining; (ii) the deposit was known to have metal-rich waters in local streams; and (iii) the deposit has atypically preserved ore zones. Surface and ground waters around the Casino deposit are anomalous with respect to Cd (up to 5.4 µg l−1), Co (up to 64 µg l−1), Cu (up to 1657 µg l−1), Mo (up to 25 µg l−1), As (up to 17 µg l−1), Re (up to 0.7 µg l−1) and Zn (up to 354 µg l−1) concentrations. Sulfur and Sr isotopes are consistent with proximal interactions with the Casino rocks and mineralization; a sulfide-rich bedrock sample from the deposit has δ34S=−1.2‰ and proximal groundwaters are only slightly heavier (0.3 to 3.1‰). These geochemical and isotopic results indicate interaction and dispersion of porphyry-related solutes in ground and surface waters and point to the suitability of hydrogeochemistry as a medium for mineral exploration for porphyry-style mineralization in the Yukon, and elsewhere in Canada.

Keywords: hydrogeochemistry; stable isotopes; groundwater; stream water; mineral exploration; porphyry

Supplementary material: Dissolved concentration data for major and trace elements for the ground and stream water samples from Casino are available at https://doi.org/10.6084/m9.figshare.c.5778911

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With much of Canada covered by glacial sediments, surficial geochemical tools including till geochemistry and indicator minerals are commonly used to discover buried mineralization at or near the bedrock interface (McClanaghan 2005; Thorleifson 2017; Salama et al. 2021). Much less attention has been paid to the use of ground and surface water geochemistry as a mineral exploration vector, particularly where potential mineralization is at significantly greater depth and thus unaffected by glacial transport, or in parts of Canada not obscured by the last glaciation. The use of groundwater as a sample medium in Canadian mineral exploration has a long history (Boyle et al. 1971; Cameron 1978; Leybourne et al. 2003; Phipps et al. 2004; McClanaghan et al. 2015); however, it is only in the last two decades that analytical technologies with sufficiently low detection limits have become commercially widespread (Leybourne 2007; Leybourne and Cameron 2010; Buskard et al. 2020). More recently, emphasis has been placed on the use of isotopic techniques to assist in the interpretation of aqueous geochemical data or to provide direct vectors to mineralization (Kirste et al. 2003; Kirste et al. 2017; Leybourne and Cousins 2005; Mathur et al. 2005, 2012, 2013; de Caritat et al. 2009; Leybourne et al. 2009; Skierszkan et al. 2019; Kidder et al. 2021). To build on previous work within this region, the objectives of this study are threefold: (i) to demonstrate the usefulness of hydrogeochemistry in the exploration of porphyry copper deposits; (ii) to identify the most diagnostic suite of pathfinder elements and isotopic fractionation patterns; and (iii) to establish natural hydrogeochemical baselines for the study area.

The Casino deposit in the west-central Yukon (Fig. 1a and b) is one of Canada’s largest and highest-grade porphyry Cu–Au–Mo deposits (Roth et al. 2020). It provides an ideal site for testing modern stream water and groundwater geochemical methods because the deposit has only been minimally disturbed by exploration (not yet mined) and is known to have metal-rich waters and sediments in creeks draining the deposit (Archer and Main 1971).

The earliest exploration in the Casino area took place in 1911 for placer gold in the lower reaches of Canadian Creek (Bostock 1959) (Fig. 1a). Further upstream, a gold–tungsten placer at the junction of Canadian Creek and Patton Gulch on the NW flank of the deposit was first worked to mine the tungsten in 1916. When the upper placer was worked again in the 1940s, the following minerals were recovered from the black sand: ferberite, gold, magnetite, hematite, scheelite, molybdenum, zircon, cassiterite, tourmaline and titanite (Bostock 1959; Archer and Main 1971). Over the years, placer gold mining also occurred on Rude Creek (Fig. 1a), SE of the Casino.
Other early exploration in the Casino area focused on the silver–lead–zinc veins at the Bomber occurrence on the south periphery of what is now known as the Casino deposit (Fig. 1b).

Prior to the initial diamond drilling that resulted in discovery of the Casino deposit, surface indications of the presence of the deposit included: the prominent (730 m long) limonite gossan along a small creek on SE side of the deposit that empties into upper Casino Creek; the presence of the local gold–tungsten placer; intense hydrothermal alteration and presence of limonite, jarosite and weak malachite staining in leached rocks at the surface; the peripheral silver–zinc–lead veins; and anomalous Cu concentrations in −80 mesh stream silt samples in Casino Creek as compared to values for the Dawson Range compiled over several years by Archer and Main (1971). Anomalous contents of Cu and Mo in −80 mesh soil samples collected in 1966 were used to guide the exploration drilling in 1969 that led to the discovery of Cu–Au mineralization (Archer and Main 1971). Current total measured and indicated resources of the deposit are 2.173 billion tonnes grading 0.16% Cu, 0.18 g/t Au, 0.17% Mo, and 1.4 g/t Ag (Roth et al. 2021).

Archer and Main (1971) reported that the Casino deposit had an obvious geochemical signature in stream sediments (Cu, Mo, Au and Ag) and waters overlying the deposit at the time of its discovery. Subsequent reconnaissance-scale stream water and sediment sampling in NTS map sheets 115J and 115K by the Geological Survey of Canada (GSC) (pH, E. Ll. in waters; 19 elements in <0.177 mm stream sediment), showed that a multi-element geochemical anomaly (Ag, Cu, Mo, Pb, Sb, W) is obvious in the local creeks draining the Casino deposit. A stream sediment and water study was carried out around the deposit in 2017 as part of a larger GSC study of the indicator mineral and surficial geochemical signatures of this very large deposit (Beckett-Brown et al. 2019; McClenaghan et al. 2020).

Regionally, many studies have been undertaken to assess the impact of ground and surface water interaction with a range of mineral deposits spanning a variety of commodity types, including: (i) volcanogenic massive sulfide (Hunt 1999; Nordstrom 2015), (ii) gold and silver deposits (Gleeson and Boyle 1976; Mueller et al. 2004, 2007; Verplanck et al. 2007) and (iii) porphyry deposits (Eppinger et al. 2012, 2013; Skierszkan et al. 2020; Kelley and
the porphyry is rhyodacite, with phenocrysts of dacite composition
porphyry and Dawson Range Batholith. The overall composition of
discontinuous dykes (up to 10 s of m wide) that cut both the
breccia at its outer contacts (Casselman and Brown 2016). Elsewhere, the porphyry consists of
its contacts (Casselman and Brown 2016). The porphyry is locally
the small porphyry into these older rocks caused brecciation along
Dawson Range Batholith and Paleozoic Yukon Crystalline
(72
deposit and is centred on the Patton Porphyry, a Late Cretaceous
from the western margin of Laurentia (Nelson
Mortensen and Friend 2020), separating the Yukon
assemblages (Fig. 1a)( Colpron
The terrane consists of rocks formed in a Mid- to Late Paleozoic
tectonic terrane that extends over 2000 km from Alaska, through
Yukon and south into British Columbia (Allan
et al. 2013). Higher-order streams occur in broader valleys and are
filled with more distally derived colluvium, loess and rounded
gravel (e.g. Dip Creek, Colorado Creek) (Bond and Lipovsky 2012).
Other mineral occurrences near the Casino deposit (Fig. 1a and b)
include the Mount Cockfield (20 km SE) and Zappa (Canadian Creek)
Cu–Mo–Au porphyry occurrences, as well as polymetallic vein
occurrences Marquerite (10 km NE), as well as Nordex and
Idaho (12 km SE, Rude Creek). Two gold occurrences have been
reported 13 to 16 km ENE of the deposit (Buck and Mascot).

Methods

Groundwater and stream water sampling

Groundwaters
Nine groundwater samples (Table 1) were collected in September
2017 from established monitoring wells in eight locations (Fig. 1b)
and a matrix of quartz lattice composition. Primary copper, gold
and molybdenum mineralization was deposited from hydrothermal
fluids in the contact breccias and fractured wall rocks and consists of
pyrite, chalcopyrite, molybdenite and minor huebnerite (Casselman
and Brown 2016). Supergene mineralization is concentrated in the
phyllic zone and surrounded by weakly developed argillic and
propylitic alteration zones. Grades decrease away from the contact
zone towards the center of the stock and outward into the wall rocks.

Groundwaters
Nine groundwater samples (Table 1) were collected in September
2017 from established monitoring wells in eight locations (Fig. 1b)
Table 1 Location and physical parameters of stream and groundwaters, including pH, Electronic Conductivity (EC), Eh, dissolved oxygen (DO), dissolved organic carbon (DOC), and total dissolved solids (TDS). Sample types characterized by 'SW' for stream water and 'GW' for groundwater

| Sample Type | Location | UTM easting | UTM northing | pH  | EC (µS cm⁻¹) | Eh (mV) | DO (mg l⁻¹) | DOC (mg l⁻¹) | TDS (mg l⁻¹) |
|-------------|----------|-------------|--------------|-----|--------------|--------|-------------|--------------|--------------|
| SW Battle Creek | 631343 | 6954446 | 7.41 | 119 | 410 | 92.3 | 3.0 | 120 |
| SW Selwyn River | 639801 | 6946601 | 7.41 | 106 | 411 | 92.7 | 3.1 | 98 |
| SW Hayes Creek | 640714 | 6956762 | 7.82 | 162 | 427 | 88.9 | 7.8 | 173 |
| SW Hayes Creek | 640714 | 6956762 | 7.23 | 238 | 88.8 | 3.8 | 138 |
| SW Colombo Creek | 617063 | 6976152 | 7.61 | 118 | 417 | 88.8 | 3.8 | 138 |
| SW Casino Creek | 609922 | 6947632 | 7.7 | 194 | 392 | 82.2 | 4.1 | 227 |
| SW Casino Creek | 611144 | 6951000 | 7.86 | 213 | 401 | 84.3 | 4.2 | 251 |
| SW unnamed tributary of Dip Ck | 597923 | 6945670 | 7.87 | 199 | 347 | 81.7 | 9.9 | 252 |
| SW Casino Creek | 612518 | 6953864 | 7.81 | 225 | 383 | 6.1 | 3.2 | 248 |
| SW unnamed tributary of Coffee Creek | 600541 | 6958104 | 7.38 | 124 | 393 | 81.1 | 5.2 | 148 |
| SW Meloy Creek | 611972 | 6953572 | 7.75 | 162 | 350 | 83.1 | 6.1 | 250 |
| SW Casino Creek | 613398 | 6956248 | 7.71 | 208 | 338 | 83.6 | 2.7 | 221 |
| SW Excelsior Creek | 603857 | 6968696 | 7.84 | 302 | 412 | 77.1 | 8.5 | 371 |
| SW Sunshine Creek | 626132 | 6964413 | 7.86 | 311 | 321 | 81.6 | 8.4 | 392 |
| SW Isaac Creek | 626826 | 6963830 | 7.62 | 124 | 363 | 80.7 | 6.0 | 155 |
| SW Mascot Creek | 630818 | 6962786 | 7.79 | 158 | 423 | 80.9 | 3.4 | 124 |
| SW Canadian Creek | 610240 | 6963647 | 7.13 | 120 | 457 | 80.9 | 3.4 | 124 |
| SW Tributary to Britannia Ck | 617609 | 6965203 | 8.1 | 419 | 444 | 83.1 | 6.8 | 557 |
| SW unnamed creek east of Excelsior Ck | 605254 | 6974187 | 8.32 | 548 | 444 | 83.6 | 8.5 | 654 |
| SW Canadian Creek | 617754 | 6972333 | 7.63 | 314 | 427 | 81.3 | 5.9 | 339 |
| SW Canadian Creek | 617754 | 6972333 | 7.63 | 314 | 427 | 81.3 | 5.9 | 339 |
| SW Canadian Creek | 616283 | 6968644 | 7.74 | 289 | 436 | 81.6 | 6.3 | 303 |
| SW Canadian Creek | 615961 | 6966522 | 7.65 | 249 | 435 | 79.7 | 5.1 | 256 |
| SW Canadian Creek | 615961 | 6966522 | 7.65 | 249 | 435 | 79.7 | 5.1 | 256 |
| SW Canadian Creek | 618699 | 6965014 | 7.75 | 290 | 380 | 78.3 | 8.0 | 345 |
| L1992155-1 GW East side of deposit | 611593 | 6958186 | 6.55 | 875 | 210 | 0.52 | 1.0 | 1309 |
| L1992155-3 GW Middle of deposit | 611533 | 6958503 | 5.41 | 125 | 392 | 0.15 | 1.1 | 135 |
| L1992155-4 GW East side of deposit | 611504 | 6958186 | 6.68 | 859 | 203 | 0.19 | 1.0 | 1314 |
| L1992155-5 GW Upper Canadian Creek | 609888 | 6959341 | 5.58 | 54 | 405 | 0.18 | 1.0 | 74 |
| L1992155-6 GW West of adit | 601022 | 6955865 | 7.6 | 126 | 304 | 6.69 | 1.1 | 197 |
| L1992155-7 GW Near mouth of adit | 611446 | 6956176 | 7.15 | 187 | 153 | 0.15 | 1.0 | 309 |
| L1992155-8 GW Near mouth of adit | 611433 | 6956171 | 8.16 | 188 | 159 | 3.53 | 1.4 | 309 |
| L1992155-9 GW East side of deposit | 611684 | 6958225 | 6.36 | 514 | 212 | 1.2 | 673 |
| L1992155-10 GW East side of deposit | 611684 | 6958225 | 6.36 | 514 | 212 | 1.2 | 670 |

by Western Copper and Gold Corporation (2020). Sample water was recovered using a low flow (0.2 to 0.5 l min⁻¹) submersible pump positioned 1 m above screen casing height in the well (Knight-Piesold Ltd 2015). Field parameters for well waters were measured using a calibrated multi-parameter probe attached to a flow-through cell (Knight-Piesold Ltd 2015). Sample water was filtered in the field through 0.45 μm disposable filters and preserved with laboratory-supplied ultrapure nitric acid immediately after filtration. To establish quality assurance/quality control (QA/QC) a single blank (sample L1992155-2) was included in the sample suite consisting of deionized water and added to the sample bottle using the same field techniques as the other samples, including field filtration and field preservation. A single field duplicate was included, with sample L1992155-10 being a field replicate of sample L1992155-9.

Stream waters

During the same period, the GSC collected 24 stream water samples from 22 sites downstream of the deposit (Fig. 1a) and regionally in background areas. Samples were collected using GSC National Geochemical Reconnaissance sampling protocols similar to those previously reported (Day et al. 2013; McCurdy and McNeil 2014). Two water samples were collected in the mid-channel of streams at each site: a filtered, acidified sample and a filtered, un-acidified sample. On-site, 60 ml of water was collected by filling the syringe from the active part of the stream channel and filtered through a single-use Millipore Sterivex-HV® 0.45 μm filter unit attached to a 60 ml sterile plastic syringe into each of the triple-rinsed 60 ml Nalgene® bottles. In situ water measurements were completed using a YSI Pro Plus® multi-parameter meter. The instrument simultaneously measured temperature, pH, specific conductivity, dissolved oxygen (DO), oxidation-reduction potential with automatic temperature compensation for pH and DO. Colour photographs of each water sample site are presented elsewhere (McCurdy et al. 2019). Two field duplicates were collected at two sites: 115J1005 is a duplicate of sample 115J1004 and 115J1024 is a field duplicate of 115J1023.

Analytical methods

Groundwaters

Samples collected from monitoring wells were transported under cooled conditions and analysed by ALS Environmental at laboratories located in Vancouver (British Columbia) and Whitehorse (Yukon). Full details of ALS laboratory methods are included in Knight-Piesold Ltd (2015). Specific conductivity and pH were determined using bench-top electrodes. Total dissolved solids (TDS) were determined gravimetrically by filtering a sample...
though glass fibre and evaporating the filtrate to dryness. Chloride, $\text{SO}_4^{2-}$ and $\text{F}^-$ were analysed by ion chromatography with conductivity detection. Alkalinity was determined using potentiometric titration and used to calculate values for $\text{HCO}_3^-$, $\text{CO}_3^{2-}$ and $\text{OH}^-$. Dissolved metals were determined from a filtered and acidified ($\text{HNO}_3$) aliquot and analysed by a collision/reaction cell induced coupled plasma mass spectrometer (CRC ICP-MS). Mercury concentrations were determined on a filtered and acidified (HCl) aliquot using the cold-oxidation method followed by reduction using stannous chloride, with analysis using cold vapour atomic absorption spectrometry.

**Stream waters**

Two water samples were collected and filtered (0.45 µm Durapore) at each site. They were kept in a cool dark container until being received at the GSC’s Inorganic Geochemistry Research Laboratory in Ottawa. One sample was acidified within 48 hours of arrival to 0.4% v/v with Ultrapure $\text{HNO}_3$ and stored at room temperature for two to four weeks prior to analysis.

Filtered acidified samples, labelled FA, were analysed for dissolved cations. Major element concentrations were measured using a Spectro Arcos EOP inductively coupled plasma emission spectrometer, and minor and trace elements were measured using a Thermo × Series II quadrupole ICP-MS. Further details on ICP analysis can be found in Hall *et al.* (1995, 1996). Data for Hf and Zr are not published because these elements are not sufficiently stabilized in water by the addition of nitric acid. Data for In, Se, Ag, Ta and Tl are not published because of inadequate detection limits and/or precision.

Filtered unacidified samples, labelled FU, were analysed for anions, dissolved organic carbon (DOC), alkalinity, pH, and specific conductivity. Determinations of anion concentrations were made with a Dionex ICS-2100 ion chromatograph using an AS-18 column and gradient elution. DOC was measured on a Shimadzu TOC-L analyser using high-temperature combustion and infrared detection. Alkalinity (measured by potentiometric titration with 0.02 N $\text{H}_2\text{SO}_4$), pH and specific conductivity measurements of the waters were completed using a MAN-TECH PC-Titräte™ system.

**Stable isotopes**

Water samples were analysed for $\delta^{18}\text{O}$, $\delta^{2}H$, and $\delta^{34}\text{S}_{\text{SO}_4}$ (for samples with sufficient $\text{SO}_4^{2-}$) and $\delta^{34}\text{S}_{\text{Sr}}$ at Queen’s Facility for Isotope Research (QFIR). $\delta^{34}\text{S}_{\text{SO}_4}$ was determined using CO$_2$ equilibration. Approximately 2 ml sample aliquots were loaded into 10 ml exetainer vials, purged with a mixture of 3% CO$_2$ in He and allowed to equilibrate for three days. The equilibrated CO$_2$ was analysed using a Thermo-Finnigan Neptune DeltaPlus XP Continuous-Flow Isotope-Ratio Mass Spectrometer. The $\delta^{18}\text{O}$ values are reported using the delta ($\delta$) notation in permil ($\%$o), relative to Vienna Standard Mean Ocean Water (VSMOW), with a precision of 0.2‰. The $\delta^{2}H$ values were determined using thermo-chemical reduction. Samples were loaded into 1 ml vials and introduced into a Thermo-Finnigan H-Device via an airtight syringe, flash vaporized and reduced by contact with a chromium reaction furnace at 850°C. The hydrogen isotopic composition of the H$_2$ gas was measured via the dual inlet system of a Thermo-Finnigan MAT 253 IRMS. The $\delta^{2}H$ values are reported using delta ($\delta$) notation in permil ($\%$o), relative to VSMOW, with a precision of 1‰.

Analysis of $\delta^{34}\text{S}$ was undertaken on both groundwater sulfates and a single sulfide mineral, liberated from a bedrock sample using a dental drill. Water samples were precipitated as BaSO$_4$ by adding excess BaCl$_2$ to sample aliquots and the precipitate extracted. A single chalcopyrite sample was extracted from a sulfide-rich bedrock specimen using a dental drill and crushed to homogenize. Samples were then weighed into tin capsules and the sulfur isotopic composition was measured using a MAT 253 IRMS coupled to a Costech ECS 4010 Elemental Analyser. The $\delta^{34}\text{S}$ values are calculated by normalizing the $^{34}\text{S}/^{32}\text{S}$ values in the sample to that in the Vienna Canyon Diablo Troilite (VCDT) international standard. Values are reported using the delta ($\delta$) notation in units of permil ($\%$o) and are reproducible to 0.2‰.

Strontium isotope separation was achieved using a method adapted from Smet *et al.* (2010), utilizing a prepFAST-MC™ automated column chromatography system (Romaniello *et al.* 2015). Strontium-specific exchange resin Sr Spec™ was loaded into a Poly-Prep column (3 cm × 200 µl) and pre-washed with 4 ml of 8 N HNO$_3$ and 1 ml of 3 N HNO$_3$, at a flow rate of 500 µl min$^{-1}$. Dried samples were dissolved in 3 N HNO$_3$ and a 1 ml sample aliquot loaded onto the column at a flow-rate of 250 µl min$^{-1}$. Matrix elements were eluted using 3 ml of 3 N HNO$_3$ and a purified Sr aliquot was eluted using 1 ml of 0.05 N HNO$_3$, both at a flow rate of 500 µl min$^{-1}$. Procedure blanks, along with certified reference materials NASS-7 (NRC, 2016) and SRLS-5 (NRC, 2015), were included in each batch. Isotopic measurements were conducted using a ThermoFinnigan Neptune™ Series High Resolution Multicollector ICP-MS (MC-ICP-MS) coupled with an Elemental Scientific Inc (ESI, Nebraska) Microfast autosampler at QFIR. Prior to analysis all samples were refluxed with 200 µl of 15.8 N HNO$_3$ at 180°C, evaporated at 80°C and dissolved into 2% HNO$_3$. Samples were delivered at 30 µl min$^{-1}$ using a PFA nebulizer and a cyclonic double-pass spray chamber composed of quartz. External measurement precision was monitored using the NIST-SRM-987 isotopic standard and mass bias correction achieved using $^{86}\text{Sr}^{88}\text{Sr}$ values ($^{86}\text{Sr}^{88}\text{Sr}$) = 0.1194).

**Results**

**Major ions and field chemistry**

Groundwater and surface water pH values range from 5.4 to 8.3 (Table 1). Sub-acidic values are associated with groundwater samples located proximal to Casino. Comparatively, surface waters are all circum-neutral, values that are typical for ground and surface waters in crystalline rock systems (Leybourne *et al.* 2006). Groundwater samples typically have higher salinities, with TDS ranging from 74 to 1320 mg l$^{-1}$, whereas surface waters range from 98 to 654 mg l$^{-1}$. Groundwater salinities are also higher proximal to the Casino deposit (Table 2), whereas surface water salinities are highest in streams draining to the north of the deposit. Ground and surface waters from the Casino study area are dominantly Ca–HCO$_3$ to Ca–SO$_4$-type waters (Fig. 2) and are dominated by Ca (and Mg) as the major cations. Only four samples showed slightly elevated Na concentrations (14–20 mg l$^{-1}$; Fig. 3a and b) and only three water samples trended to the Na (+K) apex of the piper plot (Fig. 2). All waters had low Cl (<1 mg l$^{-1}$) and fluoride (<1 µg l$^{-1}$) concentrations (Fig. 4g and h). Anions were dominated by HCO$_3$ and, for groundwaters close to the Casino deposit, SO$_4^{2-}$ (groundwaters were up to 800 mg l$^{-1}$ SO$_4^{2-}$). Thus, Ca, Mg, HCO$_3$ and SO$_4^{2-}$ are the dominant constituents (Fig. 4a–b).

Calcium concentrations in stream waters display a lithological control; concentrations of more than 40 mg l$^{-1}$ (median 38 mg l$^{-1}$) appear to be associated with a Neoproterozoic and Paleozoic aged Snowcap assemblage (Ryan *et al.* 2013) (Fig. 1a), composed of quartzite, mica schist and metaconglomerate. Generally, there does not appear to be a spatial correlation between Ca concentration and mineralized occurrences in the district. Concentrations of NO$_3$ range from 1.22 to 1.91 mg l$^{-1}$ (dataset median 1.2 mg l$^{-1}$) in Casino Creek. The highest concentrations were observed at sites 115J2017-1008 and 115J2017-1010, at the intersection of the Meloy and
Casino Creeks. Anomalous concentrations more than 1.5 mg l$^{-1}$ are also present in Mascot Creek, downstream of the Mascot Au–Ag–As prospect, and in the Isaac Creek, downstream of the Buck Au–As–Sb–Hg–Ba prospect.

Iron concentrations for most waters are generally low (<0.1 mg l$^{-1}$) (Fig. 3a and b), typical of surface waters exposed to atmospheric O$_2$. By contrast, the more saline, higher sulfate groundwaters have elevated dissolved Fe and Mn concentrations (>40 mg l$^{-1}$ and 5000 µg l$^{-1}$, respectively) (Fig. 5). Iron concentrations are elevated in stream waters of Casino Creek (Fig. 3b), ranging from 0.01 to 0.07 mg l$^{-1}$ compared to a dataset median of 0.01 mg l$^{-1}$. The highest Fe concentrations (>0.2 mg l$^{-1}$) occur in sites 115J2017-1004 and 1005 (Hayes Creek), draining into the Selwyn River, and site 115J2017-1009, located in an unnamed tributary of Dip Creek (Fig. 3b). Similarly, Mn concentrations in Casino Creek are elevated, ranging from 35 to 104 µg l$^{-1}$ (Fig. 3a and b), as well as site 115J2017-1009 (79 µg l$^{-1}$). Elsewhere in the district, Mn concentrations are generally below the dataset median of 5 µg l$^{-1}$.

Trace elements

Groundwaters proximal to the Casino deposit have elevated dissolved trace cation and oxyanion concentrations. There is a spatial control on concentrations, with samples located in the west of the deposit displaying anomalous values of Co, Cu, Mo, As, Re, Zn (Fig. 3a and b), B and U to up to 64, >1500, 25.2, 17, 0.71, 11.7, 39.6 and 354 µg l$^{-1}$, respectively. In particular, sample L1992155-3, located in the centre of the deposit displays the most anomalous concentrations. With the exception of Cu, samples with the highest sulfate concentrations have the highest metal and metalloid concentrations (Fig. 5a–f), along with significant concentrations of Fe and Mn. In comparison, sample L1992155-5 (located in upper Canadian Creek) has the lowest salinity, along with trace cation and oxyanion concentrations close to or below the median values for the groundwaters (Fig. 3).

Establishing background concentrations for the stream waters is complicated by the abundance of mineralized occurrences in the area (Fig. 1a). Due to the small dataset available, a simple statistical approach was used to establish the upper threshold for natural background levels (NBLs) for a set of common pathfinder elements (SO$_4^{2-}$, Cd, Cu, Co, Ni, Pb, Zn, As, Mo, Re, Se and Sb). Samples pre-selected ($n = 10$) based on location in stream catchments with no known mineralized occurrences, including Hayes, Colorado, Excelsior Creeks, as well as upper potions of the Selwyn River (Fig. 1a). The 90th percentile was calculated for each element representing the upper threshold of NBLs (dashed lines on Fig. 5a–f). Values were considered anomalous where concentrations exceeded twice the NBLs.

Stream waters from Casino Creek, draining the south side of the deposit, have elevated concentrations of Co, Cu, Mn, Mo (Fig. 5a–f), Re and Zn up to 14 km downstream of the deposit. Surface waters around the Casino deposit are not anomalous in SO$_4^{2-}$; the highest surface water SO$_4^{2-}$ concentrations occur in streams to the

| Sample | Type | δ$^{18}$O % v. VSMP | δ$^{18}$H % v. VSMP | δ$^{34}$S (sulfate) % v. VCDT | δ$^{18}$O (sulfate) % v. VSMP | TDS | $^{87}$Sr/$^{86}$Sr |
|--------|------|---------------------|---------------------|---------------------|---------------------|------|----------------|
| 115J171002 SW | -22.5 | -168 | 120.06 | 0.70782 |
| 115J171003 SW | -22.3 | -165 | 98.1 |
| 115J171004 SW | -21.9 | -165 | 14.1 | 173.17 |
| 115J171005 SW | -21.8 | -164 | 9.8 | 170.64 |
| 115J171006 SW | -22.5 | -168 | 138.08 |
| 115J171007 SW | -22.5 | -168 | 9.2 | -16.7 | 227 | 0.71167 |
| 115J171008 SW | -22.6 | -164 | 3.9 | -25.4 | 250.53 |
| 115J171009 SW | -22.6 | -164 | 251.56 | 0.70807 |
| 115J171010 SW | -22.6 | -167 | 5 | -24 | 247.87 |
| 115J171012 SW | -22.4 | -162 | 9.9 | 148.06 | 0.70765 |
| 115J171013 SW | -22.9 | -169 | 214.7 | 0.70801 |
| 115J171014 SW | -22.6 | -169 | 4.6 | -25.1 | 221.26 |
| 115J171015 SW | -22.5 | -167 | 6.4 | -21.2 | 371.03 | 0.71331 |
| 115J171016 SW | -22.6 | -172 | 5.8 | 392.24 | 0.71077 |
| 115J171017 SW | -22.7 | -170 | 154.95 |
| 115J171018 SW | -22.2 | -161 | 6.6 | 188.36 | 0.70775 |
| 115J171019 SW | -22.4 | -166 | 124.31 |
| 115J171020 SW | -23 | -170 | 6.7 | -29.3 | 556.69 |
| 115J171022 SW | -22.9 | -165 | 7.6 | 653.97 |
| 115J171023 SW | -22.5 | -167 | 338.8 |
| 115J171024 SW | -22.6 | -168 | 6.6 | -23.4 | 342.26 | 0.71224 |
| 115J171025 SW | -22.4 | -169 | 6.4 | -23.6 | 302.71 | 0.7075 |
| 115J171026 SW | -22.3 | -167 | 7.8 | -23.2 | 255.82 | 0.71151 |
| 115J171027 SW | -22.6 | -160 | 6 | -25.1 | 344.55 | 0.71031 |
| L1992155-1 GW | -22.8 | -171 | 2.1 | -21.8 | 1,308.70 |
| L1992155-2 FB | -20 | -150 | 0.70683 |
| L1992155-3 GW | -22.7 | -162 | -0.3 | 135.22 | 0.70792 |
| L1992155-4 GW | -22.7 | -167 | 3.1 | -35.1 | 1,314.08 | 0.70682 |
| L1992155-5 GW | -22.5 | -165 | -0.1 | -29.3 | 74.21 | 0.70689 |
| L1992155-6 GW | -22 | -166 | 197.27 | 0.7078 |
| L1992155-7 GW | -22.9 | -170 | 295.2 | 0.70735 |
| L1992155-8 GW | -23 | -171 | 7.4 | 308.79 |
| L1992155-9 GW | -22.7 | -170 | 0.4 | -31.8 | 672.54 | 0.70708 |
| L1992155-10 GW | -22.8 | -170 | 0.4 | -35 | 669.93 |
Fig. 2. Piper plot of ground and surface waters from the Casino deposit area. Waters closest to the Casino deposit have proportionally higher $\text{SO}_4^{2-}$ and Ca concentrations and the highest total dissolved solids (TDS).

Fig. 3. Histogram of dissolved metal load concentrations for (a) groundwater samples and (b) surface water samples.
north of the Casino area (Fig. 4). However, sites 115J2017-1008, 115J2017-1010 and 115J2017-1014 close to the Casino deposit have the lowest $\delta^{34}S$ values of the surface waters, approaching the values observed in the metal- and sulfate-rich groundwaters from the deposit. Site 115J2017-1002, about 20 km east of the Casino deposit, shows moderately anomalous Cd and Cu concentrations, and the highest Mo concentrations (2.91 µg l$^{-1}$) of all the surface waters in this study. This site is downstream from the Cockfield porphyry Cu–Mo–Au occurrence.

Rare-earth element (REE) concentrations were above detection limit for most of the waters. General REE profiles allow for the evaluation of the interconnectivity of groundwaters and surface waters (Fig. 6a). All waters have relative flat to slightly light REE (LREE)-enriched profiles normalized to North American Shale Composite (NASC; Gromet et al. 1984), and slightly LREE-enriched normalized to chondrite (McDonough and Sun 1995). Groundwaters proximal to the Casino deposit have higher total REE concentrations compared to the surface waters (up to 22 µg l$^{-1}$ v. up to 1.5 µg l$^{-1}$).

Fig. 4. Plots of TDS for Casino surface and groundwaters compared to (a) Ca (mg l$^{-1}$); (b) Na (mg l$^{-1}$); (c) Mg (mg l$^{-1}$); (d) Fe (mg l$^{-1}$); (e) SO$_4^{2-}$ (mg l$^{-1}$); (f) HCO$_3^-$ (mg l$^{-1}$); (g) Cl (mg l$^{-1}$); (h) F (mg l$^{-1}$).
δ¹⁸O and δ²H values of surface water samples range from −23.0 to −21.8‰ and −172 to −160‰, respectively. The data are tightly clustered around the mean annual weighted average for precipitation in the Yukon, as recorded at stations in Mayo and Whitehorse (Fig. 7a). Groundwaters are isotopically indistinguishable from the surface waters; all data plot on or slightly above the global meteoric water line, with excess ‘d’ values of 13.5 ± 2.84‰ (range = 9.2 to 21.1‰) (Fig. 7b).

**Stable isotopes**

δ¹⁸O and δ²H values of surface water samples range from −23.0 to −21.8‰ and −172 to −160‰, respectively. The data are tightly clustered around the mean annual weighted average for precipitation in the Yukon, as recorded at stations in Mayo and Whitehorse (Fig. 7a). Groundwaters are isotopically indistinguishable from the surface waters; all data plot on or slightly above the global meteoric water line, with excess ‘d’ values of 13.5 ± 2.84‰ (range = 9.2 to 21.1‰) (Fig. 7b).
There was sufficient SO$_4^{2-}$ to measure the S isotopes in 16 of the surface waters samples, with resulting $\delta^{34}$S values ranging from 3.9 to 14.1‰ (Fig. 8). Seven groundwater samples had variable $\delta^{34}$S values, ranging from $-0.3$ to 7.4‰, with lowest values in groundwaters proximal to mineralization and having the highest SO$_4^{2-}$ concentrations (Fig. 8). A single $\delta^{34}$S value for chalcopyrite obtained from a mineralized bedrock sample yielded $-1.2$‰.

Nineteen waters were analysed for their Sr isotopic composition. Surface waters were more variable, ranging from $^{87}$Sr/$^{86}$Sr = 0.70750 to 0.71331 (Fig. 9a–c), compared to the groundwaters with values from 0.70682 to 0.70792 (Fig. 9a). The least radiogenic groundwaters and surface waters had the highest Cu and Mo concentrations (Fig. 9c) and highest Rb/Sr values (Fig. 9b).

**Discussion**

**Water provenance**

Stable isotope data for the surface and groundwater samples show a tight clustering of $\delta^{18}$O$_{VSMOW}$ and $\delta^{2}$H$_{VSMOW}$ values around the mean annual weighted average for the precipitation monitoring...
stations in Whitehorse and Mayo (Fig. 7a). The isotopic composition of the groundwaters indicates that these are modern meteoric recharge waters, consistent with the low salinities of the waters at Casino. There is a slight enrichment in δ¹⁸O SMOW compared to δ¹³C SMOW, which could represent a fractionation during snow or permafrost melt events (Leybourne et al. 2006). However, the clustering of the surface waters with the groundwaters (Fig. 7b) indicates that the surface waters represent shallow groundwater discharge, with dampened seasonal fluctuations, rather than being influenced by seasonal precipitation (Leybourne et al. 2006). Further, regional deep groundwater discharge is estimated to contribute 0.08 m³ s⁻¹ of water along the upper 7 km of Casino Creek (Knight-Piesold Ltd 2015); however, mini-piezometer water level and calculated vertical gradients indicate fluctuating interconnection between groundwaters and surface waters, with upward gradients increasingly prevalent during fall months (Knight-Piesold Ltd 2015).

**Water–deposit interaction: sources of dissolved solutes characteristic of porphyry Cu deposits**

The groundwaters and surface waters proximal to the Casino deposit are differentiated by anomalous concentrations of Fe, Mn, SO₄²⁻, Co, Cu, Mo, As, Re and Zn concentrations. This generally correlates to the Casino primary and supergene mineralization, which includes disseminations of pyrite, chalcopyrite, chalcocite and molybdenite, along with trace sphalerite and bornite (Casselman and Brown 2016). Sources of As, Sb and Se are typically constrained to the structure of primary sulfide minerals such as pyrite (Manceau et al. 2020) and are therefore likely to have been leached and remobilized from the upper portions of the deposit. In comparison, Mo-bearing sulfide minerals are reported to be unaffected by supergene processes at Casino (Casselman and Brown 2016). There are several lines of evidence to indicate sulfide oxidation is an important solute source at Casino. Anomalous SO₄²⁻ and Fe concentrations in groundwater samples proximal to Casino and stream waters from Casino Creek (sample 115J171014) correlate with pH values down to 5.4. Water samples collected proximal to Casino display δ³⁴S (SO₄) values ranging from −0.3 to +3.1‰ (Fig. 8), similar to a δ³⁴S value of −1.2‰ obtained from a Casino bedrock-sourced chalcopyrite specimen. However, there is also evidence of mixing or source differentiation, with a decrease in sulfate concentrations and increase in δ³⁴S values with increasing distance from Casino (Fig. 8), most likely representing the input of atmospheric SO₂ (Clark and Fritz 1997). However, it is not possible to discount SO₄²⁻ input from the dissolution of hypogene sulfates, which can occur as a function of S disproportionation of hydrothermal fluids during formation and be isotopically heavier than sulfides (Seal 2006), as well as likely more soluble below the water table than primary sulfides.

Typically, Mo and Re concentrations in stream and groundwaters are low (Leybourne and Cameron 2008; Smedley et al. 2014), with average global surface waters estimated to be 0.5 µg l⁻¹ Mo (Reimann and de Caritat 1998) and aqueous Re concentrations generally encountered <1 µg l⁻¹ (Leybourne and Cameron 2008). Elsewhere, highly anomalous concentrations of both elements have been encountered in groundwaters around mineral deposits. Proximal and down-gradient of the Spence porphyry Cu deposit in the Atacama Desert of northern Chile have been shown to have up to 100s of µg l⁻¹ Mo and 31 µg l⁻¹ Re (Leybourne and Cameron 2008). In comparison, at Casino, Mo concentrations show weak anomalism in proximal groundwaters (<25 µg l⁻¹) and are all close to NBL (1.1 µg l⁻¹) in surface waters. The only anomalous concentration in surface waters was identified in Battle Creek
(Fig. 1a) downstream of the Cockfield Cu–Mo occurrence. In comparison, Re concentrations range from 5 to 37 ng l⁻¹ and groundwater Re concentrations are up to 710 ng l⁻¹ with higher concentration anomalies occurring proximal to Casino. Rhenium typically occurs substituted into the structure of molybdenite crystals (Rathkopf et al. 2017) and its occurrence around Casino is likely the result of molybdenite oxidation. Despite this, there is no correlation between Mo and Re concentrations in the Casino waters, which likely reflects a mobility contrast between both (oxy)anions. However, other lithological sources are feasible, with Re concentrations that vary from c. 0.1 to 23.2 ng l⁻¹ in water samples collected from rivers in India, resulting from the weathering of black shales, mafic-rock associated pyrite and, at higher Re/K values, elevated Re was attributed to anthropogenic contributions (Rahaman et al. 2012). Essentially identical ranges of Re (1.3 to 26 ng l⁻¹) were observed in groundwaters from the Nevada Test Site, attributed to dissolution of marine carbonate rocks (Hodge et al. 1996).

Further evidence of water–deposit interaction is displayed in ⁸⁷Sr/⁸⁶Sr values. Strontium isotopes are useful in hydrogeochemical studies because surface processes such as evaporation, precipitation or adsorption do not fractionate strontium isotopes (McArthur 1994), which can be used to differentiate solute sources, be it rainfall, water–rock interaction, or wind-dispersed materials such as dust, and identify fluid pathways and mixing zones. Additional tracing tools include ratios of Rb/Sr, with ⁸⁷Sr/⁸⁶Sr values primarily varying according to the age of parent material and initial Rb/Sr values because ⁸⁷Sr is generated by radiogenic growth from the beta-decay of ⁸⁷Rb (Kendall and McDonnell 2012), and Na/Cl, which behaves conservatively in aqueous solution with low chemical reactivity potentially allowing for source differentiation. Finally, comparisons with pathfinder minerals potentially allow for metalloid concentrations to be associated with a particular mineral or lithology. Around the Casino deposit, groundwaters and surface waters have relatively non-radiogenic ⁸⁷Sr/⁸⁶Sr values (0.706 to 0.708), within range of values (0.70551–0.70834) of hydrothermal K-feldspar from the Casino, Mt Nansen, and Cash plutons (Selby et al. 2001) (Fig. 9a–c). However, there is potential overlap with the magmatic ⁸⁷Sr/⁸⁶Sr composition of country rocks from the Dawson Range batholith and metamorphic rocks of the Yukon–Tanana terrane, which range 0.707 to 0.722 (average 0.709, n = 70) (Selby et al. 1999). A second grouping consists of more radiogenic ⁸⁷Sr/⁸⁶Sr values (Fig. 9a–c), all located proximal to occurrences of the Snowcap Assemblage (Fig. 1a). These waters also have the lowest Rb/Sr, Na/Cl, Cu and Mo values (Fig. 9a–c), indicating either mixing between Sr derived by water–pluton/deposit interaction with Sr derived from precipitation, or perhaps more likely the dissolution of Sr derived from minerals of the Snowcap Assemblage.

Halogen elements are commonly found as components in the alteration shells of porphyry deposits, occurring in the hydroxyl sites of hydroxilicate minerals (e.g. apatite, fluorite, biotite and hornblende; Idrus 2018). Selby and Nesbitt (2000) determined the chemical composition of biotite at Casino within both the magmatic host rock and secondary, hydrothermal phases, reporting a marked increase in the F and Cl concentrations in biotite from the potassic and phyllic alteration zones. Fluoride concentrations in groundwaters proximal to Casino range from 0.03 to 1.00 mg l⁻¹ (median 0.39), which is at the lower end of the published ranges for mineral dissolution related to granitic and metamorphic rocks (0.2 to 10.3 mg l⁻¹; Brindha and Elango 2011). However, compared to distal ground or surface waters, molar ratios of F/Cl are elevated proximal to Casino, suggesting water–rock interaction with rock-forming minerals from the alteration suite.

Controls on solubility and dispersion

The major ion and trace metal and metalloid composition of the groundwaters and surface waters around the Casino deposit are consistent with water–rock interaction with the deposit. The ⁶⁸Sr isotopic compositions of waters proximal to the Casino deposit are consistent with this interpretation. Compared to other case studies (Gray 2001; Kirste et al. 2003; Jorquera et al. 2014) dissolved anomalies (SO₄²⁻, Fe, Mn, Cu, Co, Zn, As, Mo and Re) are relatively low, which could reflect either dilution from higher rainfall or the extent of supergene development and leached capping at Casino, with the readily leachable solutes already flushed from the deposit over time.

The depth of oxide and supergene mineralization in relation to water table is a likely control on variation in the hydrogeochemical signature across the deposit. The highest concentration anomalies (SO₄²⁻, Fe, Mn, Co, Cu, Mo, Re and Zn) and lowest pH (5.4) occur in sample L1992155-3, a groundwater sample collected from within the eastern edge of the deposit footprint (near Casino Creek) and the phyllic alteration halo. In this location (Fig. 1b), depth to primary mineralization is less than 70 m from surface (Fig. 10), combining shallow weathering, a water table of less than 10 m, and deep groundwater flow (Knight-Piesold Ltd 2015), suggesting potential heightened water interaction with reactive primary sulfide minerals during seasonal water table fluctuations. In comparison, in the west

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**Fig. 10.** Conceptual model with east–west section with deposit mineralogy, host geology and hydrology. Black stars represent endmember compositions and vertical lines represent drillholes with depths marked.
of the deposit (near Canadian Creek) depth to primary sulfide minerals extends down to 280 m (Casselman and Brown 2016) (Fig. 10). In this location, groundwaters and surface waters are predominantly interacting with supergene oxide and sulfide minerals with significantly lower dissolved concentrations.

The mobility of dissolved metals is majorly controlled by pH, which has large impacts on aqueous chemistry, controlling variation in carbonate geochemistry, element adsorption and desorption, mineral precipitation and dissolution, speciation, nitrification and microbial growth (Nimick et al. 2011). At Casino groundwaters are sub-acidic and surface waters are circum-neutral. There are several possible controls on the limited pH gradient. Firstly, the lack of near-surface sulfide to oxidize likely results in limited acid generation. Secondly, buffering of the acids generated from reaction with the Casino sulfides may occur either through interaction with calcite reported in the phyllic and propylitic alteration zones (Casselman and Brown 2016) or flushing events from enhanced seasonal precipitation or snow and ice melt. In oxygenated and circum-neutral waters the likely fate of redox elements is precipitation as hydroxide phases (e.g. Fe(OH)_3) (Kysel et al. 2015), which has an impact on the mobility of trace metal cations (Cd, Co, Cu, Ni, Pb and Zn), which are typically adsorbed on reactive surfaces at higher pH.

Another potential control on the stream water concentrations is the effect of diurnal cycling (Nimick et al. 2011) of stream water pH and temperature. Key impacts on stream water chemistry include changes to physicochemistry, speciation and trace element load, particularly with variation in temperature and pH (Nimick et al. 2011). Diurnal cycling can also occur from freeze–thaw variation during snow and ice melting events (Caine 1992), particularly at Casino where permafrost is a discontinuous source of recharge to streams and aquifers (Knight-Piesold Ltd 2015).

Surface waters at sites 115J2017-1008, 115J2017-1013 and 115J2017-1014 may be influenced by a pipe draining water from the Bomber prospect into the headwaters of Meloy Creek (Huss et al. 2013), upstream from site 115J2017-1013. However, Archer and Main (1971) collected surface waters and stream sediments in the Casino deposit prior to any disturbance and reported Cu concentrations in creek waters that were anomalous compared to other streams in the area, with Cu values up to 2030 µg l⁻¹, only seen in groundwaters in this study. Archer and Main (1971) also reported that Taylor Creek had a flowing spring with a pH of 2.6 (much lower than any sample in this study) associated with a limonite gossan. Although they were unable to measure Mo in the waters, stream sediments were also anomalous in Mo (Archer and Main 1971).

**REE mobility**

All water samples show subtle to significant Ce anomalies (where Ce* = [Ce]_NASC[Gd]_NASC+ [Gd]_NASC0.5–, with Ce* ranging from 0.18–0.82. There is a positive correlation (r = 0.841; p < 0.0001 for Ce* v. Log10[Mn]) between the Ce* value and Mn concentrations in the waters; groundwaters with higher Mn and have a less pronounced Ce* anomaly than surface waters (Fig. 6b). This represents a physicochemical control on Ce speciation due to the interaction of Ce with Mn oxides, which catalyse the conversion of Ce⁴⁺ to Ce³⁺ and the complexion of Ce⁴⁺ on reactive surfaces (Takahashi et al. 2000; Tanaka et al. 2010). Less pronounced effects, with greater uncertainty, have been reported for Ce⁴⁺ complexion to Fe oxyhydroxides (Bau and Koschinsky 2009), and organic ligands (Tanaka et al. 2010; Loges et al. 2012). Similar patterns have been reported around mineral deposits, with Leybourne et al. (2000) reporting similar correlations in Ce anomalis and concluding oxidation and complexation to be a key control.

**Implications for mineral exploration**

This study represents a rare opportunity to assess the potential of both surface waters and groundwaters as vectors to mineralization. The study area has not been disturbed by Pleistocene glaciation, which results in atypical preservation of the porphyry and, in comparison, to many other sites in Canada where glacial activity has occurred, exposures of fresh bedrock to enhance water–mineral chemical activity. The hydrogeochemistry of Casino shares similarities with the Taurus porphyry in Alaska, with also displays exceptional preservation (Kelley and Graham 2021). In comparison, the ground and stream waters at Casino generally have lower salinity, higher pH, and lower concentration dissolved trace metal anomalies which form a smaller dispersion halo. This may reflect the deeper weathering and leached horizon at Casino and reduced ligand availability for complexing. In both study areas dissolved trace metals loads of sampled waters are significantly lower than those reported from the Pebble porphyry (Eppinger et al. 2012), a study area impacted by Pleistocene glaciation, with trace element concentrations in stream and seeps somewhat comparable to groundwater samples from Casino.

In waters proximal to Casino, Taurus and Pebble porphyries Re is a notable pathfinder, likely sourced from the oxidation of molybdenite. Rathkopf et al. (2017) noted that there are large variations in Re content in molybdenite with total variation <15 to 4450 ppm in some 45 samples of 11 rock units at the Bagdad porphyry Cu–Mo deposit in Arizona, but variation of <15 to 1215 ppm in a single molybdenite crystal. These authors noted that there was no systematic variation in Re content of molybdenite as a function of lithology, degree of alteration, distance to ore, or ore grade, suggesting that Re content of molybdenite may not be easily applied as a vector to porphyry Cu mineralization (Rathkopf et al. 2017). However, in aqueous systems, elevated Re may well prove an effective exploration tool, as shown here and in northern Chile (Leybourne and Cameron 2008); i.e. the low background values for most groundwaters and surface waters mean that readily detectable Re in a water sample is likely an indicator of molybdenite. Groundwaters proximal to the Casino deposit have Re concentrations more than an order of magnitude higher than groundwaters from Nevada, for example (Hodge et al. 1996).

The hydrogeochemical stream water anomaly in Casino Creek approaches concentrations close to natural background levels within 7 km of the Bomber occurrence, when the water body flows into Dip Creek (Fig. 1a), a third-order stream. Stream water anomalies resulting from the interaction with sulfide metal deposits are generally of low concentration in the highly meteoric waters in Yukon, and in most cases are discernible only due to trace analysis with ICP-MS. However, such analysis is now a mainstream technique in many commercial laboratories with costs reflecting that. There is potential for enhancing the intensity and dispersion of anomalies by measuring ‘total’ or unfiltered samples, which will include trace metals adsorbed on to reactive surfaces carried in suspension (Clements et al. 2000; Gray et al. 2000).

**Conclusions**

At Casino, porphyry-related solutes are dispersed in both groundwaters and surface waters but at relatively low concentration compared to well-known examples from the region. This is almost certainly due to the unique preservation of Casino and demonstrates the potential for varied hydrogeochemical signatures for the sample styles of mineralization within Yukon and beyond. Irrespective of concentration, stable isotope systems are particularly effective at discerning the water provenance at Casino as well as fingerprinting interaction between host rock and ore minerals. Ultimately, the atypical geochemical signature (Mo, Se, Re, As, Cu) of these types
of deposits are typically reflected in the water chemistry and δ34S isotopes provide a more local vectoring tool for mineral exploration.

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Data availability The physicochemical, major, trace, and isotopic data of stream and groundwaters used in this manuscript is publicly available as an Open Data availability (supporting), methodology (lead), data curation (supporting), writing – original draft (supporting), writing – review & editing (supporting); MG: formal analysis (supporting), original draft (supporting), writing – review & editing (supporting); DL: formal analysis (supporting), resources (supporting), supervision (supporting), writing – review & editing (supporting).

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