

Organic-Compound Pathfinders in Soil for Base- and Precious-Metal Exploration in British Columbia

P.M. Luck, Mineral Deposit Research Unit, The University of British Columbia, Vancouver, BC, pluck@eoas.ubc.ca

R.L. Chouinard, Mineral Deposit Research Unit, The University of British Columbia, Vancouver, BC

P.A. Winterburn, Mineral Deposit Research Unit, The University of British Columbia, Vancouver, BC

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Introduction

Hydrocarbon pathfinders are a promising and under-researched tool for nonpetroleum-based mineral exploration through cover. Historically, most economic mineral deposits were discovered as showings of visibly altered or mineralized outcrop. Currently in British Columbia (BC), economic geologists explore for deposits in terrain that may be covered by tens to hundreds of metres of till and glaciolacustrine deposits. Traditionally, commodity and pathfinder elements analyzed by a variety of partial-extraction techniques were integrated with other information, such as geophysical or geological evidence, to potentially improve drilling outcomes. When sampling soils that developed over poorly understood glacially derived surface sediments, geochemical signals may be complex and far travelled. This challenge has driven innovation and development of other exploration techniques to explore through transported overburden. Hydrocarbon concentrations in soil may increase in response to economic mineralization and have the potential to identify targets beneath cover.

The purpose of this research is the advancement of hydrocarbon-pathfinder techniques as an open geochemical exploration tool to explore for Cu-porphyry and related deposits in BC. The goals of this project are to

- identify the physical, chemical and biological links between buried economic mineralization and hydrocarbon concentrations and compositions at surface;
- develop robust, commercially viable and cost-effective analytical techniques for hydrocarbon analysis; and
- optimize hydrocarbon-sampling methodologies and strategies.

This research draws on datasets and sample suites generated by previous research in the Exploration Geochemistry Initiative research group at the Mineral Deposit Research

Unit (MDRU), primarily from soils overlying the Highmont South Cu-Mo calcalkalic porphyry deposit in south-

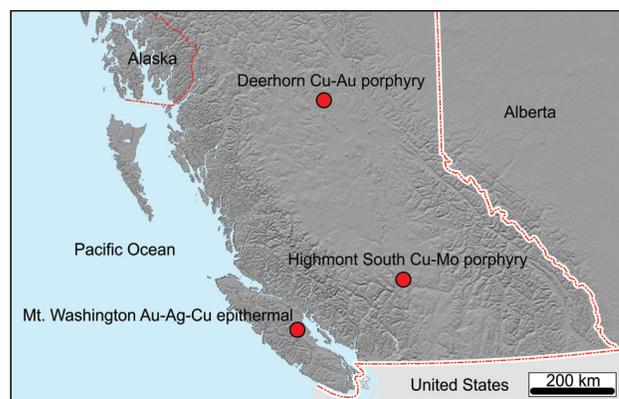


Figure 1. Locations of orientation studies for organic compounds in base- and precious-metals exploration, southern British Columbia.

central BC (Chouinard, 2018) and the Deerhorn Cu-Au alkaline porphyry deposit (Rich, 2016) in central BC (Figure 1). An integrated study of available traditional geochemistry, bedrock and Quaternary geology, and physiography data for these study areas will define hydrocarbon behaviour in proximity to mineralized systems. Data analysis aims to discriminate areas with elevated hydrocarbon abundances generated by barren geology from those of economic interest. Additionally, new fieldwork to be undertaken in the fourth quarter 2018 at the Mount Washington epithermal Au-Cu-Ag deposit on Vancouver Island will test the applicability of organic-compound pathfinders across the continuum of Cu-porphyry systems.

Methods

Pioneering research in organic-compound pathfinders demonstrated changes in the abundance of organic compounds in soil related to underlying hydrocarbon resources, geothermal anomalies and mineral deposits (Klusman, 1993).

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There are two strategies utilizing organic-compound pathfinders that are currently practised in mineral exploration: passive and soil sampling. The passive-sampling technique utilizes collectors made of various sorbents, such as activated charcoal, encased in a water-resistant casing. With this approach, sampling is conducted by auguring a 60–100 cm deep hole in the soil, in which the sampler is buried for 120 days or more. Upon retrieval, the passive sampler is analyzed by thermal-desorption gas chromatography–mass spectrometry (GC-MS). Amplified Geochemical Imaging LLC (AGI) distributes collectors that were once termed ‘Gore Sorbers’ (Figure 2), and it also performs the C2–C20 analysis. At the Miitel Ni-sulphide deposit in western Australia, 2-methylbutane, 1-pentene and pentane were reported as being anomalous above known mineralization using this method (Noble et al., 2017).

In the soil-sampling technique, the B horizon is typically used as sampling medium (Hamilton, 2007), although lake bottom sediments, peat and humus have also been evaluated (Sutherland, 2007). Samples undergo a hexane-acetone leach to extract surface-bound hydrocarbons, and concentrations are determined by GC-MS (Cayer, 2017). This method type is sometimes referred to as a time-integrated technique, as it is considered that the organic compounds accumulate in soil over time. Soil techniques have the advantage over passive techniques of requiring only a single visit to the field and a faster turnaround time. The Activation Laboratories Ltd. proprietary Spatiotemporal Geochemical Hydrocarbons (SGH) technique, as evaluated at the Mount Milligan Cu-Au porphyry (Heberlein, 2010), is one such technique. Historically, SGH results were reported as generic compound classes, rather than compound-specific results. Currently, the SGH technique results are reported as a contoured interpretation map; no compound concentrations are shared with the end user.

Biogeochemical Links Between Organic Compounds and Ore Deposits

A growing body of evidence suggests that organic compounds form and accumulate in mineralized environments through microbial biosynthesis. A number of bacterial species have been identified in acid mine-drainage leachates (Southam and Saunders, 2005; Harneit et al., 2006), where they commonly grow as biofilms on the surfaces of sulphide minerals. Examples include the sulphide oxidizer *Acidithiobacillus thiooxidans*, iron and sulphide oxidizer *A. ferrooxidans* and iron oxidizer *Leptospirillum ferrooxidans* (Edwards et al., 1999). These bacteria enhance sulphide dissolution, playing a crucial role in supergene environments (Enders et al., 2006).

Sulphur- and iron-oxidizing bacteria use extracellular polymeric substances (EPS) to attach themselves to mineral surfaces (Harneit et al., 2006; Konhauser, 2007). For



Figure 2. An AGI Gore Module activated-charcoal organic-compound collector being retrieved after two months (Image: M. Bodner).

A. ferrooxidans, the EPS and outer cell membrane contain lipopolysaccharide (LPS; Figure 3), which has a slight positive charge under acidic conditions that results in an attraction to the negative surface charge of sulphide grains. As the LPS degrades, the lipid functional groups may contribute to the concentration of alkanes in the subsurface and soils.

In a sediment-column copper-sulphide bioleaching experiment (Luca et al., 2008), hydrocarbons formed as byproducts of bacterial metabolism. Columns were spiked with Cu-bearing ore from the Andina hydrothermal breccia and El Teniente Cu-porphyry deposits in Chile. A bacterial consortium taken from the El Teniente ore leachate and a pure strain of *A. ferrooxidans* were used to inoculate the sediment columns. Gas exiting the column was passed through

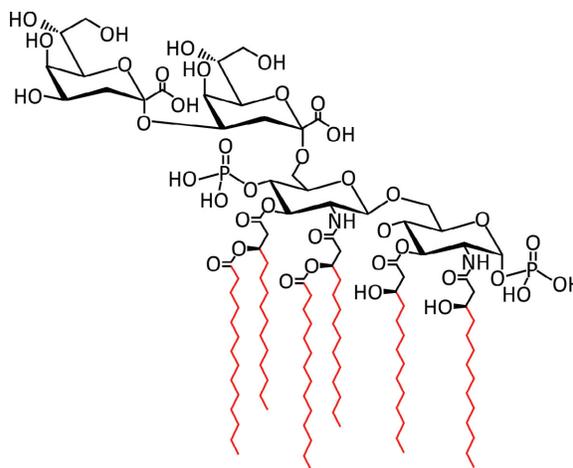


Figure 3. Lewis diagram of lipopolysaccharide (LPS), with lipid functional groups shown in red. This compound is part of the outer cell membrane of microbes, such as *Acidithiobacillus ferrooxidans*, that enable them to adhere to sulphide grains. After decomposition, the lipid functional groups may contribute to alkane concentrations in soil. Alkanes, such as decane, dodecane and tridecane, are pathfinders for sulphide-bearing ore deposits.

an adsorbent for 90 days. Bacterial species were identified with terminal-restriction fragment-length polymorphism analysis. The autotrophs *A. ferrooxidans* and other bacterial species were identified. Organic compounds in the adsorbent material were analyzed by Activation Laboratories Ltd. using GC-MS (Luca et al., 2008). Measurable concentrations of methyl-benzenes (20–350 ppt) and branched alkanes (10–120 ppt) were observed (Luca et al., 2008).

Previous MDRU Studies

Highmont South Cu-Mo Porphyry Deposit, Highland Valley Copper District, South-Central BC

High-molecular-weight alkanes, such as decane ($C_{10}H_{22}$), dodecane ($C_{12}H_{26}$) and tridecane ($C_{13}H_{28}$), are elevated in the surface B-horizon soil over mineralization in the southern section of the study area (Chouinard, 2018). Anomalous high concentrations also occur in areas overlying bedrock-fault projections to surface and topographic lows where soils are saturated with water (Figure 4). Fault zones are known to transport fluids containing trace amounts of organic compounds (Klusman, 1993).

Deerhorn Cu-Au Porphyry Deposit, Woodjam Cu-Au-Mo Porphyry District, Central BC

At the Deerhorn-Cu-Au porphyry deposit, one of three north-northwest-trending passive-gas transects showed anomalous hydrocarbon concentrations at the margins of the mineralization (Figure 5; Rich, 2016). Dodecane concentrations were highest in two samples directly northeast of the deposit footprint. Concentrations of the branched alkanes 2-methylbutane and 1-ethyl-2/3-methylbenzene were anomalous in samples adjacent to mineralization in the northwest and southeast. The cyclic compounds cyclopentene and o-xylene, which have a moderate correlation across the dataset ($R^2 = 0.7$), share a similar ‘rabbit-ears’-style anomaly pattern with respect to the deposit.

The inconsistent results between the three transects suggests that the passive samplers did not reach equilibrium with soil gasses. The samplers were deployed for a period of 63 days. Since then, the manufacturer has suggested a sampling interval of at least 120 days. Additional evaluation is required to make this methodology logistically feasible in an exploration setting.

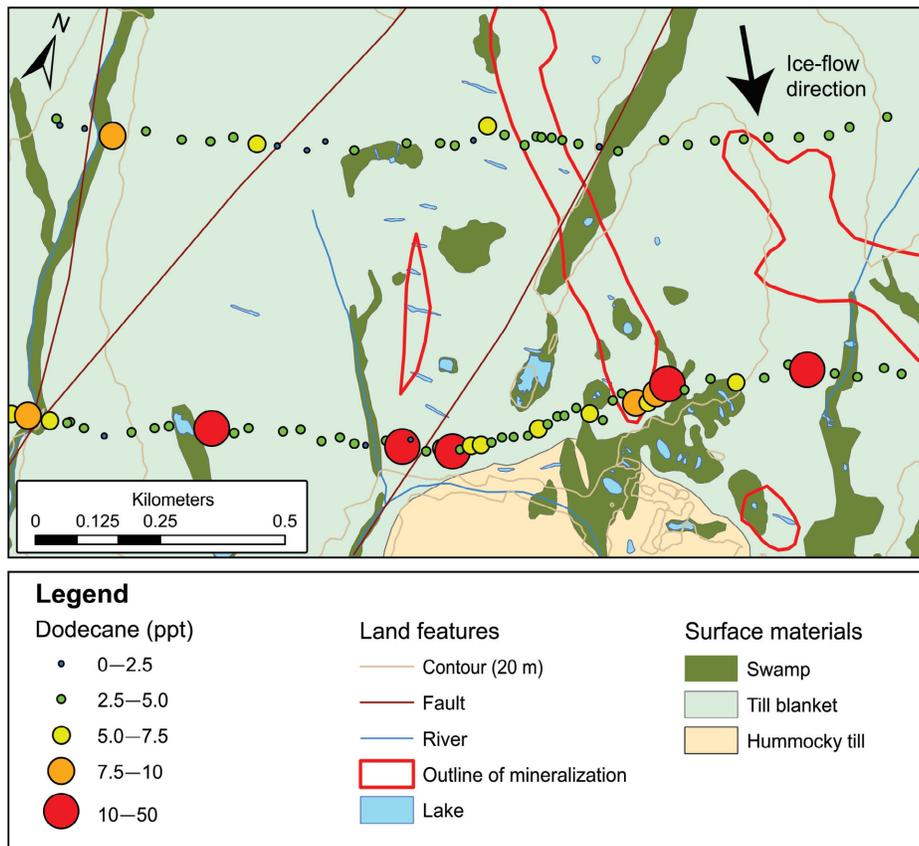


Figure 4. Passive sampler transects of the Highmont South Cu-Mo porphyry deposit. An anomalous response in dodecane detected the mineralized outline on the southern transect. Data from Chouinard (2018).

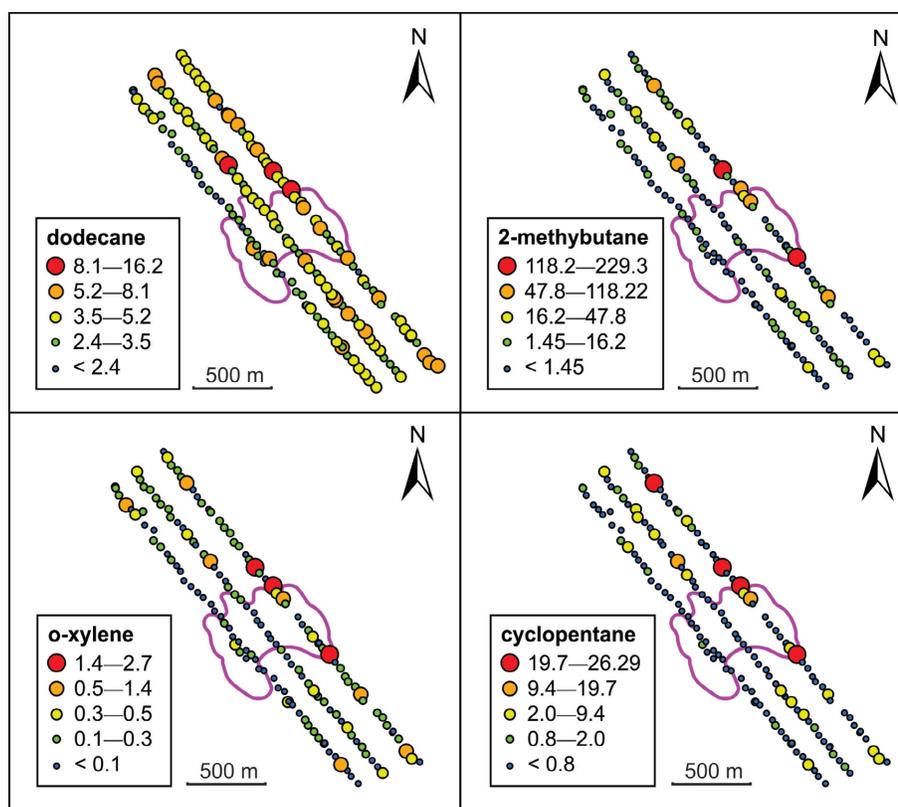


Figure 5. Results (in ppt) for AGI passive-sampler survey at the Deerhorn Cu-Au porphyry deposit. In total, 152 samplers were deployed for 63 days. Data from Rich (2016).

Current Research Directions

The Mount Washington high-sulphidation, epithermal Au-Ag-Cu deposit has historically produced 381 733 tonnes grading 0.34 g/t Au, 19 g/t Ag and 0.93% Cu (Houle, 2013, 2014). The main geological units in the study area include Triassic Karmutsen Group basalts, Cretaceous Nanaimo Group sedimentary rocks and the Eocene Mount Washington Plutonic Suite (Muller, 1998; Massey et al., 2005; Figure 6). These units are cut by a series of north-northwest-striking extension faults. The Lakeview-Domineer resource area contains a mineralized breccia zone and the Domineer vein (Houle, 2013). A previous geochemical orientation study at Mount Washington tested the response of halogens and volatile compounds in soil, snow, mountain hemlock and yellow cedar to mineralization (Heberlein et al., 2017).

As part of this project, a soil geochemical survey was carried out to test the hydrocarbon response over the Mount Washington mineralization. The grid design runs perpendicular to the strike of country rock and extends beyond the extension faults to the east and west of mineralization. A grid spacing of 50 m was centred over a mineralized breccia zone. Sample sites were selected to favour undisturbed soils, as the area is cut by a network of resource roads. At each sampling station, site duplicates were collected for

four-acid and aqua-regia ICP-MS, organic compounds and genomics analysis. Five sites were selected for vertical-profile sampling. At these sites, representative samples were taken from each soil horizon. In the Bm horizon, where practical, samples were taken at 10 cm intervals to a depth of 1 m (Figure 7). Additionally, sulphide-mineralized surface-rock samples were collected for hydrocarbon analysis. For this study, samples will be extracted in a hexane-based solvent followed by GC-MS analysis of the extract for C2–C20 hydrocarbons.

Conclusion

While results thus far have been promising, the use of organic-compound pathfinders in exploration for mineral deposits beneath cover requires more research to evaluate the hydrocarbon link between the buried mineral deposit and surface, and also to establish that anomalies are reproducible through analysis-of-variance experiments. Orientation studies by the MDRU Exploration Geochemistry Initiative have shown the effectiveness of passive collectors for identifying Cu-porphyry mineralization through cover. Key organic compounds, including long-chain alkanes, branched alkanes and aromatic compounds, show anomalous responses in soils above and adjacent to ore-deposit footprints. These compounds are linked to mineralization by microorganisms such as *Acidithiobacillus ferrooxidans*,

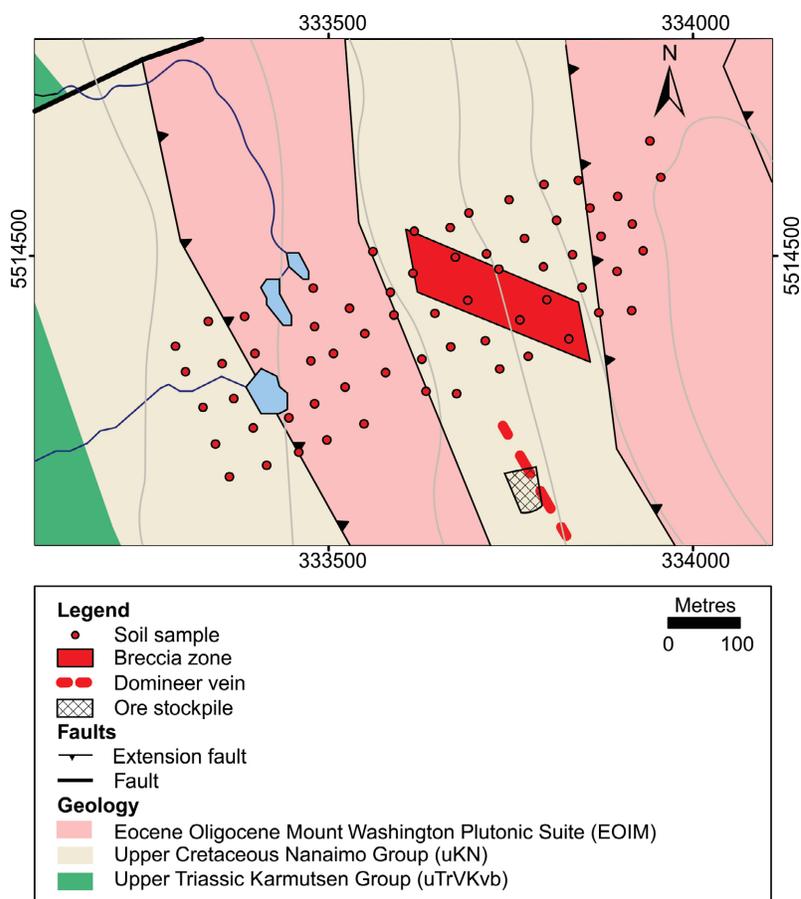


Figure 6. Geology of the Mount Washington Au-Ag-Cu epithermal deposit after Muller (1998) and Massey et al. (2005). Mineralized footprint after McDougal (1987) and Heberlein et al. (2017). A grid spacing of 50 m perpendicular to strike was chosen to target the deposit footprint and test the response of faults cutting mineralized and barren geology.

which attach to sulphides and gain energy by facilitating redox-based sulphide dissolution. Further research aims to develop and improve solvent-extraction methodologies so that organic-compound analyses may be integrated with traditional soil-sampling workflows. Upcoming results from the Mount Washington Au-Ag-Cu epithermal deposit will test the applicability of organic compounds across the Cu-porphry continuum.

Acknowledgments

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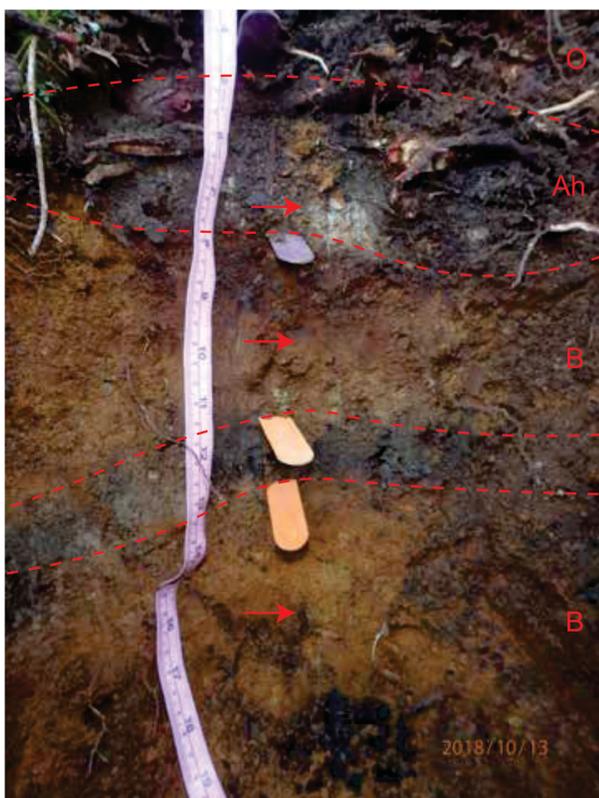


Figure 7. Representative soil profile at the Mount Washington Au-Ag-Cu epithermal deposit. Each horizon was sampled; where horizon thickness allowed, additional samples were taken at 10 cm intervals.

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