

Host phases of redox-sensitive trace metals and an evaluation of trace metal ratios as
redox proxies in Ordovician organic-rich sedimentary rocks.

by

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Author's Declaration

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Abstract

Methods for classifying bottom water redox conditions using trace metal ratios are currently being developed, which has increased the importance of identifying primary host phases. Past studies are not in agreement regarding the primary host phases of Thallium (Tl), Rhenium (Re), Molybdenum (Mo), Uranium (U), and Vanadium (V) in organic-rich sediments. Tl is thought to be predominately hosted by pyrite and clay minerals, particularly illite. The central debate for Re and Mo host phases is between pyrite and organic matter, with clay minerals being a less important host. U is found in a wide variety of host phases including carbonates, pyrite, phosphates, or organic matter. Finally, V enrichment is hypothesized to be influenced by organic matter and clay minerals. The concentrations of redox-sensitive trace metals, when normalized to Al content, have been used to identify the bottom water redox conditions during sediment deposition. In a few recent studies, researchers developed enrichment parameters of V, Re, U, and Mo, as well as Re/Mo ratios, which could be used to classify ancient depositional environments. However, it is unclear to what extent ocean redox classification schemes developed based on observations of modern marine sediments can be applied to ancient oceans.

A 2M HNO₃ acid leach was the procedure used in this study and is based on methods summarized in past work. The 2M HNO₃ leach is very effective at dissolving pyrite and can target reactive forms of organic matter and some clay minerals (especially metals adsorbed to clay mineral surfaces). For a subset of samples, total digestions were performed on the residue left behind following 2M nitric acid digestions to evaluate the amount of trace metals remaining. After the 2M nitric acid leach and subsequent total digestion of the residues, the multi-elemental analysis was done using the Agilent 8800 Triple Quadrupole Inductively Coupled Plasma Mass Spectrometer (QQQ-ICP-MS). A total of 19 rock powder samples were

sent to Activation Laboratories Ltd (ActLabs) for quantitative X-ray diffraction analysis. All samples were also previously analyzed using whole rock digestions. The mineral analysis was used in tandem with elemental data (organic and inorganic carbon, sulfur, aluminum, phosphorus) to identify the primary host phase for each redox-sensitive trace metal.

The prominent host phases for Tl are organic matter and pyrite, with some hosted in clay minerals. Re can be found within organic matter and pyrite but also exhibits the potential to be hosted in certain clay minerals. The results from this study support the previous studies that organic matter is the primary host of Mo in non-euxinic environments. U was found to have been primarily hosted by organic matter and pyrite, with some being hosted in clay minerals. The primary host phases for V within these shales are organic matter and pyrite.

Regarding local redox conditions, the trace metal ratios did not agree with each other for most cores. All cores had Mo/Al values of $<5 \mu\text{g g}^{-1}/\%$ which indicates the sediments were deposited in settings that could have been oxic, suboxic, or dysoxic. However, the V/Al and Re/Mo ratios contradict this interpretation, suggestive of anoxic and/or euxinic local redox conditions at multiple localities. The U/Al values that are between $1\text{-}5 \mu\text{g g}^{-1}/\%$ ambiguously indicate either euxinic, suboxic, or dysoxic conditions. Only one core from the Collingwood Member showed consistent agreement among proxies, pointing to oxygenated bottom waters in this case. These thresholds probably should not be used to establish the local redox conditions of bottom waters during the Early Paleozoic or Precambrian when paleogeography and global ocean redox states were significantly different from the modern ocean.

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List of Abbreviations

Al	Aluminum
Auth	Authigenic
CW	Collingwood Member
CWD	CWD
LC	Little Current Core
MF	Mount Forest Core
mL	Milliliter
Mo	Molybdenum
Mya	Million years ago
PI	Pickering Core
PS	Port Stanley Core
Re	Rhenium
RR	Rouge River Member
Tl	Thallium
TIC	Total inorganic carbon
TOC	Total organic carbon
TS	Total sulfur
U	Uranium
V	Vanadium

Chapter 1

Introduction

There is still a great deal of debate about what controls the deposition of redox-sensitive trace metals in organic-rich sediments and their lithified equivalents (Paul et al., 2023). Methods for classifying bottom water redox conditions using trace metal ratios are currently being developed, which has increased the importance of identifying primary mineral and organic host phases (Bennett & Canfield, 2020; Fan et al., 2020; Ostrander et al., 2017). Past studies are not in agreement regarding the primary host phases of Thallium (Tl), Rhenium (Re), Molybdenum (Mo), Uranium (U), and Vanadium (V) (Foltyn et al., 2022; Kiseeva & Wood, 2013; Paul et al., 2023). Chemical and environmental factors also influence the deposition of trace metals in organic rich sediments. Chemical and environmental properties include solubility, binding affinities, pH, and the type and redox states of particulates sinking through the water column. The redox states of chemical species can be influenced by bottom water and sediment conditions at deposition or early diagenesis (Bennett & Canfield, 2020). Metal concentrations in organic-rich sediments are also influenced by the size of the dissolved metal reservoir in the sedimentary basin, which in turn is determined by multiple factors including local continental, atmospheric, volcanic, and hydrothermal metal inputs into the basin, relative magnitude of the different sedimentary sinks for that metal in the basin, and the frequency of water exchange with the open ocean.

There are debates about what hosts each trace metal in organic-rich sedimentary rocks. Tl is thought to be predominately hosted by pyrite and clay minerals, particularly illite (Martin et al., 2018). The central debate for Re and Mo hosts phases is between pyrite and organic matter (Algeo & Liu, 2020). Recent data suggested that the primary host phase of Mo could be influenced by the redox conditions at the time of deposition. In environments where there was an abundance

of aqueous H_2S it was inferred that the primary hosts phases of Mo were clay minerals and pyrite. When there was limited available aqueous H_2S it was inferred that the primary host phase of Mo was organic matter (Ardakani et al., 2024; Zhou et al., 2024). In previous studies, these trace metals are often considered to be enriched in both major host phases, sometimes without clear supporting evidence. U is a well-studied and widely used trace metal for paleoredox assessment and is found in a wide variety of host phases including carbonates, pyrite nodules, or organic matter (Algeo & Liu, 2020; Romaniello et al., 2020; Vyalov et al., 2013). Finally, V enrichment is hypothesized to be influenced by organic matter and clay minerals in organic-rich sedimentary rocks (Lewis et al., 2010; Wu et al., 2021; Yongbin Zhang et al., 2015).

In previous studies, methods such as laser ablation, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), electron microprobe, atom probe tomography, and X-ray spectroscopy have been utilized to try to identify the host phases of these trace metals in organic-rich sediments and mudrocks (Algeo & Liu, 2020; Helz et al., 2011; Lewis et al., 2010; Reddy et al., 2020). Comparison of mineralogical information (e.g., from X-ray diffraction (XRD) data) with elemental concentration data is one approach but XRD detection limits are high, preventing precise quantification of small amounts of important mineral host phases like pyrite that may dominate the trace element budget of sedimentary rocks (Atienza et al., 2023). Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and electron microprobe analyses can measure the elemental compositions of solid geological materials in situ (Ardakani et al., 2024; Zhou et al., 2024). For example, current LA-ICP-MS instruments can precisely measure elements down to the ppb level using a laser spot size of $<10\text{ }\mu\text{m}$, enabling the targeting of individual minerals (Chew et al., 2021; Foltyn et al., 2022). The electron microprobe can be used to obtain geochemical data down to 300 nm spot size (Zhou et al., 2024). A variety of sequential leaching experiments followed by

ICP-MS and ICP-OES analyses have also been used to infer host phases for metals. These approaches are generally time-consuming and labor-intensive and typically do a poor job of distinguishing between pyrite and organic matter (Reddy et al., 2020). Atom probe tomography (APT) is a promising technology that can potentially distinguish between element incorporation into the pyrite crystal lattice or as nano-inclusions. However, the APT technique does have experimental limitations that are still being researched, and there are currently no existing standards for APT trace element analysis (Atienza et al., 2023; Reddy et al., 2020).

To further contribute to efforts to infer redox-sensitive metal host phases in organic-rich sediments, this study used a different approach compared to past studies: a 2M nitric acid leach in combination with elemental data from bulk digestions and mineralogical analysis. This approach was applied to two different upper Ordovician rock units of contrasting composition, and at multiple localities within a sedimentary basin to evaluate the influence of changes in depositional conditions. The dilute nitric acid leach procedure was used previously by Owens et al. (2017) to target authigenic Tl in sediments deposited under euxinic conditions. This procedure was selected for Tl primarily because of its ability to destroy pyrite, typically considered to be the main host phase of Tl. The 2M nitric acid leach will remove trace metals absorbed onto clay minerals but is not as effective in removing trace metals that substitute into the clay mineral structure. Nitric acid has weak oxidizing power below 2M concentrations (Hu & Qi, 2013) so a 2M nitric acid leach will preferentially dissolve more acid-soluble forms of organic matter. As these three phases (pyrite, organic matter, and clay minerals) are important potential host phases for the redox-sensitive trace metals of interest (Groenenberg et al., 2017; Hseu, 2004; Hu & Qi, 2013; Owens et al., 2017), the 2M nitric acid leach may provide new insights on trace metal partitioning into organic-rich sediments under different depositional conditions. This leaching procedure is also simple to use, rapid, and cost-effective. It provides

information about the relative importance of host phases at a bulk-rock scale, complementing the microscale approaches provided by laser ablation and electron microprobe analyses.

Determining the host phases for these trace metals is of interest to paleo-redox researchers working with sediments deposited in conditions quite different from the modern world. The concentrations of redox-sensitive trace metals, when normalized to Al content, have been used to identify the bottom water redox conditions during sediment deposition. In a few recent studies, researchers developed enrichment parameters of V, Re, U, and Mo, as well as Re/Mo ratios, which could be used to classify ancient depositional environments (Bennett & Canfield, 2020; Kunert & Kendall, 2023). These methods were developed by calibrating the geochemical behavior of trace metals in modern settings with already-known redox conditions (Bennett & Canfield, 2020; Kunert & Kendall, 2023). However, it is unclear to what extent ocean redox classification schemes developed based on observations of modern marine sediments can be applied to ancient oceans whose metal reservoirs may have been quite different from the modern ocean because of more widespread anoxia. This problem is particularly acute for the Early Paleozoic and Precambrian intervals of Earth's history when deep ocean anoxia was thought to be widespread (Lenton et al., 2012; Pohl et al., 2021; Yan et al., 2015).

The Ordovician Period was a time characterized by rapid paleogeography, biodiversity, climate, and ocean redox changes. During this period, there were increases in oxygen that led to more hospitable environments, leading to the Great Ordovician Biodiversification Event (GOBE). Then, in the Late Ordovician Period, one of the most significant mass extinction events recorded in Earth's history, known as the Late Ordovician Mass Extinction (LOME), occurred. Trace metals from the sediments deposited during these events have been used to track the ocean redox conditions (Algeo et al., 2016; Servais et al., 2010). It is unclear if the techniques

used by Bennett and Canfield (2020) are applicable to environments from the Early Paleozoic. The Early Paleozoic is hypothesized to have experienced ocean anoxia in epicontinental seas, an environment not well represented in the modern world (Elias et al., 2013; He et al., 2020; Pohl et al., 2021).

The samples collected for this study are from the Blue Mountain and Lindsay formations, deposited in an epi-continental sea on the continent of Laurentia (Figure 1) during the Katian. Previous studies of these samples have determined that the local redox conditions during deposition ranged from anoxic to suboxic to oxic by Lu et al. (2024) using more classical local redox indicators: metal-TOC and rhenium-molybdenum trends, sedimentary Fe speciation, organic carbon to phosphorus ratios, and molybdenum to uranium ratios. Using the methods outlined in Bennett and Canfield (2020) and Kunert and Kendall (2023), trace metal enrichments normalized to Al and Re/Mo ratios will be used to identify the bottom water redox conditions for comparisons with the interpretations reached using the more classical local redox indicators by Lu et al. (2024).



Figure 1: Map of the continents during the Late Ordovician (Katian). The continent Laurentia is marked by a pink rectangle. Modified from Cocks and Torsvik, 2021.

Research Objectives

The first objective is to place further constraints on the host phases for the trace metals Re, Tl, Mo, U, and V. It is currently debated as to what the primary host phases of these trace metals are in organic-rich sedimentary rocks. This study aims to identify the host phases of these metals by using a combination of mineralogical, bulk rock elemental data, and dilute nitric acid leach elemental data from two different Upper Ordovician organic-rich sedimentary rock units from southern Ontario. The Collingwood Member has overall higher carbonate and total organic carbon contents and was deposited in more anoxic conditions. In contrast, the Rouge River Member is richer in clay minerals, has overall lower carbonate and total organic carbon contents, and was deposited in a generally more oxidizing environment (Béland-Otis, 2015; Lu, et al. 2024; Macauley & Snowdon, 1984; Russell & Telford, 1983). In using the combination of the 2M nitric acid leach and the whole-rock digestion to identify host phases, the effectiveness of the 2M nitric acid leach at removing trace metals from organic-rich sedimentary rocks can also be evaluated.

The second objective is to use the trace metal data to identify the bottom water redox conditions using the recently published parameters outlined in Bennett and Canfield (2020) and Kunert and Kendall (2023) to determine if parameters developed based on modern world observations can be effectively applied to Ordovician marine environments. See Table 1 for a summary of the different water column classifications based on O₂ concentrations. A previous study identified the bottom water redox conditions using a combination of Fe speciation and classical elemental redox proxies (Lu et al. 2024). The results using the methods from the Bennett and Canfield (2020) and Kunert and Kendall (2023) studies will be compared to the interpretations of Lu et al. (2024) to see if there is an agreement between the two.

Table 1: Water column classifications based on O₂ concentrations

Classification	O₂ μM
Oxic	> 90 μM
Dysoxic	15-90 μM
Suboxic	0-15 μM
No O₂ Present in Water Column	
Anoxic	Non-sulfidic water column
Euxinic	Sulfidic water column

Chapter 2

Background Information

2.1 Ordovician Period

The Ordovician Period began after the end of the Cambrian Period (~485.4 Ma) and ended after nearly 42 Myr at the start of the Silurian Period (~443.8 Ma). During the Ordovician, the supercontinent Gondwana existed along with three smaller continents, Siberia, Baltica, and Laurentia (Figure 1; Servais et al., 2010). This period saw a diverse range of atmospheric oxygen levels. Cambrian and Ordovician atmospheric O₂ levels fluctuated between 2% and 11% (Krause et al., 2018). In the mid-Ordovician, an increase in oxygen levels contributed to rapid changes in biodiversity and climate that began in the Darriwilian (~467 Ma) and is hypothesized to have peaked in the mid-Katian (~457 Ma) (Edwards et al., 2017). The Ordovician Period saw an overall decrease in global temperatures, leading to changes in ocean temperatures and mixing patterns (Krause et al., 2018).

Katian Stage

The Katian began after the Sandbian (453 Ma) and ended at the start of the Hirnantian (445.2 Ma). Around the mid-Katian, decreases in global temperatures created a steep climatic gradient, enhanced organic carbon burial during expanded ocean anoxia, and increased continental weathering in a warmer climate caused CO₂ drawdown resulting in global cooling (Algeo et al., 2016; Cocks & Torsvik, 2010). Decreasing atmospheric temperatures caused increased ocean mixing, disrupting previously stratified layers. By contrast, warmer ocean temperatures slow ocean mixing and reduce the transportation rate of oxygen and other nutrients through the water column, resulting in ocean stratification (Pohl et al., 2021; Shen et al., 2018). Increased ocean ventilation resulted in nutrients and oxygen being delivered deeper into the water column, and this began a positive feedback loop in which the enhanced

ocean circulation stimulated primary productivity and thus organic carbon burial, leading to further CO₂ drawdown (Algeo et al., 2016; Marilaure et al., 2023).

Evidence of enhanced drawdown and burial of CO₂ as organic matter is the elevated TOC concentrations of Katian organic-rich sedimentary rocks (Chen et al., 2024; Lenton et al., 2012; Zhao et al., 2018). Increased TOC levels are caused by elevated organic matter burial rates, driven by enhanced primary productivity in response to the recently increased abundance of nutrients circulated by enhanced ocean mixing, and the resulting expansion of anoxic zones (oxygen minimum zones). Anoxic zones are areas where organic matter can be buried and preserved instead of decomposed (Chen et al., 2024; Zhao et al., 2018). As the drawdown and burial of CO₂ as organic matter continued, the amount of dissolved O₂ in the oceans increased. Dissolved oxygen was not consumed during the breakdown of organic matter, as the organic matter was buried instead.

There is evidence for a dramatic shift to lower global temperatures in the late Katian before the start of the Hirnantian. This shift is reflected by the change from high levels of chemical alteration via weathering (chemical index of alteration; CIA) recorded in the sedimentary rock record to low values (P. Wang et al., 2020). Higher CIA values, 70 to 80, indicate warmer, moist soil conditions (Zhang et al., 2021). In moist soil conditions, soluble cations like K⁺, Ca²⁺, and Na⁺ are removed, enriching them in less soluble cations such as Al³⁺ (P. Wang et al., 2020). Sediments within sedimentary rocks that were deposited under climates that are cool and arid have CIA values that range between 50 to 70. Some areas deposited in the late Katian record a transition from ~80 to ~65, which suggests a 10°C change (Zhang et al., 2021). Some paleo-tropical regions recorded maximum CIA value drops of ~26 in the Late Katian (Yan et al., 2010; Zhang et al., 2021).

2.2 Geochemical Background

2.2.1 Thallium

The trace metal thallium (Tl) is a newer paleo-redox proxy with a well-understood oceanic mass balance framework (Newby et al., 2021). Tl can be used as an ocean redox proxy as it has a modern ocean residence time of 18.5 kyr, which is longer than the ocean mixing time of 1500 years (Newby et al., 2021; Ostrander et al., 2017). Tl is one of the more sensitive redox proxies. Rapid stratigraphic changes in Tl isotope ratios are connected to variations in ancient global seawater Tl isotope composition (Ostrander et al., 2017). Tl has a higher sensitivity to changes in the ocean compared to other commonly used proxies such as uranium, molybdenum, and rhenium, which have longer ocean residence times of $\sim 10^5$ years (Ahrens et al., 2021). The enrichment of Tl isotopes in sediments is directly tied to the burial rates of manganese oxides in oxic conditions.

In these conditions, Tl (I) can be adsorbed onto the manganese oxide hexagonal birnessite and oxidized to Tl (III). This is one of the mechanisms in which Tl is scavenged from seawater (Nielsen et al., 2013). In anoxic conditions, Tl can be sequestered in pyrite (Fan et al., 2020; Newby et al., 2021; Owens et al., 2017; Them et al., 2018). Tl adsorption has also been observed in clay minerals and sheet silicates. Tl has a large ionic radius similar to K^+ , Rb^+ , and Cs^+ . Of the clay minerals, illite has a high affinity for Tl (Martin et al., 2018; Vaněk et al., 2020). Previous studies have shown that Tl can substitute for K^+ in biotite and K-feldspar in igneous rocks. Tl preferentially adsorbs to sheet silicates because the K site in micas is slightly larger than in K-feldspar (Coggon et al., 2014).

2.2.2 Rhenium

Rhenium is a useful redox proxy as enrichment occurs under suboxic, anoxic/non-sulfidic, and anoxic/sulfidic (euxinic) conditions (Miller et al., 2015). Re is enriched through diffusion into the sediment, and reduced Re solid phase precipitation appears to occur within sediment pore water, not in the water column (Bennett & Canfield, 2020). It is thought that this happens even in strong reducing environments such as euxinic basins. However, it has also been argued that Re may precipitate as part of sulfide minerals in the water column of euxinic basins (Helz & Dolor, 2012).

Previous studies have found that the rate of organic C respiration primarily controls Re enrichment, which influences the reducing conditions required for Re precipitation. The positive correlations between Re enrichment and shallow O₂ penetration depths have reinforced this (Morford et al., 2005). The precipitation of Re occurs in the sediment porewater, even in euxinic conditions. This is thought to be influenced by slower reaction kinetics (Bennett & Canfield, 2020; Miller et al., 2015; Ostrander et al., 2019). Re was also found to be enriched in anoxic sediments beneath productive oxygenated water columns (Bennett & Canfield, 2020; Ostrander et al., 2019). Currently, there is debate about whether the primary host phase for Re is organic matter or pyrite (Helz et al., 2011; Helz & Vorlicek, 2019; Ostrander et al., 2019; Stein & Hannah, 2014; Vyalov et al., 2013).

2.2.3 Molybdenum

Molybdenum (Mo) is a widely used paleo-redox proxy as it is soluble in oxygenated waters and becomes insoluble in sulfidic conditions (Erickson & Helz, 2000; Kendall, 2021). Previously, in numerous studies, Mo has been used to further the understanding of paleo-ocean and atmospheric redox conditions (Algeo & Tribovillard, 2009; Erickson & Helz, 2000; H. Fan et al., 2020; Ostrander et al.,

2019). However, although widely used as a redox proxy, there is still debate about what hosts Mo (Hlohowskyj et al., 2021). In some cases, ferromanganese crusts and nodules can scavenge small amounts of Mo through adsorption and co-precipitation in oxic waters (Morford & Emerson, 1999; Scott et al., 2008). The particulate Fe-Mn oxyhydroxide shuttle can increase the transfer of Mo to the seafloor when the chemocline is fluctuating and near the sediment-water interface (Algeo & Li, 2020; Lu et al., 2024; Yano et al., 2020). The result of this accelerated transfer is the enrichment of Mo_{auth} in relation to U_{auth} in anoxic sediments (Lu et al. 2024; Algeo and Tribovillard, 2009).

Molybdate converts to thiomolybdate under sulfidic conditions in the sediment pore waters or the water column. In sulfidic conditions where $H_2S_{[aq]}$ is $>11\mu M$, Mo (VI) undergoes sulfidation that produces Mo-polysulfide through reactions with sulfur. This increases Mo's vulnerability to scavenging as its geochemical behavior has been altered (Dahl et al., 2013; Erickson & Helz, 2000). Hence, Mo can be captured by Fe-sulfide minerals (e.g., pyrite), clay minerals, and organic matter (Ardakani et al., 2024; Chappaz et al., 2014; Dahl et al., 2017; Erickson & Helz, 2000; Helz et al., 2011). Restricted environments tend to have decreased sedimentary Mo enrichments even if there is bottom water anoxia because the rate of resupply of Mo from the open ocean to stratified deep waters of the basin is slow (Algeo & Lyons, 2006; Bennett & Canfield, 2020; Yano et al., 2020). In euxinic conditions, some studies have found that pyrite is the primary host for Mo (Helz et al., 2011; Helz & Vorlicek, 2019; Lewis et al., 2010; Shi et al., 2021), whereas organic matter may be the more important Mo host in non-euxinic environments (Ardakani et al., 2024; Zhou et al., 2024). It was found that in conditions Mo was mainly sequestered in the sedimentary matrix surrounding the pyrite nodules (Ardakani et al., 2024).

2.2.4 Uranium

Uranium (U) is another widely used redox proxy. Under oxygenated conditions, U(VI) is soluble, whereas in anoxic conditions, U(IV) is insoluble. In anoxic basins, U removal occurs beneath the sediment-water interface (Y. Lu et al., 2019; Shaw et al., 1994). It is dependent on metal-reducing bacteria (MRB) and common abiotic reductants such as Fe (II) (Smedley & Kinniburgh, 2023). U is commonly found in silicates and is classified as a lithophile, and in specific environments, U can also be found in carbonates (Howari et al., 2016; Romaniello et al., 2020). It has become a popular paleo-redox proxy used in paleo-ocean redox studies (Romaniello et al., 2020; Shi et al., 2021). U can be found in phosphorites, carbonates, and organic-rich sedimentary rocks within phosphate-bearing minerals, carbonate minerals, organic matter, and pyrite (Shi et al., 2021).

2.2.5 Vanadium

Vanadium (V) is enriched under anoxic conditions. In reducing continental shelf environments, it is mainly scavenged from seawater by clays (Shi et al., 2021). There are three common oxidation phases for V: V(V), V(IV), and V(III) (Bian et al., 2022; Huang et al., 2015). V(V) occurs under oxic conditions, whereas V(IV) is found under moderately reducing conditions, and V(III) can be found in anoxic conditions (Bian et al., 2022; Huang et al., 2015). Under euxinic conditions, V(V) and V(IV) can be reduced to V(III) in the presence of H₂S, which can be incorporated into organic matter or into clay minerals by replacing Al³⁺ (Bian et al., 2022). In anoxic ocean conditions, organic-rich shales deposited under anoxic seawater often contain high levels of vanadium, which is hypothesized to be influenced by black shale's high organic carbon content (Ardakani et al., 2024; Breit & Maynard, 2006; Hirner & Xu, 1991; Riley & John, 1982).

Several studies have demonstrated that V can complex with organic matter (Ardakani et al., 2024; Bian et al., 2022; Ferrer & Baran, 2001; Huang et al., 2015; Templeton & Chasteen, 1980). Bian et al. (2022) proposed that V(IV) can become associated with organic matter under moderately reducing conditions. In contrast, in anoxic and euxinic conditions, V(III) can become incorporated into clay minerals or associated with organic matter and pyrite (Ardakani et al., 2024; Bian et al., 2022). Typical host phases for V in sediments include magnetite, Fe-Mn oxyhydroxides, illite, and black shales with phosphate and organic matter (Ardakani et al., 2024; Bian et al., 2022; Huang et al., 2015; Shi et al., 2021). In modern oceans, Mo, U, Re, Tl, and V have been observed to be enriched together in euxinic basins (Bennett & Canfield, 2020).

Table 2: Redox-sensitive trace metals and possible host phases in organic-rich sedimentary rocks

Redox-sensitive Trace Metal	Possible Host Phases
Thallium	Fe-sulfide Minerals, Clay Minerals
Molybdenum	Fe-sulfide Minerals, Organic Matter, Clay Minerals
Rhenium	Fe-sulfide Minerals, Organic Matter
Uranium	Fe-sulfide Minerals, Organic Matter, Carbonates, Phosphates
Vanadium	Fe-sulfide Minerals, Clay Minerals, Organic Matter

2.3 Redox Classification using Trace Metal Ratios

In Bennett and Canfield (2020), data collected from marine environments with diverse oxygen conditions were compiled from published and unpublished sources. Only data that was from sediments that were less than 10,000 years old and were from areas that have been well-characterized were considered. The oxygen conditions ranged from oxic environments to permanently euxinic basins to unrestricted continental margins, which can have oxic conditions, perennial oxygen minimum zones (P-OMZ), or seasonal oxygen minimum zones (S-OMZ). Data from uncertain depositional environments were excluded. It was explained that sediments deposited on the upper or lower margin of a P-OMZ were excluded to minimize possible chemocline influence.

In comparison, data from oxic environments were only included if there was no evidence of anaerobic respiration in the water column. The data from different environments were analyzed together so that enrichment trends of trace metals could be observed. Trace metal concentration data were normalized by dividing it by Al concentration to account for variable terrigenous detrital inputs to different environments. It was argued that due to the variety of environments being analyzed, normalization using Al (wt%) was the most objective approach to determine the threshold values used to differentiate the environments (Bennett and Canfield, 2020).

It was suggested that the sediment was locally deposited under euxinic conditions if the enrichment of Mo was $>5 \mu\text{g g}^{-1}/\%$ and V was between $46\text{--}23 \mu\text{g g}^{-1}/\%$. However, if the enrichment of V was $>46 \mu\text{g g}^{-1}/\%$ in combination with the enrichment of U $>5 \mu\text{g g}^{-1}/\%$ and Mo $>5 \mu\text{g g}^{-1}/\%$, the sediments were deposited under anoxic non-euxinic conditions. Finally, if the enrichment of V was $<23 \mu\text{g g}^{-1}/\%$, Mo $<5 \mu\text{g g}^{-1}/\%$, and U $>1 \mu\text{g g}^{-1}/\%$, this was indicative of oxygenated waters under a perennial OMZ (P-OMZ). In oxic environments, Re values are $<1.3 \text{ ng g}^{-1}/\%$, and Mo values are $<0.4 \mu\text{g g}^{-1}/\%$ (Bennett and Canfield, 2020).

Based on the same dataset for modern environments used by Bennett and Canfield (2020), Kunert and Kendall (2023) also explored thresholds to identify redox conditions using Re/Mo. It was determined that low-O₂ environments within P-OMZs (O₂ < 5 μM) could be identified by Re/Mo_{auth} ratios of 2-10 ppb/ppm. Oxic and dysoxic environments below P-OMZs could be differentiated by ratios > 10 ppb/ppm. Because fully anoxic environments within P-OMZs and euxinic environments both contain low Re/Mo_{auth} (< 2 ppb/ppm), the V/Al and U/Al ratios identified by Bennett and Canfield (2020) can be used as proxies to distinguish between these environments (Kunert & Kendall, 2023). The application of these techniques to ancient marine environments, particularly the Paleozoic and Precambrian, has not undergone evaluation, and it is uncertain if the outlined thresholds are appropriate for the Ordovician.

Chapter 3 Geological Setting

3.1 Laurentia

During the breakup of Rodinia (750-633 Ma), Laurentia had separated from the rest of the continents and became situated along the equator, resulting in the opening of the Iapetus Ocean (Cawood, 2005; Elias et al., 2013; Meert & van der Voo, 1997). Through the Ordovician Period, Laurentia underwent significant changes after colliding with a volcanic arc during the final phase of the Taconic Orogeny. This orogenesis event resulted in continental uplifts, mountain building, and the development of a foreland basin, which altered the structure of the Iapetus Ocean and inland seas (Cawood, 2005; Theses & Banas, 2012). The restructuring of inland seas transformed the currents and degree of oxygenation which decreased the biodiversity of the marine biota (Elias et al., 2013).

3.2 Southern Ontario during the Ordovician Period

During the Paleozoic, parts of the Southern Ontario area were covered by a marine environment which is why most of the rocks in Southern Ontario consist of nearly flat-lying marine Paleozoic rocks overlying the Precambrian basement (Frizzel et al., 2011; Gbadeyan & Dix, 2013; Hamblin, 2008). These Paleozoic rocks are primarily carbonates, evaporites, and clastic sediments that range in age from Cambrian to Devonian (Armstrong & Carter, 2010; Brigham, 1971; Frizzel et al., 2011). During the Late Ordovician, Laurentia was at the equator, so the climate of this area has been hypothesized to have been subtropical with the potential to be seasonally arid before the Katian. During the Late Ordovician, changes began to occur. The Taconic Orogeny resulted from several volcanic island arcs colliding along the eastern cratonic margin of Laurentia (Hamblin, 2008; Van Staal et al., 2009). This collision resulted in the development of the Appalachian Foreland Basin (Hamblin, 2008). The

geological landscape of Southern Ontario has two other notable structural features that are a result of tectonic activity, the Algonquin Arch and the intracratonic Michigan Basin (Brigham, 1971; Frizzel et al., 2011; Gbadeyan & Dix, 2013; Hamblin, 2008).

3.2.1 Algonquin Arch

The Algonquin Arch is a forebulge that spans from northeast to southwest southern Ontario. The arch, as a result of tectonic forces, separated and acted as a structural control for the Michigan Basin and the Appalachian Basin depositional patterns (Frizzel et al., 2011). The underlying Southwestern Ontario bedrock strata dip shallowly southwest along the Algonquin Arch and then down the flank of the arch. The dip changes directions to the west into the Michigan Basin and south into the Appalachian Basin (Armstrong and Carter, 2010).

3.2.2 Michigan and Appalachian Basins

The Michigan Basin is a carbonate-dominated circular intracratonic and evaporite basin (Armstrong and Carter, 2010). The central portion of the Michigan Basin was deposited during the existence of an inland sea, while the outer part is hypothesized to have formed because of tectonic expansion in the Cambrian and is the result of crustal subsidence (Frizzel et al., 2011; Howell & van der Pluijm, 1990). The siliciclastic-dominated Appalachian foreland basin formed because of tectonic loading during the Taconic Orogeny. The Appalachian Basin is elongated and has siliciclastic-dominated geology (Armstrong and Carter, 2010).

3.3 Formations of Interest

The Upper Lindsay, Blue Mountain, Georgian Bay, and Queenston Formations were deposited in a shallowing upward succession during the Taconic orogenesis event. The succession begins with the upper Lindsay Formation's marine black shale

to grey shale and ends with the Queenston Formation's coarse nonmarine red siltstone and sandstone (Hamblin, 1999; Russell & Telford, 1983).

Global Division		Time Slice	Age (Ma)	North America Stages	Graptolite Zone (southern Ontario)	Conodont Zone (southern Ontario)		Stratigraphy (southern Ontario)
Series	Stages					North Atlantic	Midcontinent	
Late Ordovician	443.4 ± 1.5 Hirnantian	Hi2	445	Gamachian	?	?		?
		Hi1						
	445.2 ± 1.4 Katian	Ka4		Richmondian	?	?	<i>R. symmetricus</i>	Queenston Fm.
								Georgian Bay Fm.
		Ka3			<i>A. grandis</i>			
		Ka1		Edenian	?	?	?	Cobourg Fm.

Figure 2: Stratigraphic column of Southern Ontario. Modified from Lu et al. (2024). Formations of interest are marked with a red outline.

3.3.1 The Lindsay Formation

The Lindsay Formation is the uppermost formation of the Trenton Group. It is comprised of grey limestone and dark brown to black calcareous organic-rich sedimentary rocks. The Upper Lindsay Formation, known as the Collingwood Member, is interpreted as having been deposited below a storm wave base (Brett et al., 2006). The marine organic-rich sedimentary rocks of the Upper Lindsay Formation were deposited around the time of the Taconic Orogeny and indicate a semi-deeper water depositional environment (Brett et al., 2006; Hamblin, 1999). The Upper Lindsay Formation contains regionally anoxic facies that developed after the foundering of the underlying Trenton carbonate ramp following sea-level rise. It has

mixed lithology, including shaly limestone, calcareous shales, and organic-rich marlstone, with some fossiliferous interbeds (Hamblin, 2008). The transition from carbonates to the lower member of the Lindsay Formation to the organic-rich sedimentary rocks of the Collingwood Member is interpreted to result from the deepening of shelf areas. This was either caused by an increase in the sea level or the existence of a peripheral foreland basin that was produced by subsidence as a result of orogenic thrust and increased sedimentation (Brett et al., 2006).

3.3.2 The Blue Mountain Formation

The Blue Mountain Formation is the lowermost formation of the Nottawasaga Group and is primarily interpreted as having been deposited in both shallow and deep marine environments (Hamblin, 1999; Russell & Telford, 1983). This formation is comprised of uniform dark grey shales at the base with sandstones and coarse siltstones towards the upper portion, reflecting an overall trend towards shallower water conditions. It contains very few fossils and ranges from 35m to 75m in thickness, with a general thinning trend towards the north (Hamblin, 1999). The Blue Mountain Formation is enriched in terrigenous sediment, resulting from an influx of siliciclastic sediment caused by the Taconic Orogeny. The Blue Mountain Formation's lowest portion is called the Rouge River Member. The Rouge River Member comprises dark grey to black siliciclastic shales and several carbonate-rich interbeds (Armstrong & Carter, 2010; Russell & Telford, 1983). Above the Rouge River Member is the Thornbury Member, characterized by bluish-grey siliciclastic shales with carbonate and siltstone interbeds (Armstrong & Carter, 2010; Hamblin, 2008).

3.3.3 The Collingwood Member

Composition and Notable Features

The Collingwood Member has a maximum thickness of 12 m that spans from Toronto to Georgian Bay. This member gradationally overlies the lower member (equivalent to the Cobourg Formation) limestones. The composition of the Collingwood Member is a mix of shaly limestone, calcareous mudstone, and finely laminated black organic-rich marlstone, which are ‘cyclically’ packed. This depositional pattern has been interpreted to result from short-term sea-level variations (Brett et al., 2006; Russell & Telford, 1983). The most common minerals found in the Collingwood Member by weight % are calcite (50-58%) and clays (29-35%). Other minerals found within the member include quartz, dolomite, pyrite, ankerite, and potassium feldspar (Béland-Otis, 2015). Across the Collingwood Member’s contact with the Rouge River Member, it has been noted that there is an abrupt decrease in carbonate and organic carbon content (Armstrong & Carter, 2010; Russell & Telford, 1983).

The Collingwood Member’s TOC content ranges from 0.9-11% with an average of 3.9%, which indicates the past environment had a high organic productivity rate and was likely deposited along the platform edge (Hamblin, 1999; Russell & Telford, 1983). Past work done on the Collingwood Member has focused on hydrocarbon exploration, and it was found that this member would be a promising source due to the kerogen content and thermal maturity. The member ranges from marginally mature in the Georgian Bay area to mature in the Toronto area. Normal marine type II kerogen, dominated by bituminite and alginite, is found throughout the member (Brett et al., 2006; Russell & Telford, 1983). A rich fossil abundance has been observed within the Collingwood member, with an average of five species in each bed (Brett et al., 2006).

Fossils Found in the Collingwood Member

Common organisms that are found within the Collingwood Member are trilobite species such as *Pseudogygites latimarginatus* and *Triarthrus eatoni*, brachiopods, which were the most diverse in species, graptolites, and cephalopods, the largest being *Endoceras proteiforme* (Brett et al., 2006; Verma, 1979). *T. eatoni* is a Late Ordovician trilobite that is preferential to O₂-depleted environments, evidence that the platform environment could be suboxic (Brett et al., 2006; Cisne, 1973). The *P. latimarginatus* trilobite is commonly found in Upper Ordovician rocks. Based on the species found within the formation, it has been proposed the Collingwood Member was deposited during the Maysvillian (~452-449.5 Ma), which is within the timeframe of the Katian (George et al., 2003). Researchers also noticed that some of the fossils found in the Collingwood Member had well-developed eyes, which indicate low light conditions. Overall, the low levels of marine biodiversity within this member imply that a portion of the Collingwood Member was deposited in a deep-water environment with low O₂ and light conditions (Brett et al., 2006).

3.3.4 The Rouge River Member

The Rouge River Member (449 Ma) is another significant source of hydrocarbons. The Rouge River Member is thermally mature and has 1-5% TOC. It also contains normal marine type II kerogen dominated by bituminite and alginite (Hamblin, 1999).

Composition and Notable Features

It has a maximum thickness of 60 m and is comprised mainly of dark grey to black non-calcareous siliciclastic shales and carbonate-rich interbeds (Armstrong & Carter, 2010; Friedman, 1996; Russell & Telford, 1983). The Rouge River Member's upper contact is with the bluish-to-greyish siliciclastic shales of the Thornbury Member (Armstrong & Carter, 2010). The underlying contact with the Collingwood Member may be gradational or sharp. There is also a phosphatic bed along the bottom

contact, which has been interpreted to be a maximum flooding surface (Béland-Otis, 2015; Brett et al., 2006; Russell & Telford, 1983). The Rouge River Member has a high concentration of terrigenous clays, and this is thought to have been influenced by an increase of siliciclastic sediments during the Taconic Orogeny (Béland-Otis, 2015). It has been interpreted that this member was deposited below the storm wave base because of the lack of storm-wave induced sedimentary structures (Johnson, et al. 1992).

3.4 Previous Geochemical Work (Rouge River and Collingwood Members)

Extensive geochemical work was previously done on the Rouge River (RR) and Collingwood (CW) Members. Both members were analyzed using strontium isotope ratios, which correlated with geological and climatic events (Hannigan et al., 2010). The bottom water conditions of both members were previously analyzed using redox-sensitive trace metals and sedimentary Fe speciation (Lu et al., 2024). Paleosalinity was determined using Sr/Ba and S/TOC ratios (Lu, 2022). U isotopes were also applied to both members as global ocean redox tracers (Lu et al., 2024).

3.4.1 Strontium Isotope Ratios

The strontium isotope ratios recorded from Upper Ordovician rocks in southern Ontario initially decreased and then sharply increased. When the Sr isotope curve was compared with global seawater, the lower Collingwood Member and lower-middle Blue Mountain Formation (including the RR Member) indicate a primary seawater $^{87}\text{Sr}/^{86}\text{Sr}$ signal. Comparatively, an abrupt increase of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was observed in the middle-upper Blue Mountain Formation and overlying Georgian Bay Formation. The sharp increase has been correlated with basin isolation from the open oceans and an influx of freshwater caused by the Taconic Orogeny. The changes in Sr isotope ratios also correlate with brachiopod oxygen isotope data that correspond with

cooling in the Katian starting in the late Maysvillian from $\sim 30\text{-}35^{\circ}\text{C}$ to $\sim 28^{\circ}\text{C}$ in the Richmondian (Brookfield & Hannigan, 2021). This temperature change has been hypothesized to have been the catalyst for the ‘Richmondian Invasion.’ The Richmondian Invasion was an influx of species into the more hospitable environment of the Cincinnati region in Ohio during the Katian (Brookfield & Hannigan, 2021; Hannigan et al., 2010).

3.4.2 Paleosalinity

The salinity of the water column during the deposition of the CW and the RR Member was determined to be brackish/marine using Sr/Ba ratios (Lu, 2022). Seawater has higher concentrations of Sr than freshwater, whereas the reverse is true of Ba. These elements are not redox-sensitive, so clay minerals can capture enrichments of Ba and Sr that are representative of the overlying water column (Wei & Algeo, 2020). Brackish/marine paleosalinity is also supported by sedimentary sulfur to total organic carbon ratios (S/TOC). S/TOC ratios can also be used as paleosalinity proxies because of the significant difference between the seawater S concentration (higher) and freshwater S concentration (lower). S/TOC ratios are not dependent on clay mineral adsorption dynamics but instead rely on reduced sulfur (sulfide) and organic carbon accumulation in the sediment. The drawback of using S/TOC is that it can only distinguish freshwater from brackish/marine conditions (Wei & Algeo, 2020). The CW Member had a S/TOC ratio of 0.21 ± 0.17 (1SD), and the RR Member had a ratio of 0.66 ± 0.37 (1SD). Both ratio values support the above hypothesis of brackish/marine conditions and that there was some water exchange between the local basin and the open ocean (Lu, 2022).

3.4.3 Iron Speciation Data and Trace Metal Data

Iron speciation is commonly used to differentiate local bottom water redox conditions during sediment deposition (Dahl et al., 2010; Hammarlund et al., 2012;

Poulton & Canfeld, 2011; Raiswell et al., 2018; Y. Wang et al., 2019). The values of the four groups of Fe minerals, specifically carbonate, pyrite, ferric oxide, and magnetite, are summed together to form highly reactive Fe (Fe_{HR}) (Y. Wang et al., 2019). Carbonate, ferric oxide, and magnetite have the potential to react with sulfide in the water column or in the sediment pore water fluids during early diagenesis to form pyrite. The iron groups can distinguish between oxic, ferruginous, and euxinic conditions using two ratios, Fe_{HR}/Fe_T , and Fe_{py}/Fe_{HR} where Fe_T is total iron and Fe_{py} is pyrite iron (Y. Wang et al., 2019).

The value of the Fe_{HR}/Fe_T ratio can be used to determine local bottom water redox conditions (Lu et al., 2024; Y. Wang et al., 2019). Fe_{HR}/Fe_T ratios distinguish between oxic and anoxic bottom water conditions. Agreed upon ranges are >0.38 is indicative of anoxic bottom water conditions, whereas <0.22 may indicate oxic bottom water conditions. Values that fall between 0.22-0.38 are unclear and can mean either anoxic or oxic bottom waters (Poulton & Canfeld, 2011; Raiswell et al., 2018). Fe_{py}/Fe_{HR} ratios are used when it has been determined that the water column is anoxic using Fe_{HR}/Fe_T ratios. The values of Fe_{py}/Fe_{HR} ratios can further identify the water column state: >0.8 = euxinic, <0.7 = ferruginous, 0.7-0.8 = ambiguous (Y. Wang et al., 2019). In addition to Fe speciation, the $C_{org}:P$ molar ratios can be applied to organic-rich sedimentary rocks to determine the bottom water conditions during deposition. $C_{org}:P$ molar ratios that are <50 generally indicate oxic-suboxic conditions, and those that are >50 indicate anoxic conditions, with the actual threshold depending on local sedimentary basin environmental conditions (Algeo & Liu, 2020; Lu et al., 2024).

The CW had Fe_{HR}/Fe_T values between 0.12-0.36 and $Fe_{py}/Fe_{HR} <0.7$. These values could indicate either oxic or anoxic local conditions, so more classical redox

indicators like trace metal EFs, covariation patterns between trace metal enrichment factors ($EF = [metal / Al]_{sample} / [metal / Al]_{detrital\ background}$), and each of TOC and sulfur content, and Mo/U ratios were also considered. Higher redox-sensitive EFs and higher Mo/U ratios suggest more reducing conditions in the sediments but are more ambiguous regarding the lower water column redox state. The average $C_{org}:P$ ratio was 100.3 ± 63.1 (SD). Collectively, the data suggested that deeper water samples from the CW were deposited in anoxic conditions, whereas shallow water samples were deposited under oxic conditions (Lu et al., 2024). The RR had $Fe_{HR}/Fe_T < 0.30$ and Fe_{py}/Fe_{HR} values that ranged between 0.00 and 0.85. Most of the Fe speciation data suggested oxic-suboxic bottom water conditions, except for a few outliers. Finally, the average $C_{org}:P$ ratio was 32.5 ± 14.6 (SD), which also indicates oxic-suboxic bottom water conditions (Lu et al., 2024).

3.4.4 Global Ocean Redox Dynamics Determined by Uranium Isotope Data

The $\delta^{238}U_{non-detrital}$ was used to constrain the coeval global seawater $\delta^{238}U$ (Lu et al., 2024). The estimated seawater $\delta^{238}U$ during deposition was $-0.87 \pm 0.05\text{‰}$ to $-0.64 \pm 0.08\text{‰}$ and, compared to the modern seawater value of $-0.39 \pm 0.04\text{‰}$, suggests more widespread ocean euxinia during deposition of the CW Member.

In the RR Member, the $\delta^{238}U_{non-detrital}$ estimated the $\delta^{238}U$ coeval seawater. A narrow range of $\delta^{238}U_{non-detrital}$ values was observed for the RR, with an average of $-0.32 \pm 0.12\text{‰}$. The contemporaneous global seawater $\delta^{238}U$ was estimated to be between $-0.62 \pm 0.12\text{‰}$ and $-0.42 \pm 0.12\text{‰}$. The estimated seawater $\delta^{238}U$ increased from the CW to the RR, which indicates a decrease in the global extent of euxinia during the deposition of the RR (Lu et al., 2024).

Chapter 4: Sample Descriptions and Methodology

4.1 Sample Descriptions

Drill core samples of the RR and CW Members were collected from multiple cores housed at the Ontario Oil, Gas, and Salt Resources Library (London, Ontario) and the Ministry of Energy, Northern Development and Mines (Sudbury, Ontario). The St. Joseph (SJ), CLGD No. 7A Collingwood (CWD), Pickering (PI), and Little Current (LC) cores from the CW Member were uniformly deposited as black to brown organic rich marl. This contrasts with the Mount Forest core (MF) which had cyclical depositional patterns of TOC-poor and TOC-rich layers (Lu et al., 2024). Sharp phosphatic contacts were observed between the RR and CW Members in the Port Stanley (PS) and MF cores. A gradational contact between the RR and CW members was observed in the SJ, CWD, PI, and LC cores (Lu et al., 2024). In all drill cores, the Rouge River Member comprises monotonic grey, dark grey, or black shales.

The PS and PI cores originated from the Appalachian Basin, the LC and SJ cores from the Michigan Basin, and the MF and CWD cores from nearby the Algonquin Arch. The sediments from cores that were collected from the two basins farther from the arch were determined to have been deposited in deeper water environments, while the sediments from cores from near the arch were deposited in shallower water environments (Lu et al., 2024). Samples of organic-rich calcareous marls were selected from the CW Member whereas samples of organic-rich shale were selected from the RR. Samples with macroscopic pyrite nodules, carbonate/quartz veins, and fossils were not used. The samples used in this study were previously assessed for diagenetic influences using petrographic and geochemical indicators (Lu et al., 2024). Rocks that have undergone significant diagenetic alteration would not have been considered for this study, as diagenesis can

alter the chemical composition and physical form of the rock. There was evidence that the carbonate-rich samples did experience minor diagenetic alteration, as there were lower $\delta^{18}\text{O}$ values for all samples and higher Mn/Sr ratios for some. However, it was concluded that there was no compelling evidence for significant diagenetic alteration (Lu et al., 2024).

From the RR, 56 samples were analyzed from the PS core, 10 from the MF core, 17 from the SJ core, and 16 from the PI core. The analysis of the CW Member consisted of 11 samples from the SJ core, 15 from the LC core, 14 from the MF core, and 7 from the CWD core. As mentioned, all the listed samples have already been analyzed for bulk elemental concentrations, and some were also analyzed for uranium isotopes and Fe speciation. Using numerous cores across the two members can show how spatial variations in the depositional environment, such as water depth and local redox conditions, may have influenced the sediment and trace metal deposition (Lu et al., 2024).

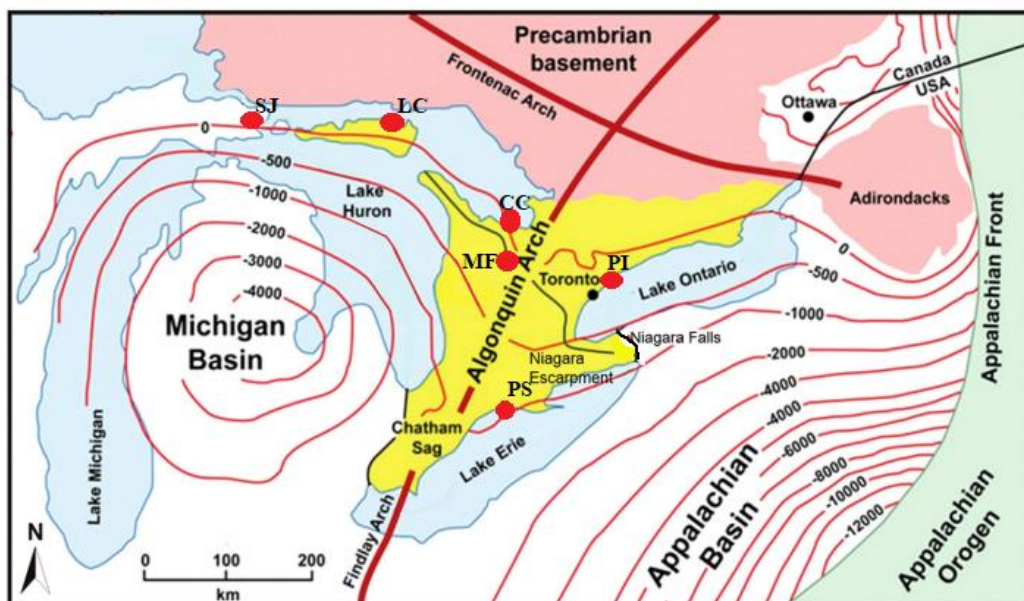


Figure 3: Regional geological setting of Southern Ontario, with sample collection sites (red dots). PS- Port Stanley, LC- Little Current, PI- Pickering, and CC- Collingwood (modified from Perras et al. 2014). Thinner red lines are contours of Precambrian basement, thicker red lines are axes of regional arches, yellow shading is Paleozoic sedimentary rocks of Southern Ontario, pink shading is the Precambrian Basement, and white are other Paleozoic sedimentary rocks (Lu, et al., 2024).

4.2 2M Nitric Acid Leach

The procedure followed is based on methods summarized in past work (Ostrander et al., 2017; Rehkämper & Halliday, 1999). A weighed amount (1.0-1.2 g) of rock powder was put into 15 mL Teflon beakers. The powder was then leached in 6 mL of 2M HNO_3 for 16 hours at 110°C. Samples were then removed from the hotplate and, after cooling, transferred into 15 mL centrifuge tubes. The original Teflon beakers were rinsed with 1 mL of ultra-pure water to ensure all the residual sediment was transferred into the centrifuge tube. Samples were centrifuged at 4500 rpm for 5 minutes at a time. The leachate was then slowly pipetted to avoid transferring solids from the centrifuge tube into a new clean 15 mL Teflon beaker. Samples were re-centrifuged when too many floating solids could not be avoided. The leachate was then dried down on a hot plate at 110°C. To ensure that any small amounts of

particulate or dissolved organic matter were destroyed (to prevent matrix effects during mass spectrometry analysis), 2 mL of concentrated, trace-metal grade HNO_3 and 2 mL of concentrated trace-metal grade HCl were added to the Teflon beakers and left for 24 hours at 110°C and then dried down. This step was repeated if there was any organic matter still present. Samples were stored in 6 mL of 6M HCl with three drops of 0.5% HF until they were ready to be analyzed.

4.3 Total Digestion of Residual Sediment

For a subset of samples, total digestions were performed on the residue left behind following 2M nitric acid digestions. The residual sediment from the centrifuge tubes was transferred into crucibles and then ashed overnight at 550°C . Once the crucibles had cooled, the powder was transferred into 15 mL Teflon beakers using ultrapure water. Samples were then digested for 48 hours in 2.5 mL of trace-metal grade concentrated HNO_3 and 0.5 mL of trace-metal grade concentrated HF . After being dried, samples were digested using 1 mL trace-metal grade concentrated HNO_3 and 3 mL trace-metal grade HCl for 48 hours, then dried on a hot plate. The final digestion uses 2 mL of trace-metal grade HCl for 24 hours at 110°C . In some instances, the samples had not fully dissolved; in this case, the HNO_3 - HCl and HCl digestions were repeated until they were fully dissolved. After fully dissolving the samples, they were stored in 6 mL of 6M HCl with three drops of 0.5% HF .

4.4 Multi-Elemental Analysis

After the 2M nitric acid leach and subsequent total digestion of the residues, aliquots were taken for multi-element analysis. The aliquot volume from the digested solution was calculated to prepare samples for analysis using a dilution factor of 5000. True dilution factors were calculated using the sample powder, digested solution, aliquot from the digested solution, and final diluted sample weights. The aliquot volume was pipetted into 7 mL Teflon beakers and dried at 110°C . 1 mL of

2% HNO₃ was added and dried to remove all the HCl. The Teflon beaker was filled halfway with 2% HNO₃, swished vigorously, left to sit for an hour, and then transferred into a 15 mL centrifuge tube. Another 3.5 mL of 2% HNO₃ was added to the Teflon beaker, swished, and then transferred to the centrifuge tube. The centrifuge tube was then filled up to 10 mL using 2% HNO₃, adding two drops of 0.5% HF.

The multi-elemental analysis was done using the Agilent 8800 Triple Quadrupole Inductively Coupled Plasma Mass Spectrometer (QQQ-ICP-MS). Elements Sc, Ge, In, and Bi were used as internal standards to correct signal drift. Blank samples were measured alongside samples to detect any contamination. Blanks accounted for <1% of the elements analyzed. The relative standard deviation values (RSD) were typically <5% and always <10%. To ensure accuracy, duplicate samples were analyzed alongside the original samples, and all duplicates were in good agreement with the original samples. Instrument accuracy was verified by multiple analyses of the United States Geological Survey water standards (T207, T211, T225, T227, T231) during each analytical session. Procedural accuracy for ashing, followed by total digestion of organic-rich sedimentary rocks, has been verified by analyses of the USGS SBC-1 (Brush Creek Shale) and SGR-1b (Green River Shale) secondary standards.

4.5 External Laboratory Procedures

4.5.1 X-Ray Diffraction

19 rock powder samples were sent to Activation Laboratories Ltd (ActLabs) for quantitative X-ray diffraction analysis. From the RR Member, there were 4 samples from the PS core, 2 from the MF core, and 3 from the SJ core. From the CW Member, there were 4 samples from the LC core, 3 from the SJ core, 1 from the MF core, and 3 from the CC core.

X-ray diffraction was performed at ActLabs. Corundum was used as an internal standard and was mixed with a portion of each sample before being loaded into the standard holder. X-ray diffraction analysis was performed on a Bruker D8 Endeavour diffractometer that was equipped with a Cu X-ray source (ActLabs, 2022). The diffractometer operated under the following parameters: 40 kV and 40 mA; range 4-70 deg 2θ ; step size 0.02 deg 2θ ; time per step 0.5 sec; fixed divergence slit, angle 0.3°; sample rotation 1 rev/sec (ActLabs, 2022).

Minerals were identified using the PDF4/Minerals ICDD database, and the quantities were determined using the Rietveld method. This method's calculations are based on the full diffraction pattern from the crystal structure data. The crystalline mineral quantities were then recalculated using a known percent of corundum, the remainder, up to 100%, was considered amorphous material (ActLabs, 2022).

Chapter 5: Results

5.1 Mineralogical Data

Table 3 reports the mineral abundances for the 19 selected samples from the RR and CW; see Appendix A for the complete dataset. The samples from the RR had high muscovite/illite content (average of 25.8 wt%) compared to the CW (average of 8 wt%) (Table 3). The average pyrite content was higher in the RR (2 wt%) than in the CW (0.8 wt%). The CW had a high average concentration of calcite, 44.9 wt%, and the RR contained a lower average calcite content of 12.7 wt%. In the sections below, the concentrations of redox-sensitive metals from bulk-rock digestions (from Lu et al., 2024) were compared with mineral abundances. The P values for each trace metal and mineral were evaluated. P-test values that were >0.05 were considered as no statistically significant correlation, whereas values <0.05 mean a statistically significant correlation.

Table 3: Mineral concentration ranges for both the CW and the RR

<i>Mineral</i>	<i>Rouge River Member</i>	<i>Collingwood Member</i>
	<i>Conc. wt%</i>	<i>Conc. wt%</i>
<i>Quartz</i>	16.4-38.6	3.0-27.7
<i>K Feldspar</i>	1.7-8.5	2.0-8.6
<i>Muscovite/Illite</i>	12-31.8	1.0-27.6
<i>Chlorite</i>	1.9-9.5	0.3-4.9
<i>Calcite</i>	1.6-47.1	3.8-95.5
<i>Dolomite</i>	0.3-12.5	0.3-24.5
<i>Fe Dolomite- Ankerite</i>	0.4-9.1	0.2-17.7
<i>Pyrite</i>	0.3-3.6	0.2-2.5

5.1.1 Thallium

Table 4 shows the correlation data between Tl and the analyzed minerals from both members of interest. No correlations were observed in the RR Member. There were notably strong positive correlations between Tl concentrations with quartz, chlorite, muscovite/illite, and pyrite in the CW Member. An inverse correlation was observed between Tl concentration and calcite abundance for the CW Member. The samples analyzed from the RR had a Tl concentration range of 0.63-0.81 ppm and an average concentration of 0.70 ppm. The concentration of Tl from the CW samples ranged from 0.05-0.8 ppm with an average concentration of 0.23 ppm.

Table 4: Tl correlations with analyzed minerals from both the RR and CW

Mineral	Rouge River Member		Collingwood Member	
	<i>p-value</i>	<i>r-value</i>	<i>p-value</i>	<i>r-value</i>
Quartz	0.37	0.34	<0.001	0.97
K Feldspar	0.74	-0.13	0.35	0.31
Muscovite/Illite	0.31	0.38	<0.001	0.97
Chlorite	0.45	0.29	<0.001	0.96
Calcite	0.48	-0.27	0.01	-0.72
Dolomite	0.16	-0.50	0.22	0.40
Fe Dolomite-Ankerite	0.07	-0.62	0.22	0.4
Pyrite	0.26	0.42	<0.001	0.94

5.1.2 Rhenium

Table 5 shows the correlation data between Re and the analyzed minerals from both members of interest. In both the CW and RR, no statistically significant correlations were observed. Re concentrations in the RR ranged from 2.06-10.71 ppb, with an average concentration of 3.97 ppb. The CW had a Re concentration range of 1.17-16.3 ppb with an average concentration of 6.68 ppb.

Table 5: Re correlations with analyzed minerals from both the RR and CW

Mineral	Rouge River Member		Collingwood Member	
	<i>p-value</i>	<i>r-value</i>	<i>p-value</i>	<i>r-value</i>
Quartz	0.99	-0.005	0.60	0.18
K Feldspar	0.19	0.48	0.06	0.58
Muscovite/Illite	0.72	0.14	0.68	0.14
Chlorite	0.82	-0.09	0.72	0.12
Calcite	0.28	-0.40	0.23	-0.39
Dolomite	0.04	0.68	0.51	-0.22
Fe Dolomite-Ankerite	0.24	0.43	0.48	-0.24
Pyrite	0.40	0.28	0.48	0.24

5.1.3 Molybdenum

Table 6 shows the correlation data between Mo and the analyzed minerals from both members of interest. A weak statistically significant correlation between Mo and quartz was observed in the RR Member. A strong correlation between Mo and pyrite was observed in the CW. No correlations were observed between Mo and the other minerals. The samples analyzed from the RR had a Mo concentration range of 1.04-8.19 ppm with an average concentration of 3.17 ppm. The CW had a Mo concentration range of 0.2-11.24 ppm, with an average concentration of 3.42 ppm.

Table 6: Mo correlations with analyzed minerals from both the RR and CW

Mineral	Rouge River Member		Collingwood Member	
	<i>p-value</i>	<i>r-value</i>	<i>p-value</i>	<i>r-value</i>
Quartz	0.02	0.74	0.64	0.16
K Feldspar	0.45	-0.29	0.44	0.63
Muscovite/Illite	0.14	0.53	0.70	0.13
Chlorite	0.74	0.13	0.81	0.08
Calcite	0.19	-0.48	0.18	-0.46
Dolomite	0.74	-0.13	0.73	-0.06
Fe Dolomite-Ankerite	0.85	-0.07	0.85	-0.10
Pyrite	0.15	0.52	0.002	0.82

5.1.4 Uranium

Table 6 shows the correlation data between U and the analyzed minerals from both members of interest. In the RR Member, a weak positive correlation was observed between U concentration and quartz whereas a weak negative correlation between U and K feldspar was observed. Borderline statistically significant correlations between U and K feldspar content (positive correlation) and between U concentration and calcite content (inverse correlation) were observed for the CW. No correlations were observed between U and the other minerals. The RR had a U concentration range of 3.35-6.65 ppm, with an average concentration of 4.71 ppm (Table 7). The CW had a concentration range of 0.93-7.56 ppm with an average concentration of 3.41 ppm.

Table 7: U correlations with analyzed minerals from both the RR and CW

Mineral	Rouge River Member		Collingwood Member	
	<i>p-value</i>	<i>r-value</i>	<i>p-value</i>	<i>r-value</i>
Quartz	0.02	0.75	0.27	0.36
K Feldspar	0.02	-0.74	0.05	0.59
Muscovite/Illite	0.30	0.39	0.27	0.36
Chlorite	0.10	0.002	0.35	0.31
Calcite	0.82	-0.23	0.05	-0.59
Dolomite	0.27	-0.41	0.82	0.08
Fe Dolomite-Ankerite	0.57	-0.22	0.93	0.03
Pyrite	0.42	0.26	0.10	0.52

5.1.5 Vanadium

Table 7 shows the correlation data between U and the analyzed minerals from both members of interest. A negative correlation between V and dolomite was observed for the RR. A negative correlation between V and calcite was observed in the CW. No correlations were observed between V and the other minerals. The RR had a V concentration range of 98.70-144.82 ppm, with an average concentration of 129.86 ppm (Table 8). The CW's concentration range was 13.43-158.91 ppm, with an average concentration of 64.95 ppm.

Table 8: V correlations with analyzed minerals from both the RR and CW

Mineral	Rouge River Member		Collingwood Member	
	<i>p-value</i>	<i>r-value</i>	<i>p-value</i>	<i>r-value</i>
Quartz	0.06	0.64	0.11	0.50
K Feldspar	0.07	-0.62	0.07	0.56
Muscovite/Illite	0.27	0.41	0.13	0.48
Chlorite	0.38	0.33	0.15	0.46
Calcite	0.79	-0.10	0.03	-0.64
Dolomite	0.01	-0.79	0.72	0.12
Fe Dolomite-Ankerite	0.10	-0.57	0.07	0.84
Pyrite	0.41	0.31	0.62	0.04

5.2 Assessing the Effectiveness of the 2M Nitric Acid Leach Using Residues

The effectiveness of the 2M nitric acid leach was assessed by comparing the quantity of trace metals remaining in the residual solid to the amount removed by the leach. It was observed that the removal of trace metals from the carbonate-rich CW Member by the 2M nitric acid leach was much more effective than from the carbonate-poor RR Member. A summary of the average % remaining in residue and standard deviation for each redox sensitive trace metal is provided below (See Table 9), a detailed sample dataset of removal rates for each element can be found in Appendix B.

Table 9: Average percentage of redox sensitive trace metals remaining in solid residuals after 2M Nitric Acid Leach

	ROUGE RIVER MEMBER		COLLINGWOOD MEMBER	
	Average	Std Dev.	Average	Std Dev.
THALLIUM	64 %	0.14	26 %	0.21
RHENIUM	23 %	0.18	9 %	0.10
MOLYBDENUM	50 %	0.25	20 %	0.12
URANIUM	67 %	0.14	30 %	0.23
VANADIUM	74 %	0.08	38 %	0.20

5.2.1 Removal of each trace metal by the 2M nitric acid leach

5.2.1.1 Thallium

The removal of Tl from the RR by the 2M nitric acid leach was not as effective as for Re and Mo, with an average of ~64% of the total quantity remaining in the residual solid after the leach. Removing Tl from the CW was much more effective, with an average of ~26% of Tl remaining in the residue after the leach.

5.2.1.2 Rhenium

The removal of Re from the RR by the 2M nitric acid leach was more effective compared to the other redox-sensitive metals considered in this study, with an average of ~23% of the total quantity remaining in the residue after the leach. The removal of Re from the CW is also high, with an average of ~9% of Re remaining in the residue after the leach. Notably, the samples from higher up within the PS core in the RR had the best removal rates. In contrast, samples from the SJ core had the poorest removal rate. In the CW, a higher average of Re remaining in the residue was observed for the CWD.

5.2.1.3 Molybdenum

The removal of Mo from the RR was not as effective compared to Re, with an average of ~50% of the total quantity remaining in the residue after the leach. Removing Mo from the CW was more effective, with an average of ~20% of Mo remaining in the residue after the leach. The samples from the deeper portions of the PS and SJ cores had the best removal rates for the RR. The removal rates of Mo from the CW were consistent, with the highest amount left being 21% in the CWD.

5.2.1.4 Uranium

The removal of U from the RR was not as effective as for Mo and Re and was similar to Tl, with an average of ~67% of the total quantity remaining in the residual solid after the leach. Removing U from the CW was effective, with an average of ~30% of U remaining in the residual solid after the leach. For the RR, the P core had better removal rates compared to other cores overall. However, three samples from lower in the PS core had the highest removal rates of U. Within the CW, the poorest removal rates were observed in the CWD, and the other cores had consistently high removal rates.

5.2.1.5 Vanadium

The removal of V from the RR was not as effective as for the other redox-sensitive metals considered in this study, with an average of ~74% of the total quantity remaining in the residual solid after the leach. Removing V from the CW was much more effective, with an average of ~38% of V remaining in the residual solid after the leach. For the RR, the P core with the highest concentration of V had the most successful removal rates, although they were still poor with over 50% of V remaining in the residue. The CW had consistent removal rates, with the highest percentage of V remaining observed in one of the SJ samples. Samples with the highest V concentration also experienced the most effective removal rates.

5.3 Whole-rock & 2M Nitric Acid Leach Data Comparison

Samples from all eight cores from both members underwent two different types of removal methods, whole-rock dissolution (Lu et al., 2024) and the 2M nitric acid leach (this study). The data from both methods are compared in this section with geochemical indicators of possible host phases for redox-sensitive metals, namely Al (clay minerals), total sulfur (TS; pyrite plus sulfurized organic matter), total organic carbon (TOC), total inorganic carbon (carbonate minerals) and P (phosphorus). For Al and P comparisons, leach Al and P were compared with leach Tl, Re, Mo, U, and V. The same was done for the whole-rock dataset, Al and P compared to Tl, Re, Mo, U, and V from that dataset. P was used to detect organic matter as a host phase, so it was not included in the figures. Only some of the *r*- and *p*-values are presented in this section; the remainder can be found in the tables located in Appendix C.

5.3.1 Thallium

5.3.1.1 Rouge River Member

The whole-rock data showed correlations between Tl and Al in the SJ ($r=0.39$, $p=0.01$) and PI ($r=0.32$, $p=0.02$) cores, and a negative correlation in the MF core ($r=-0.33$, $p=0.03$). No correlations were observed in any of the cores from the leach data.

There were correlations observed between TS and Tl in the PS core from both the whole-rock ($r=0.72$, $p<0.001$) and leach ($r=0.37$, $p=0.004$) data. One additional correlation was observed in the PI core from the leach data ($r=0.50$, $p=0.04$).

No significant correlations were observed between Tl and TOC from the whole-rock data. Two correlations were observed in the leach data, the SJ core ($r=0.83$, $p<0.001$), and PI core ($r=0.65$, $p=0.007$).

No significant correlations were observed between Tl and TIC from the whole-rock data. The leach data showed a correlation was observed in the SJ core ($r=0.59$, $p=0.01$).

A significant correlation between Tl and P was observed in the PS core using the whole-rock data ($r=0.50$, $p<0.001$). However, no significant correlation was observed between P and Tl in the PS core in the leach data. Correlations were observed in the SJ ($r=0.79$, $p<0.001$), MF ($r=0.96$, $p<0.001$), and PI ($r=0.71$, $p=0.002$) cores using the 2M leach data.

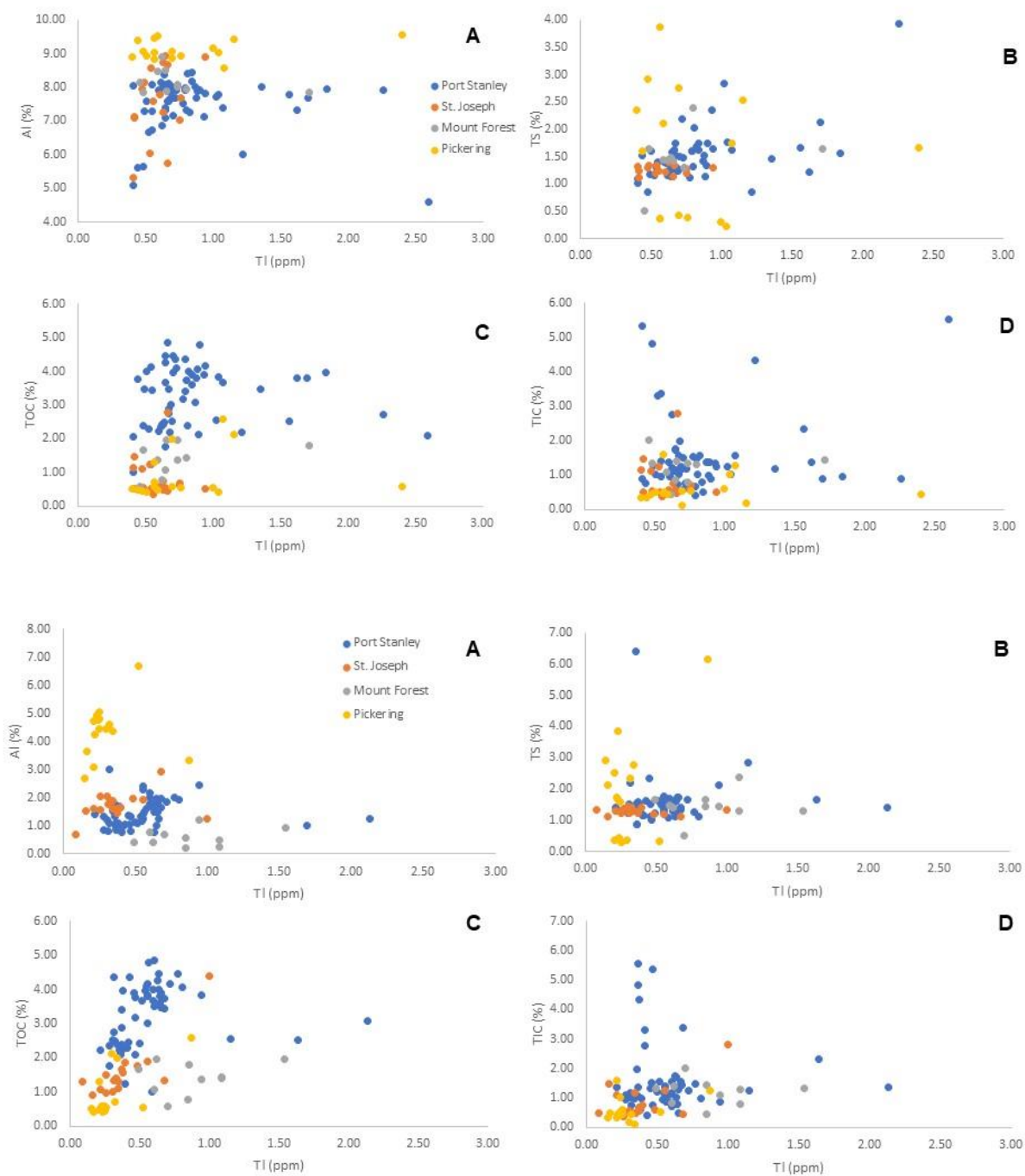


Figure 4: Cross plots between TI (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach Data from the Rouge River Member.

5.3.1.2 CW Member

Positive correlations were observed between Tl and Al in the SJ ($r=0.39$, $p=0.01$) and MF ($r=0.32$, $p=0.02$) cores, a negative correlation was observed in the CWD core ($r=-0.33$, $p=0.03$) using the whole-rock dataset. Comparatively, correlations were observed in the LC ($r=0.71$, $p=0.003$), CWD ($r=0.75$, $p=0.05$), and MF ($r=0.89$, $p<0.001$) cores but not the SJ core when using the leach dataset.

Strong correlations between Tl and TS were observed in all cores using the whole-rock data (LC $r=0.76$ & $p<0.001$, SJ $r=0.83$ & $p=0.001$, CWD $r=0.83$ & $p=0.02$, MF $r=0.8$ & $p<0.001$). The leach data agreed, and correlations were observed in all cores (LC $r=0.75$ & $p=0.001$, SJ $r=0.86$ & $p<0.001$, CWD $r=0.86$ & $p=0.001$, MF $r=0.85$ & $p<0.001$).

A correlation between Tl and TOC was observed in the SJ core from both the whole-rock ($r=0.74$, $p=0.01$) and leach data ($r=0.67$, $p=0.02$).

Negative correlations between TIC and Tl were observed in all cores using the whole-rock data (LC $r=-0.90$, $p<0.001$, SJ $r=-0.95$, $p<0.001$, CWD $r=-0.82$, $p=0.02$, MF $r=-0.54$, $p=0.05$). The leach data mostly agreed negative correlations were observed in the LC ($r=-0.81$, $p<0.001$), SJ ($r=-0.79$, $p<0.001$), and CWD ($r=-0.82$, $p=0.02$) cores. A positive correlation was observed in the MF core ($r=0.96$, $p<0.001$).

Significant correlations between Tl and P were observed in the LC ($r=0.52$, $p=0.05$), SJ ($r=0.87$, $p<0.001$), and MF ($r=0.61$, $p=0.02$) cores from the whole-rock dataset. The only significant correlations from the leach dataset were from the SJ ($r=0.60$, $p=0.05$) and MF ($r=0.53$, $p=0.05$) cores.

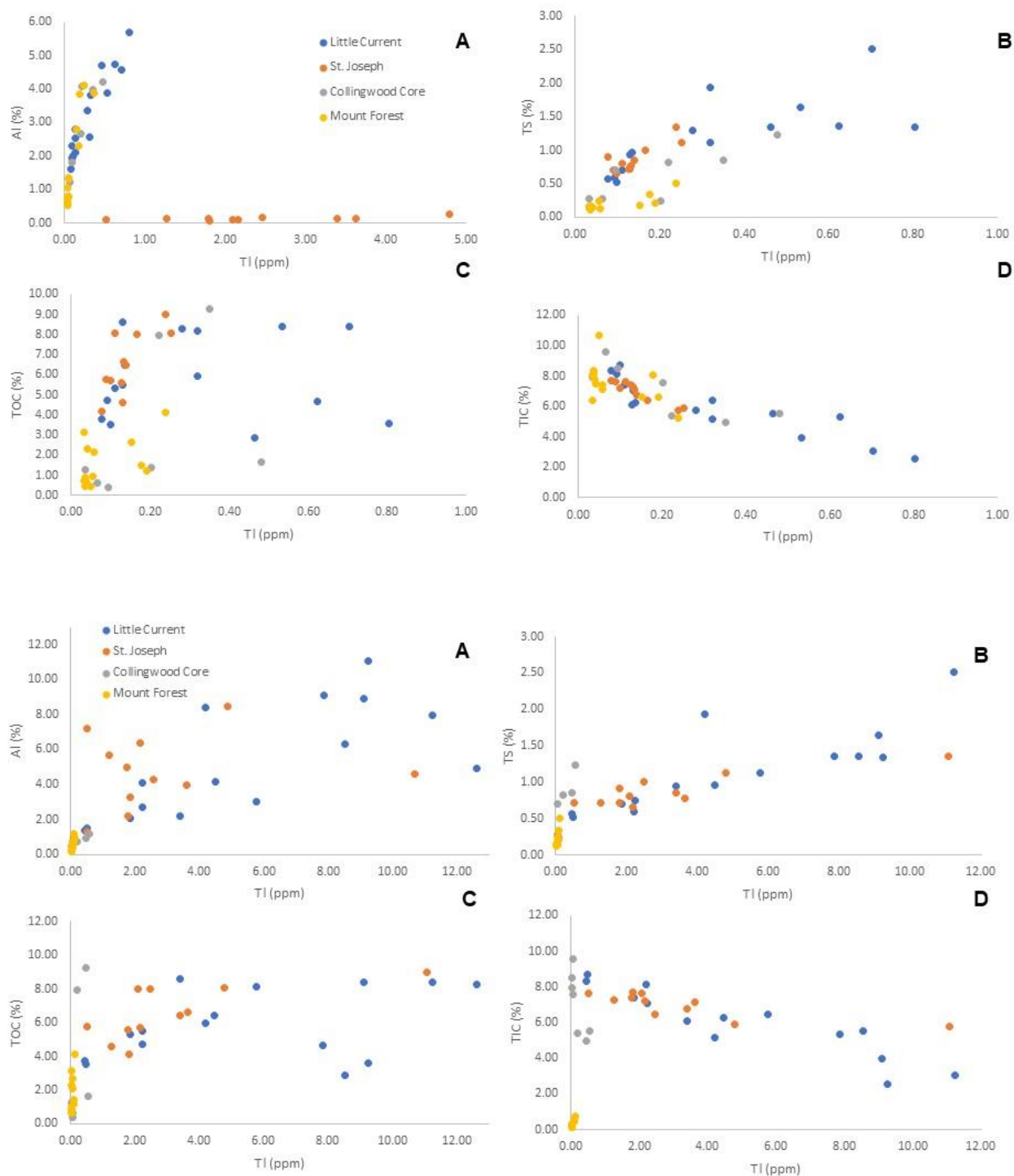


Figure 5: Cross plots between Tl (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data (BOTTOM) & Leach data from the Collingwood Member.

5.3.2 Rhenium

5.3.2.1 Rouge River Member

Both the whole-rock and leach data displayed negative correlations between Al and Re in the PS core ($r=-0.36$, $p<0.001$ and $r=-0.48$, $p<0.001$, respectively).

Only one correlation was shown between Re and TS in either of the data sets, a strong correlation was observed in the PS core ($r=0.92$, $p<0.001$) using the whole-rock data.

No correlations were observed between Re and TOC in the whole-rock data. A negative correlation was observed in the PS core ($r=-0.56$, $p<0.001$) using the leach data. Two positive correlations in both the SJ ($r=0.90$, $p<0.001$) and PI ($r=0.69$, $p<0.003$) cores were also observed.

The whole-rock and leach data agreed both displayed a correlation between Re and TIC in the SJ core ($r=0.77$, $p<0.001$).

Significant correlations were observed between Re and P in the PS ($r=0.86$, $p<0.001$) and SJ ($r=0.61$, $p=0.008$) cores using the whole-rock dataset. Using the leach dataset correlations were observed in the SJ ($r=0.75$, $p<0.001$) and PI ($r=0.57$, $p=0.02$) cores.

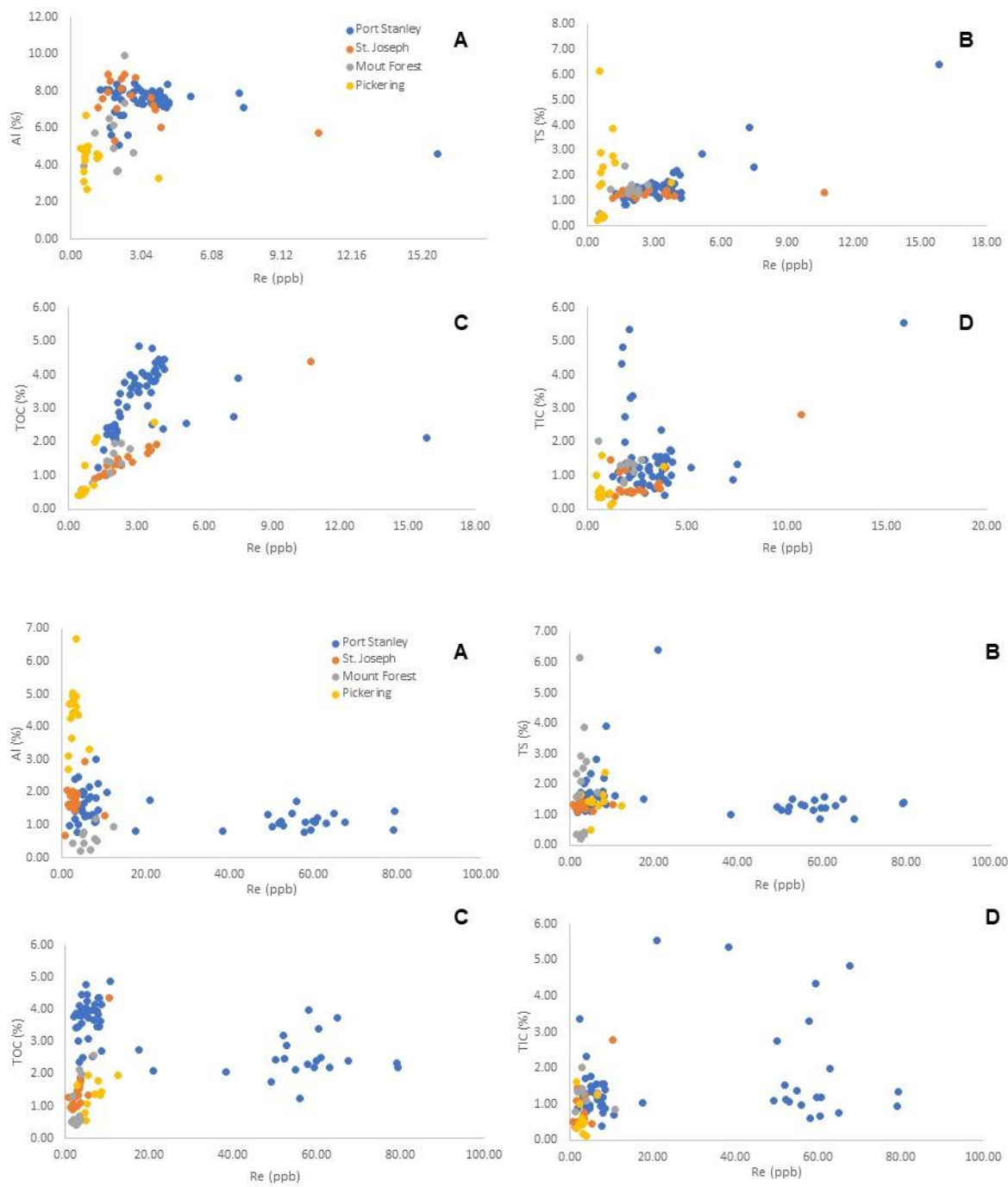


Figure 6: Cross plots between Re (ppb) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.2.2 Collingwood Member

Correlations were observed between Re and Al in the LC ($r=0.53$, $p=0.04$), SJ ($r=0.72$, $p=0.01$), and MF ($r=0.64$, $p=0.02$) cores from the whole-rock dataset. Correlations were also observed in the LC core ($r=0.8$ & $p<0.001$), SJ core ($r=0.79$, $p<0.001$), and MF core ($r=0.56$ & $p=0.02$) from the leach dataset.

The only correlation between Re and TS from the whole-rock dataset was observed in the LC core ($r=0.92$, $p<0.001$). Using the leach data correlations were observed in the LC ($r=0.80$, $p<0.001$), SJ ($r=0.79$, $p<0.001$), and MF ($r=0.84$, $p<0.001$) cores.

Correlations were observed between Re and TOC in the LC ($r=0.68$, $p=0.005$) and CWD ($r=0.99$, $p<0.001$) cores from the whole-rock dataset. The leach dataset agreed correlations were observed in both the LC ($r=0.61$, $p<0.001$) and CWD ($r=0.94$, $p<0.001$) cores as well as the SJ core ($r=0.67$, $p=0.003$).

Negative correlations were observed between TIC and Re in the LC ($r=-0.66$, $p=0.007$) and CWD ($r=-0.77$, $p=0.04$) cores from the whole-rock dataset. Using the leach data, negative correlations were observed in the LC ($r=-0.76$, $p<0.001$), SJ ($r=-0.90$, $p<0.001$), and CWD ($r=-0.75$, $p=0.01$) cores.

No significant correlations were observed between Re and P in the whole-rock dataset. Comparatively, two were observed using the leach dataset, one from the SJ core ($r=0.78$, $p=0.004$) and one from the CWD core ($r=0.78$, $p=0.04$).

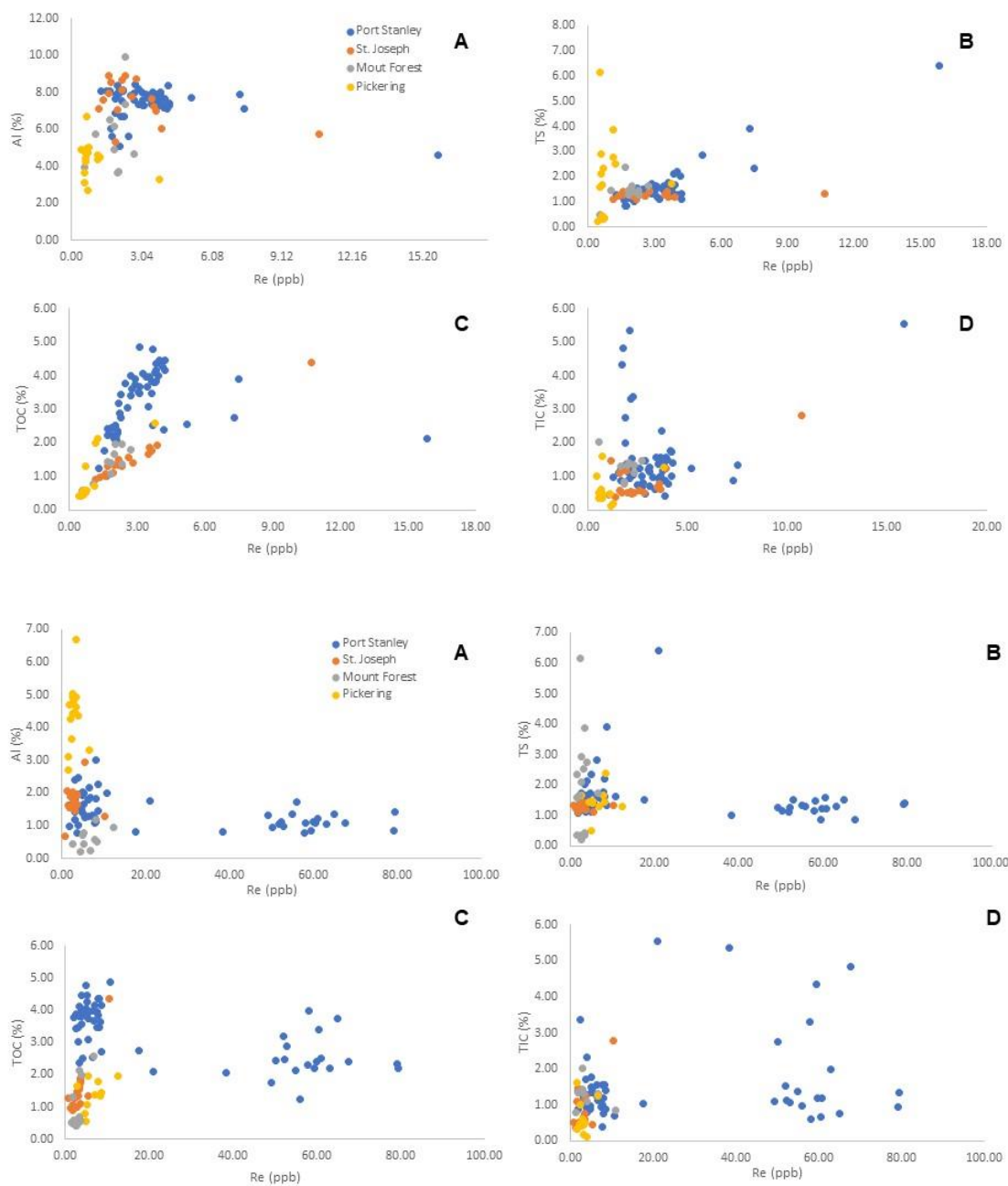


Figure 7: Cross plots between Re (ppb) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.3 Molybdenum

5.3.3.1 Rouge River Member

No correlations were observed between Al and Mo when using the whole-rock data. Two positive correlations were observed using the leach data in both the PS ($r=0.47$, $p<0.001$) and PI ($r=0.50$, $p=0.05$) cores.

Correlations between TS and Mo were observed in both the PS ($r=0.68$, $p<0.001$) and SJ ($r=0.77$, $p<0.001$) cores in both datasets. A correlation was also observed in the PI ($r=0.80$, $p<0.001$) core using the whole-rock data.

Correlations between TOC and Mo were observed in the PS ($r=0.57$, $p<0.001$), SJ ($r=0.68$, $p<0.001$), and PI ($r=0.50$, $p=0.05$) cores using the whole-rock data. Comparatively using the leach data correlations were only observed in the PS ($r=0.48$, $p<0.001$) and SJ ($r=0.61$, $p=0.008$) cores.

No correlations between TIC and Mo were observed in either dataset.

There were two significant correlations between Mo and P from the whole-rock dataset, one in the PS core ($r=0.63$, $p<0.001$) and one in the SJ core ($r=0.65$, $p=0.005$). The leach data agreed (PS $r=0.78$, $p<0.001$, SJ $r=0.77$, $p<0.001$), two additional correlations were also observed in the MF ($r=0.71$, $p=0.02$) and PI ($r=0.62$, $p=0.01$) cores.

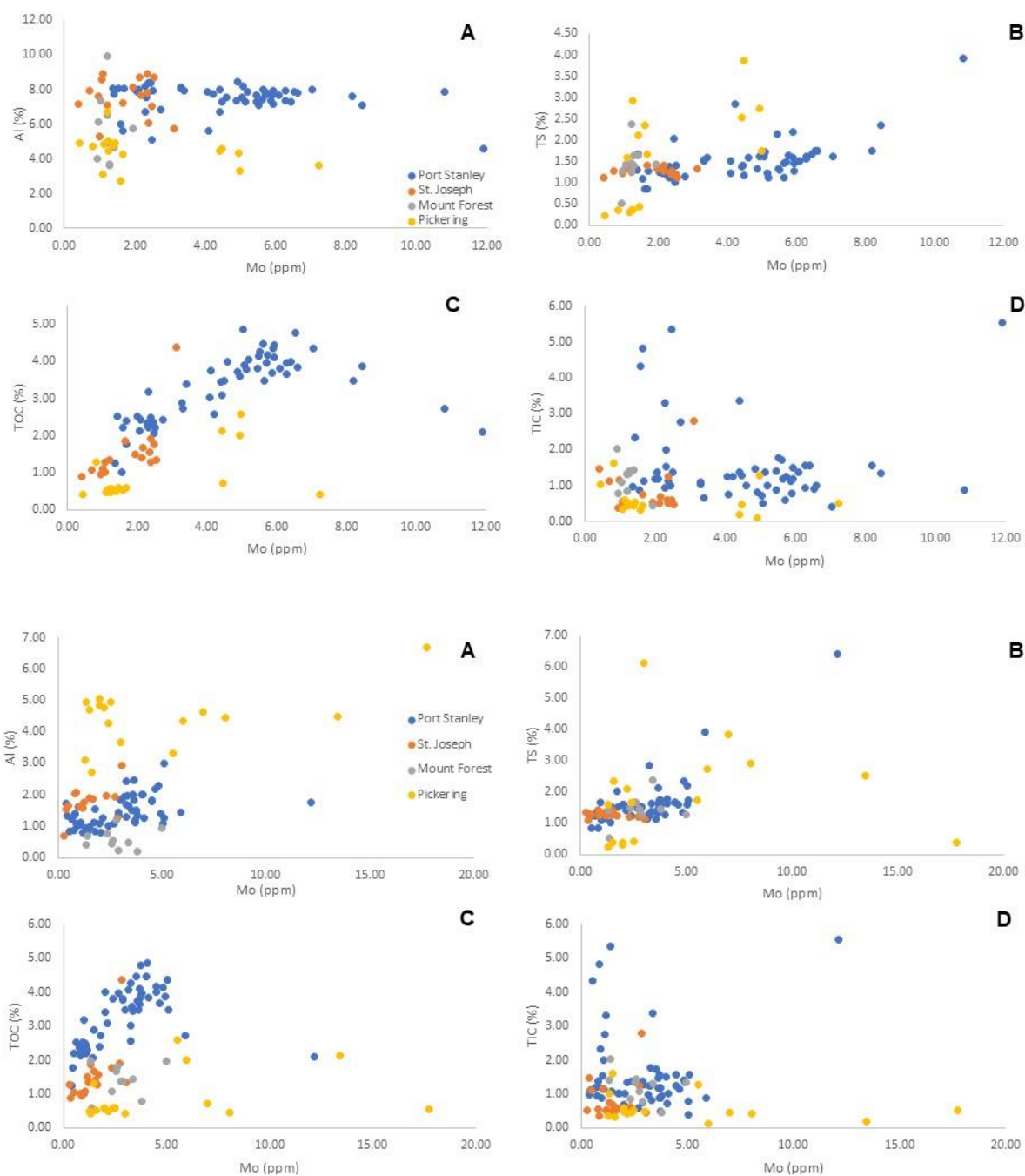


Figure 8: Cross plots between Mo (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.3.2 Collingwood Member

Only one significant correlation was observed between Mo and Al from both the whole-rock and leach datasets in the MF core ($r=0.61$, $p=0.03$ & $r=0.61$, $p=0.02$).

A strong correlation between TS and Mo was observed in the MF core using both the whole-rock ($r=0.95$, $p<0.001$) and leach ($r=0.94$, $p<0.01$) data. Additionally, a correlation was also observed in the LC core ($r=0.56$, $p<0.001$) using the leach data.

Correlations between Mo and TOC were observed in all cores from the whole-rock dataset (LC $r=0.71$ & $p<0.001$, SJ $r=0.5$ & $p=0.04$, CWD $r=0.89$ & $p<0.001$, MF $r=0.61$ & $p=0.01$). Correlations were observed in the LC ($r=0.76$, $p<0.001$), CWD ($r=0.81$, $p=0.004$), and MF ($r=0.61$, $p=0.01$) cores.

A negative correlation was observed between Mo and TIC in the CWD core ($r=-0.87$, $p=0.008$) and a positive correlation was observed in the MF core ($r=0.87$, $p<0.001$) from the whole-rock data. Comparatively, negative correlations were observed in the LC ($r=-0.48$, $p<0.001$), CWD ($r=-0.76$, $p=0.008$), and MF ($r=-0.71$, $p=0.002$) cores using the leach data.

No correlations were observed between Mo and P in either dataset from the CW member.

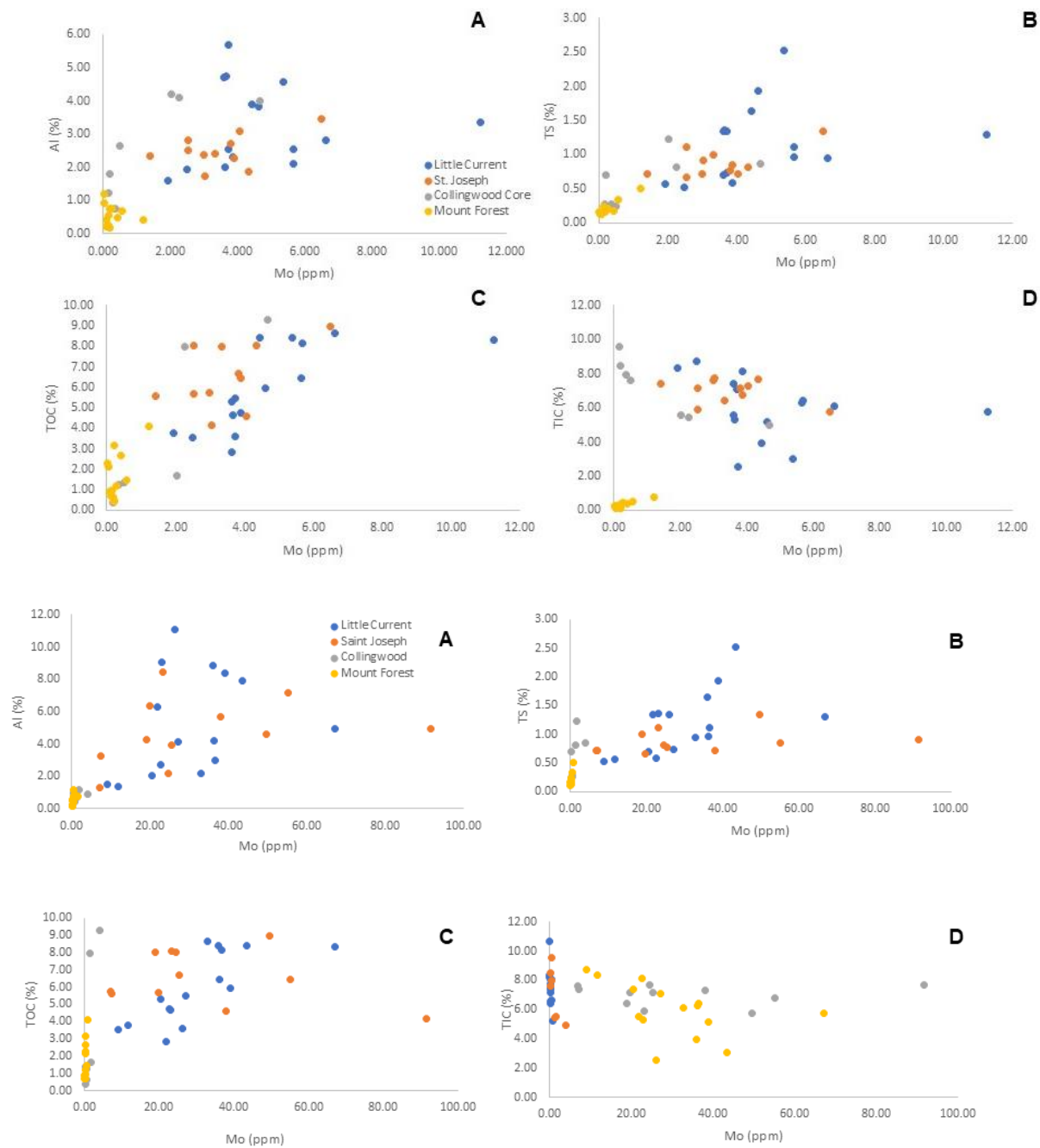


Figure 9: Cross plots between Mo (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.4 Vanadium

5.3.4.1 Rouge River Member

Strong correlations were observed between V and Al in both datasets from the PS ($r=0.76$, $p<0.001$ & $r=0.72$, $p<0.001$) and SJ ($r=0.97$, $p<0.001$ & $r=0.95$, $p<0.001$) cores. An additional correlation in the PI core ($r=0.95$, $p<0.001$) from the leach dataset was also observed.

Only one correlation was observed between V and TS. The PS core ($r=-0.28$, $p=0.04$) from the whole-rock dataset displayed a negative correlation. No correlations were observed for the leach data.

Correlations between TOC and V were observed in the PS core from both the whole-rock ($r=0.59$, $p<0.001$) and leach ($r=0.38$, $p=0.003$) data. Additionally, a correlation was observed in the PI ($r=0.58$, $p=0.02$) core from the whole-rock data.

Negative correlations between TIC and V were observed from the whole-rock data set in the PS ($r=-0.72$, $p<0.001$), SJ ($r=-0.66$, $p<0.001$), and MF ($r=-0.74$, $p=0.01$) cores. No correlations were observed in the leach data.

Negative correlations between V and P were observed in the PS ($r=-0.43$, $p<0.001$) and MF ($r=-0.65$, $p=0.04$) cores, and a positive correlation in the PI ($r=0.56$, $p=0.02$) core using the whole-rock data set. The leach data mostly did not agree, with positive correlations between V and P observed in all cores (PS $r=0.29$, $p=0.03$, SJ $r=0.61$, $p=0.009$, MF $r=0.85$, $p=0.002$, PI $r=0.74$, $p=0.001$).

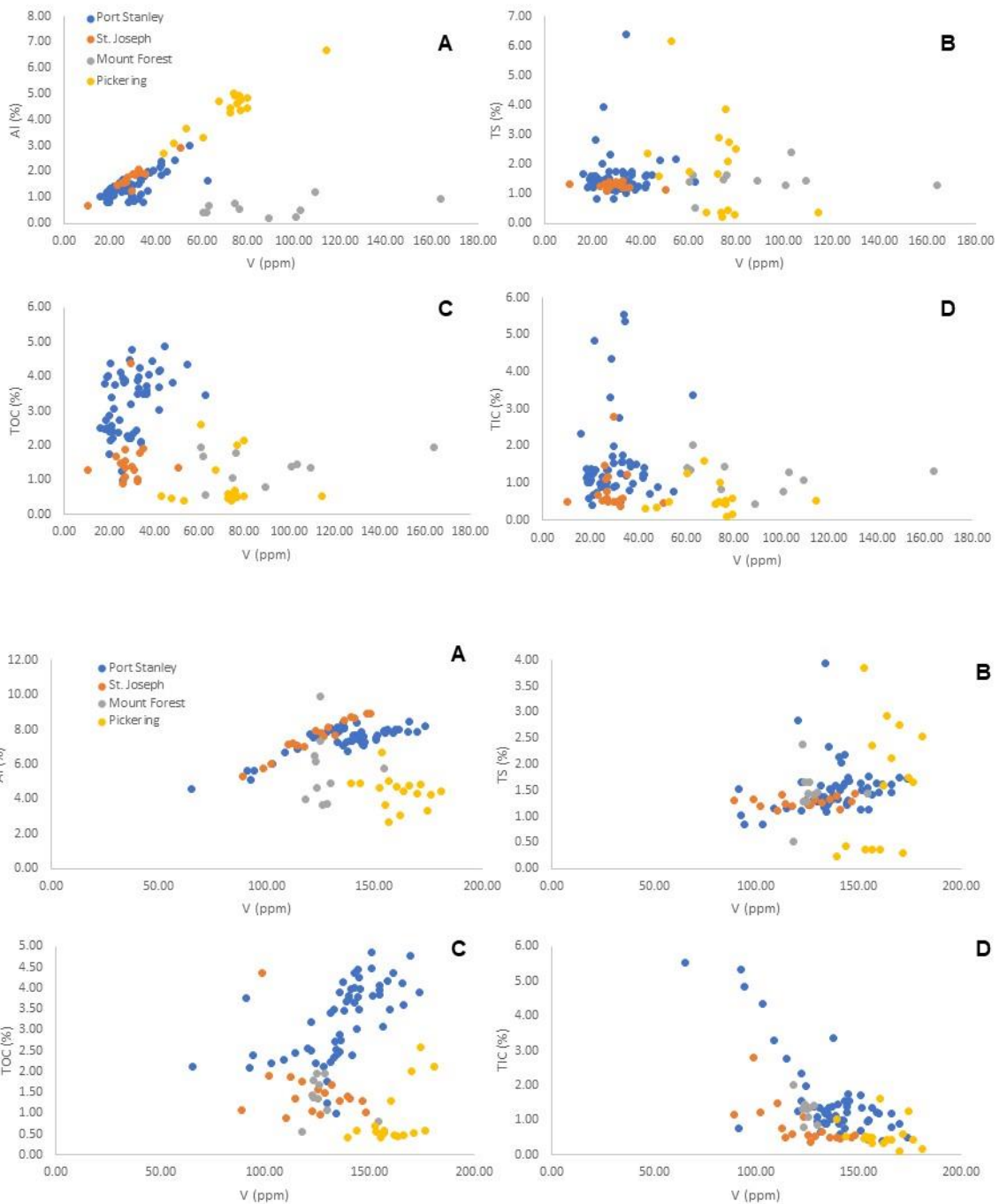


Figure 10: Cross plots between V (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.4.2 Collingwood Member

Correlations between Al and V were observed in all the cores from the whole-rock dataset (LC $r=0.53$ & $p=0.04$, SJ $r=0.67$ & $p=0.02$, CWD $r=0.98$ & $p<0.001$, MF $r=0.93$ & $p<0.001$). The leach data agreed correlations were observed in all cores as well (LC $r=0.63$ & $p=0.01$, SJ $r=0.89$ & $p<0.001$, CWD $r=0.93$ & $p<0.001$, and MF $r=0.58$ & $p=0.03$).

Correlations between V and TS were observed in all the cores from the whole-rock dataset (LC $r=0.61$ & $p=0.05$, SJ $r=0.79$ & $p=0.003$, CWD $r=0.86$ & $p=0.009$, MF $r=0.65$ & $p=0.01$). Comparatively, a correlation was only observed in the LC ($r=0.61$, $p<0.001$) and MF ($r=0.73$, $p=0.01$) cores from the leach dataset.

Correlations between V and TOC were observed in the LC ($r=0.55$, $p=0.03$) and SJ ($r=0.78$, $p<0.001$) cores from the whole-rock dataset. Comparatively, a correlation was only observed in the LC core ($r=0.50$, $p<0.001$) from the leach dataset.

Negative correlations between V and TIC were observed in the LC ($r=-0.67$, $p<0.001$), SJ ($r=-0.88$, $p<0.001$), and CWD ($r=-0.91$, $p=0.003$) cores, and a positive correlation was observed in the MF core ($r=0.83$, $p<0.001$) using the whole-rock data. A negative correlation was only observed in the MF core ($r=-0.67$, $p<0.001$) using the leach data.

Significant correlations were observed between V and P in the CWD ($r=0.83$, $p=0.02$) and MF ($r=0.76$, $p=0.001$) cores using the whole-rock dataset. The leach dataset agreed (CWD $r=0.64$, $p=0.03$ & MF $r=0.59$, $p=0.03$), with an additional correlation observed in the SJ core ($r=0.64$, $p=0.03$).

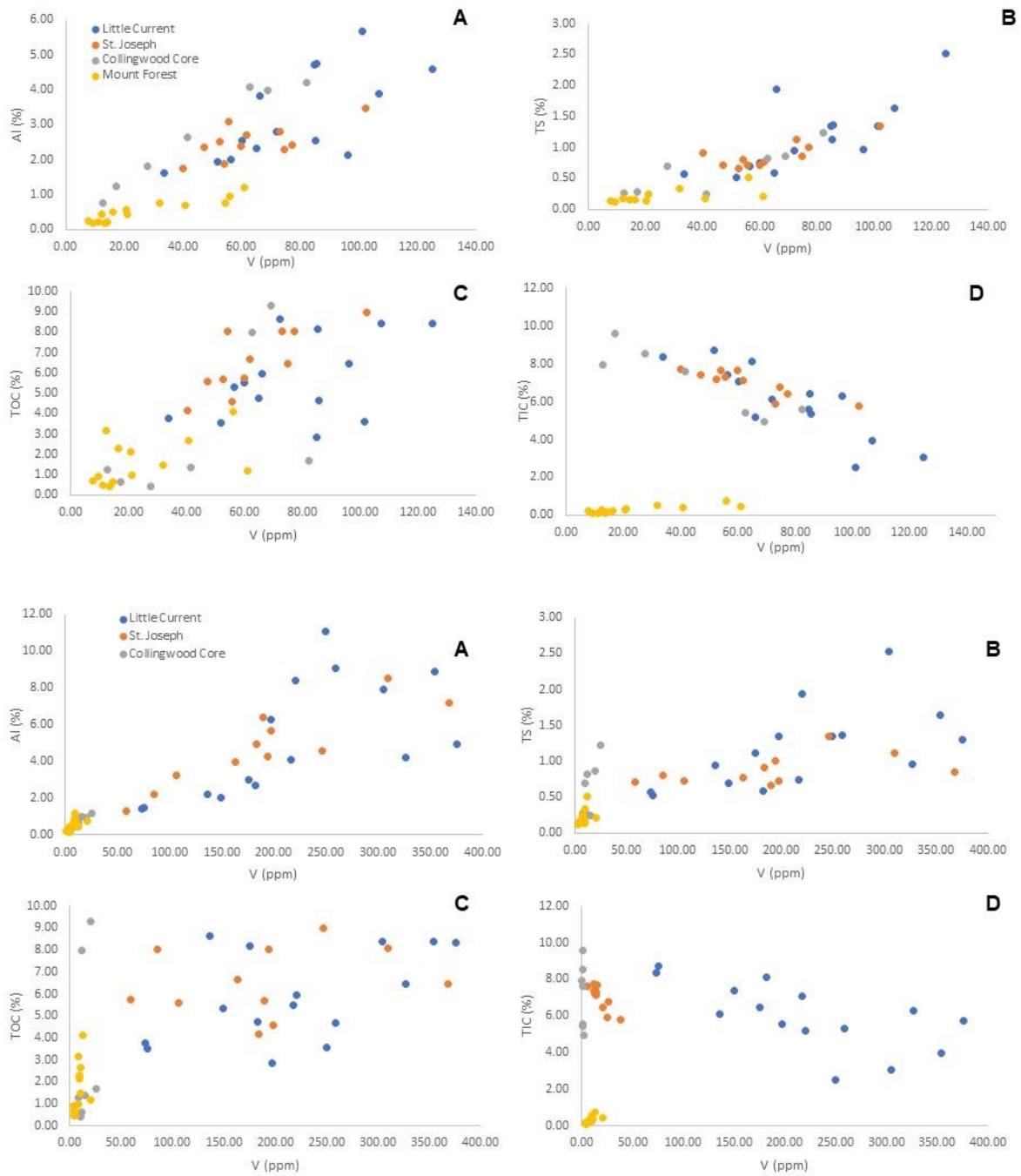


Figure 11: Cross plots between V (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.5 Uranium

5.3.5.1 Rouge River Member

Correlations were observed between U and Al in both the PS ($r=0.25$, $p<0.001$) and SJ ($r=0.59$, $p<0.001$) cores from the whole-rock data set. The leach data agreed, with correlations also being observed in the PS ($r=0.68$, $p<0.001$) and SJ ($r=0.72$, $p=0.001$) cores.

No correlations were observed between TS and U from either dataset.

Correlations were observed between TOC and U in the PS core in both the leach ($r=0.84$, $p<0.001$) and whole-rock ($r=0.79$, $p<0.001$) datasets. Additionally, a correlation was also observed in the PI core ($r=0.78$, $p<0.001$) from the whole-rock dataset.

A negative correlation between U and TIC was observed in the PS core ($r=-0.46$, $p<0.001$). No correlations were observed in the 2M nitric acid leach data.

Only one correlation between U and P was observed using the whole-rock dataset in the PI core ($r=0.60$, $p=0.01$). Comparatively, correlations were observed in all cores using the leach dataset (PS $r=0.41$ & $p=0.002$, SJ $r=0.83$ & $p<0.001$, MF $r=0.96$ & $p<0.001$, and PI $r=0.62$ & $p=0.01$).

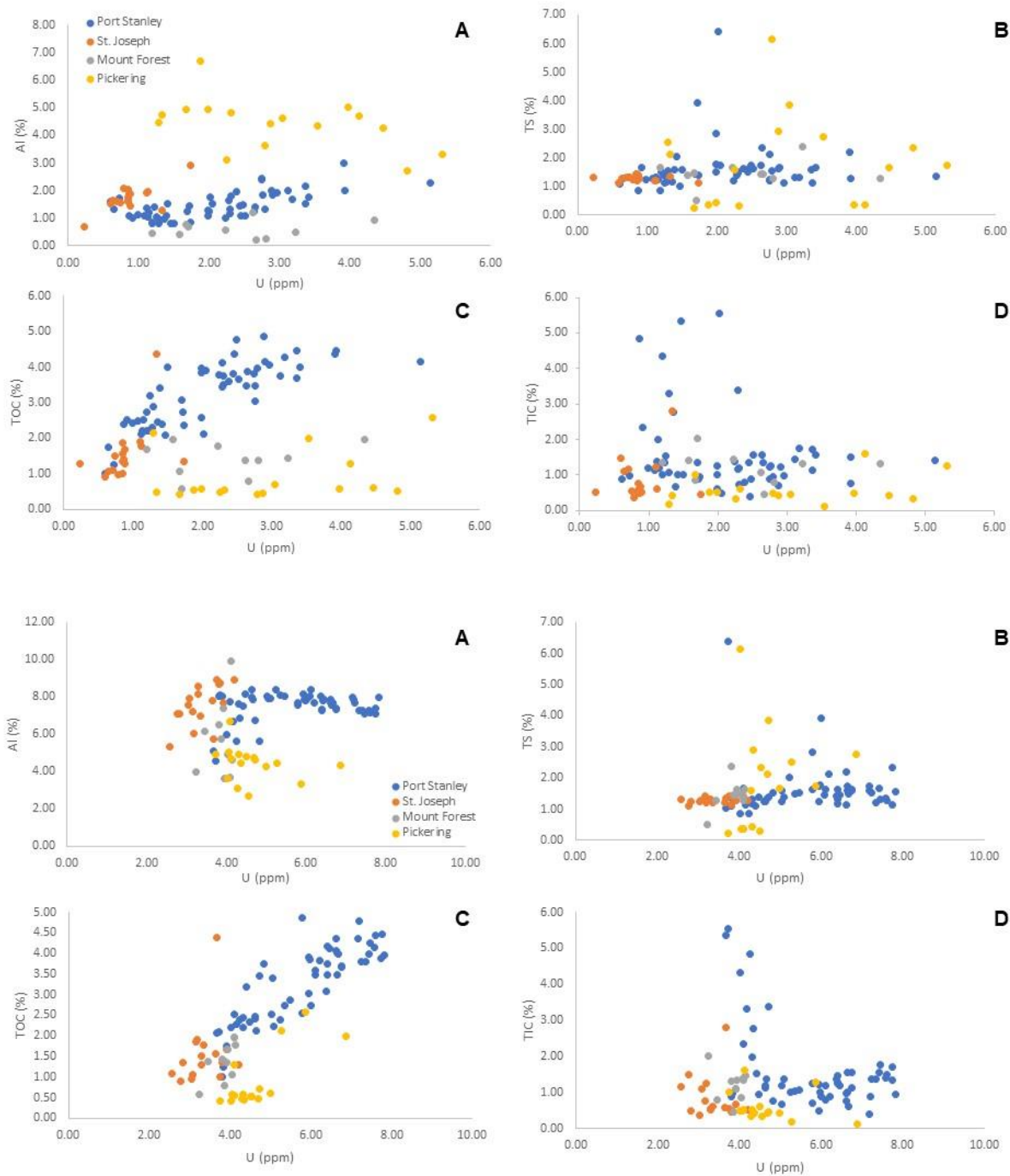


Figure 12: Cross plots between U (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

5.3.5.2 Collingwood Member

Correlations between U and Al were observed in the SJ ($r=0.66$, $p=0.02$), CWD ($r=0.98$, $p<0.001$), and MF ($r=0.72$, $p=0.01$) cores. No correlations were observed in the leach dataset.

Correlations between U and TS were observed in all the cores from the whole-rock dataset (LC $r=0.67$ & $p=0.01$, SJ $r=0.78$ & $p=0.004$, CWD $r=0.79$ & $p=0.03$, MF $r=0.77$ & $p=0.002$). Using the leach data, correlations were observed in the LC ($r=0.61$, $p<0.001$), SJ ($r=0.87$, $p<0.001$), and CWD ($r=0.66$, $p=0.04$) cores, but not the MF core.

Correlations between U and TOC were observed in the LC ($r=0.79$, $p<0.001$), SJ ($r=0.84$, $p=0.001$), and CWD ($r=0.76$, $p=0.04$) cores using the whole-rock data. Correlations were only observed in the LC ($r=0.89$, $p<0.001$) and CWD ($r=0.81$, $p=0.004$) cores using the leach data.

Negative correlations between U and TIC were observed in the LC ($r=-0.58$, $p=0.02$), SJ ($r=-0.78$, $p=0.004$), and CWD ($r=-0.94$, $p=0.001$) cores. A positive correlation was observed in the MF core ($r=0.82$, $p<0.001$). The leach data agreed negative correlations were observed in the LC ($r=-0.50$, $p<0.001$), SJ ($r=-0.88$, $p<0.001$), and CWD ($r=-0.82$, $p=0.003$) cores.

Two significant correlations were observed between U and P using the whole-rock dataset, one from the CWD core ($r=0.90$, $p=0.005$) and one from the MF core ($r=0.57$, $p=0.03$). The leach data partially agreed with one correlation observed in the CWD core ($r=0.84$, $p=0.02$).

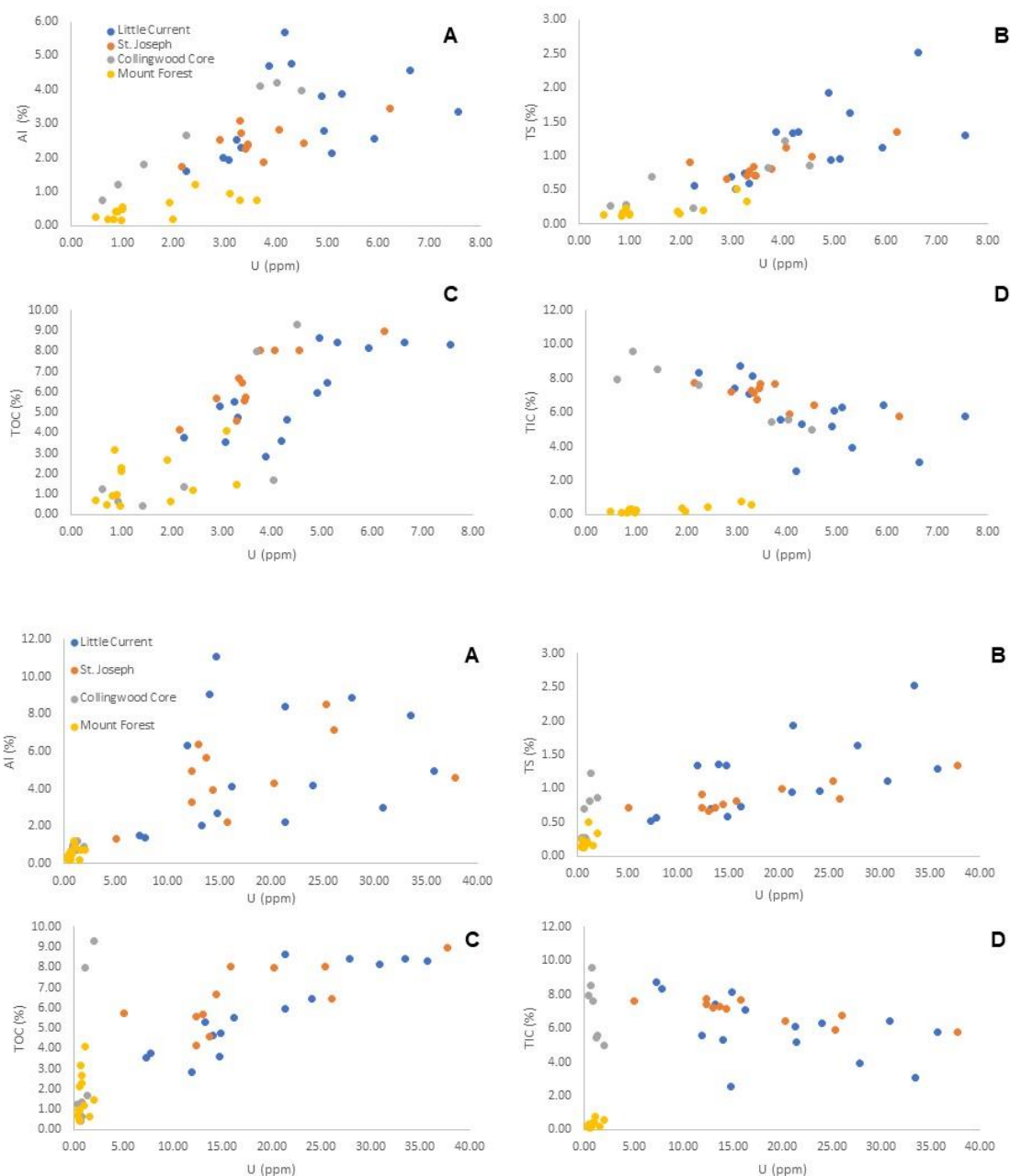


Figure 13: Cross plots between U (ppm) and host phase indicators (A) Al (%) (B) TS (%) (C) TOC (%) (D) TIC (%) using the (TOP) Whole-rock data & (BOTTOM) Leach data from the Rouge River Member.

Chapter 6: Discussion

6.1 Trace Metal Host Phases

A combination of evidence that was presented in the results was used to determine the primary host phases for each trace metal. The evidence used was the removal rates by the 2M nitric acid leach, and the strength of correlations between each trace metal and the abundances of minerals and chemical host phase identifiers (TOC, TIC, TS, Al, P). P was not used as an identifier for P-minerals as host phases because no P-bearing minerals were identified by XRD analyses. In organic-rich sedimentary rocks, P is not just found in phosphate minerals like apatite, but also in organic matter. If apatite is indeed absent, then the correlations between P and trace metals may be further used as evidence of organic matter being a host phase, as the P-bearing mineral abundance was below the XRD detection limit. The results of previous studies were also taken into consideration, particularly when unexpected results were observed.

The percentage of trace metals left within the residue after the 2M leach is lower in the CW member than in the RR member for each of the five trace metals studied. The CW member has a carbonate-dominated geology with a higher TOC content than the RR member. The carbonates are easily targeted by the 2M leach which enabled it to remove a higher percentage of trace metals. The RR member has a siliciclastic-dominated geology with a higher clay content that is more resistant to being targeted by the 2M leach. The redox conditions of each member also influenced the ability of the 2M leach to effectively remove trace metals. The RR member was overall interpreted as having been deposited in oxic-suboxic conditions whereas the cores from the CW member deposited in shallower conditions were deposited in oxic conditions, and the cores deposited in deeper water were deposited in anoxic conditions (Lu, 2022). Trace metals will be more enriched under anoxic conditions, particularly in organic matter (Bennett & Canfield, 2020; Shi et al., 2021). These combined factors made the CW member more favorable for the 2M leach to remove the trace metals.

6.1.1 Thallium

Tl is thought to be primarily hosted by clay minerals (illite) and pyrite (Fan et al., 2020; Martin et al., 2018; Newby et al., 2021; Owens et al., 2017; Them et al., 2018; Vaněk et al., 2020). No statistically significant correlations existed between Tl and any of the minerals analyzed in the RR Member. There were three significant correlations between Tl and Al in the RR from the whole-rock data. Two positive correlations were observed in the SJ and PI cores, and a negative correlation was observed in the MF core. There were no correlations observed in the leach data. This indicates that Al minerals are not the sole host phase for Tl within the RR. Significant correlations were observed between Tl and TS in the PS core from both the whole-rock and leach data, an additional correlation was observed in the PI core. This correlation indicates that Tl is held in pyrite in the PS core. However, organic matter appears to be the main host phase in the SJ and PI cores. There was one significant correlation between Tl and TIC in the SJ core, however, the correlation between Tl and TOC within this core is stronger. The PI core had correlations between Tl and TOC and Tl and TS, the correlation between Tl and TOC was stronger than the correlation between Tl and TS. In addition, there were very strong correlations between Tl and P observed in the SJ and PI cores which further supports organic matter being the main host phase of Tl in these two cores. An average of 64% of Tl was left in the solid residuals from the RR after the leach indicating that some of the Tl was being hosted by something that the leach was not targeting, which could be non-reactive (with 2M nitric acid) forms of organic matter.

The SJ and PI cores were interpreted by Lu et al. (2024) as having been deposited in oxic-suboxic conditions, but the Pickering core is thought to have been deposited in more reducing conditions. A correlation between TS and Tl was observed in the PI core as well as the PS core, which was deposited under suboxic-anoxic conditions. The results observed agree with previous studies which observed that under anoxic conditions pyrite has been observed to be the primary host phase for Tl (Martin et al, 2018).

In the Collingwood member, strong correlations were observed between Tl and muscovite/illite, chlorite, and pyrite. A high amount of Tl was removed by the leach with an average of 26% remaining in the solid residuals. There were significant correlations

observed between Tl and Al from both datasets except the SJ core from the leach dataset. The correlation from the CWD from the whole-rock dataset was negative, but a positive correlation was observed in the leach dataset. This was similar to the correlations observed between Tl and TS. However, the correlations between Tl and TS were stronger than the correlations observed between Tl and Al. These observations support the idea that pyrite is the primary host phase for Tl. Correlations were observed between Tl and TOC in the SJ core from both datasets, which could indicate that some Tl was found within the organic matter. Correlations were observed between Tl and P in the LC, SJ, and MF cores using the whole-rock dataset, and in the SJ and MF cores from the leach dataset. Although this also suggests that some Tl is being hosted in the organic matter, it is not the primary host.

The primary host phases of Tl were found to be both clay minerals and pyrite. Interestingly, the correlations between TS and Tl were strong within all the cores, even the CWD and MF cores which were interpreted as having been deposited within oxic conditions. In previous studies, it was observed that pyrite acts as a primary host in anoxic conditions. In this case, pyrite acted as a host within both oxic and anoxic conditions. Overall, the results from the Collingwood member do agree with previous studies that pyrite and clay minerals are the primary hosts of Tl (Fan et al., 2020; Martin et al., 2018; Newby et al., 2021; Owens et al., 2017; Them et al., 2018; Vaněk et al., 2020).

6.1.2 Rhenium

There is great debate as to whether the primary host phase of Re is pyrite or organic matter (Helz et al., 2011; Helz & Vorliceck, 2019; Ostrander et al., 2019; Stein & Hannah, 2014; Vyalov et al., 2013). There was only a significant correlation between dolomite and Re observed in the RR member. There was also a strong correlation observed between TIC and Re in the SJ core from both the whole rock and leach datasets. Comparatively positive correlations between Re and TOC were observed in both the SJ and PI cores. Considering there was a high average removal rate of Re by the leach with

23% remaining in the residual after the main host phases were targeted by the nitric leach, which could be reactive forms of organic/inorganic matter.

Inverse correlations were observed between Al and Re within the RR member using both the whole-rock and leach data. A strong inverse correlation was observed within the PS core using both data sets. This is an indication that clay minerals are not important as a host phase of Re. There was only one strong correlation between Re and TS in the PS core using the whole-rock data. A negative correlation was observed between Re and TOC in the PS core using the whole-rock data; however, two positive correlations were observed using the leach data, a moderate one for the PI core and a strong one for the SJ core. There were significant correlations between Re and P observed in SJ and PI cores. These correlations could be the result of the organic matter containing phosphorus, which coincides with the correlations observed between Re and TOC. However, there was also a correlation observed between Re and P in the PS core. In this core Re and TOC had an inverse correlation with TOC, so the Re-P correlation may suggest phosphate minerals are a Re host, but this cannot be confirmed with the data available (phosphate mineral abundance is below the XRD instrument detection limit). In summary, Re is hosted by both the organic matter and pyrite within the RR member, there is not a clear primary host between the two.

In previous studies, Re was observed to be primarily hosted by organic matter and pyrite in reducing conditions (Helz & Dolor, 2012; Miller et al., 2015; Morford et al., 2005). The correlation between Re and TS in the PS core demonstrates that pyrite is a host phase under reducing conditions as well as this core was interpreted as having been deposited in suboxic to anoxic conditions (Lu, 2022). The correlations between TOC and Re were observed in the PI and SJ cores which were deposited in oxic to suboxic conditions with the PI core having more O₂ deficient conditions. The PI core also had a lower TOC content than the other cores. These observations agree with previous work, that organic matter is a main host phase for Re in reducing conditions (Helz & Dolor, 2012; Miller et al., 2015; Morford et al., 2005).

The Collingwood Member Re's host phase is targeted by the leach as there was an average of only 9% of the Re content left in the residuals after the leach. The results of TIC vs Re contradicted what was observed in the RR with strong inverse correlations appearing in all cores indicating that TIC is not a host phase for Re in this member. Correlations between Re and Al were observed in the LC, SJ, and MF cores using the whole rock data. The leach data mostly agreed, except that there was no correlation observed in the SJ core. The correlations between Re and Al were moderate, with only one strong correlation observed in the SJ core from the whole rock data. These observations do indicate that clay minerals are a host phase for Re within the CW Member.

Strong correlations between Re and TS were observed in all the cores using the leach dataset, except CWD, and one strong correlation from the PS core was observed from the whole-rock dataset. The r values were all >0.78 and the p values were <0.001 . These observations are compelling evidence for pyrite being a primary host of Re within the Collingwood Member. Moderate correlations between Re and TOC were observed in the LC and SJ cores, and a strong correlation was observed in the CWD from both datasets. Correlations were also observed between Re and P in the SJ and CWDs, indicating the organic matter from these cores has P content. There is a debate about what the primary host phase of Re is, organic matter or pyrite (Helz et al., 2011; Helz & Vorlicek, 2019; Ostrander et al., 2019; Stein & Hannah, 2014; Vyalov et al., 2013). Given that the Collingwood Member has a high organic content and Re has, overall, a higher number of stronger correlations with pyrite throughout it can be interpreted that pyrite is the primary host phase for Re. There was also evidence that some Re is being hosted within Al minerals as well.

The CW member overall was interpreted as having been deposited in oxic to suboxic conditions, with the LC and SJ cores having more reducing conditions (Lu, 2022). Previous work indicated that pyrite was a more important host phase in reducing conditions (Helz & Dolor, 2012; Miller et al., 2015; Morford et al., 2005). The correlations observed in all cores from the CW member, and previously discussed

observations from the RR member, agree with the previous work, pyrite is an important host phase under reducing conditions.

6.1.3 Molybdenum

In the RR, no significant correlations existed between Mo or any of the minerals of interest. A poor average removal rate of Mo from the RR of 50% indicates that a portion of Mo is in a host phase that the 2M nitric acid leach does not target. No correlations were observed between Mo and Al using the whole-rock data. There were two correlations observed between Mo and Al from the leach data, a correlation in the PS core and the PI core. Mo and TS had significant correlations in the PS and SJ cores from the whole-rock data. Interestingly the leach data did not agree and only one correlation was observed in the PI core. Pyrite is not the main host of Mo among this member. Correlations were observed between Mo and TOC in the PS, SJ, and PI cores using the whole rock data. The leach data mostly agreed, that weak to moderate correlations were observed in the PS and SJ cores. There were correlations observed between Mo and P in all the cores as well. The poor average removal rate indicates that the majority of Mo is found in a non-reactive form of organic matter.

Mo has been observed to be hosted by pyrite in euxinic conditions, which none of the cores studied were (Chappaz et al., 2014; T. W. Dahl et al., 2017; Erickson & Helz, 2000; Helz et al., 2011). The correlations between Mo and TS observed in PS and SJ cores were not as strong as those between Mo and TOC or Mo and P. The PS core was deposited in suboxic to anoxic conditions and the SJ core was deposited in oxic to suboxic conditions. Organic matter has been observed to be the most important host in non-euxinic environments (Ardakani et al., 2024; Zhou et al., 2024). These findings agree with Zhou, et al. (2024) where Mo was found to have been primarily hosted by organic matter in non-euxinic environments. Additional correlations were observed between Mo and Al in the PI core, this core was interpreted as having been deposited in oxic to suboxic conditions and was noted to have lower TOC than the other cores, which accounts for why some Mo was located within clay minerals (Lu, 2022).

In the CW, Mo had a strong correlation with pyrite. Mo exhibited significant correlations with TS in the MF core in both datasets and a moderate correlation in the LC core from the leach dataset. Significant correlations were observed between Al and Mo in the MF core from both datasets. There were strong correlations between Mo and TOC observed in the LC and CWD cores from both datasets. Moderate correlations were observed in the SJ and MF cores from the whole-rock data, the leach data only had a moderate correlation in the MF core, not the SJ core. These findings also agree with Zhou et al., (2024) that organic matter is the primary host of Mo in non-euxinic conditions. This interpretation is based on the more consistent correlations observed in all cores from the CW Member, with pyrite and Al minerals acting as secondary hosts for Mo within certain cores.

The primary host of Mo in euxinic conditions has previously been found to be pyrite, however, none of the cores from either member were interpreted to have been deposited under euxinic conditions (Lu et al., 2024). In non-euxinic conditions, it has been found that organic matter is the more important host (Zhou et al., 2024). Organic matter was the primary host for Mo in the CW and RR members. However, additional correlations indicate that Mo is being held in clay minerals and pyrite as well. The correlations between Mo and TS were observed in the MF (more oxidizing) and LC (more reducing) cores, with an additional correlation between Mo and Al in the MF core.

6.1.4 Uranium

The primary host phases of U that have been identified in the past are carbonates, organic matter, pyrite, and phosphate minerals such as apatite (Shi et al., 2021; Howari et al., 2016; Romaniello et al., 2020). In the RR Member, no correlations were observed between U and any minerals of interest. 67% of U remained in the residuals providing evidence that most of the primary host of U was not a target of the 2M nitric acid leach. There were strong correlations observed between U and Al in the PS and SJ cores from the whole-rock dataset and in the PS and SJ cores from the leach dataset. This suggests that some U is being held in clay minerals, which is supported by the poor removal rate of U from the residuals. No correlations between U and TS are observed in any of the

cores from either dataset which indicates that pyrite is not a primary host in this member. Two strong correlations were observed between U and TOC in the PS (whole-rock data) and PI (leach data) cores. Given the high amount of U remaining in the residual solid after leaching, some U may be hosted within non-reactive forms of organic matter that the leach does not target. This does agree with Shi et al., (2021) that U is hosted within organic matter in organic-rich sediments. Strong correlations between U and P were observed in all cores from the leach data, further supporting that organic matter is the primary host phase for U within the RR Member (Wang et al., 2017; Zarasvandi et al., 2019).

U has been observed to become enriched in reducing conditions (Khaustova et al., 2022; Shi et al., 2021). The PS core was interpreted to have been deposited in suboxic to anoxic conditions, it was the expectation that U would have had strong correlations with TOC in the PS core, which was the case, however, an additional correlation was observed between U and Al (Khaustova et al., 2022; Lu, 2022; Wang et al., 2017; Zarasvandi et al., 2019). This could indicate that clay minerals are an important secondary host phase in reducing conditions. Strong correlations between U and TOC were only observed in the PS core, but correlations between U and P were observed in all cores from the leach dataset which indicates that U is being hosted in organic matter, as the phosphate mineral concentration was below the XRD detection limit. This agrees with the past literature as all cores were deposited in reducing conditions with the PS and PI cores having more O₂ deficient conditions (Lu, 2022).

In the CW Member, correlations were observed between U, chlorite, and pyrite. Inverse correlations between TIC and U were observed in the LC, SJ, and CWD cores from both datasets within the Collingwood Member, comparatively a positive correlation was observed in the MF core from the whole-rock dataset. The majority of the correlations observed were negative, which suggests that carbonate is not a primary host within this member. 30% of U remained in the residuals after the leach, which indicates that the host phase is a target of the 2M nitric acid leach, such as pyrite. There were strong to moderate correlations observed between U and TS in all cores from the whole-rock dataset and all but the MF core from the leach dataset. This further indicates the

primary host is pyrite. Strong to moderate correlations between U and Al within the SJ, CWD, and MF cores were observed using the whole-rock data. There were also strong correlations observed between U and TOC in the LC, SJ, and CWD cores. There were correlations observed between U and P in the CWD and MF cores as well. U is thought to be hosted primarily by carbonates, organic matter, and pyrite (Howari et al., 2016; Qiu et al., 2022; Romaniello et al., 2020). However, given that the samples were from shales that had a mix of minerals, not just carbonate minerals, as was the case with past studies, it is not surprising that inverse correlations were observed between U and calcite (Howari et al., 2016; Qiu et al., 2022). The correlations between U and pyrite/TS do agree with previous studies that indicate pyrite as a primary host, but the data further suggest that clay minerals could also be a potential host phase of U as well (Howari et al., 2016; Qiu et al., 2022; Romaniello et al., 2020).

The LC and SJ cores were interpreted to have been deposited in deeper waters under anoxic conditions, and the MF and CWD cores were deposited in more oxic conditions (Lu, 2022). The correlations observed between U and TS indicate that pyrite is an important host phase in various redox conditions. The strong correlations between U and TOC in the LC and SJ cores were expected based on past observations that organic matter is an important host phase for U under reducing conditions (Khaustova et al., 2022; Lu, 2022; Wang et al., 2017; Zarasvandi et al., 2019). There was an additional correlation observed in the CWD core, and a correlation was observed between U and P in the MF core which indicates that some U may be hosted in the organic matter in this core. The correlations between U and TS are stronger than those observed between U and TOC or U and P, which indicates that pyrite is the more important host phase. The CWD and MF cores were deposited under more oxic conditions so it was expected that organic matter would not have been as important of a host (Khaustova et al., 2022; Lu, 2022; Wang et al., 2017; Zarasvandi et al., 2019).

6.1.5 Vanadium

V has had two primary host phases identified in previous studies, organic matter and clay minerals (Bian et al., 2022; Huang et al., 2015; Shi et al., 2021). A strong

negative correlation was observed between V and dolomite. Negative correlations between TIC and V were also observed in the PS, SJ, and MF cores from the whole-rock data indicating that carbonates are not a host phase for V. 74% of V remained in the residuals from the RR after the 2M nitric acid leach which indicates that V was not being hosted by a primary target of the leach. Strong correlations were observed between V and Al in the PS and SJ cores from the whole-rock dataset and in the PS, SJ, and PI cores from the leach dataset which suggests that some V was being hosted in clay minerals. This is supported by the unsuccessful attempt to remove V using 2M leach, as the leach is less effective at removing trace metals from the interior of clay minerals. There was a weak negative correlation between V and TS in the PS core from both datasets, no other correlations were observed in the other cores indicating that pyrite is not hosting V in this member. Moderate correlations were observed between V and TOC in the PS and PI cores which suggest that some V is being hosted in the organic matter. To further this observation, V and P had significant correlations in all cores from this member. V is being hosted by organic matter, which would account for the poor removal rates.

V is thought to be enriched in Al minerals and TOC in reducing conditions (Bian et al., 2022; Huang et al., 2015; Shi et al., 2021). The PS core was interpreted by Lu et al. (2024) to have been deposited under suboxic to anoxic conditions, and significant correlations were observed between V and Al in this core. However, correlations between V and Al were also observed in the SJ core which was interpreted to have been deposited under oxic-suboxic conditions. This could suggest that clay minerals also are a host phase under more oxic conditions. The PI core was interpreted by Lu et al. (2024) to have been deposited under more O₂ deficient conditions, compared to the SJ core. This does account for why there were correlations observed between V and Al, as well as V and TOC. V is thought to be enriched in TOC under moderately reducing conditions, these observations agree.

The average removal rate of V from the CW by the leach was 38%, suggesting that the majority of V was hosted by a target of the leach. Strong to moderate correlations were observed between V and Al in all cores from both datasets. The leach data mostly agreed with moderate correlations observed in the LC, CWD, and MF cores suggesting

that V is being hosted by the Al minerals. Correlations between V and TS were observed in all cores from the whole-rock dataset and two cores from the leach dataset. The strength of the correlations between V & Al and V & TS were evenly matched and neither appears to be the primary host over the other. There were two correlations observed between V and TOC in the LC and SJ cores from the whole-rock dataset, and one correlation observed in the LC core from the leach dataset. This suggests that organic matter is a host phase as well. Significant correlations were observed between V and P in the SJ, CWD, and MF cores. This is evidence that further supports that the organic matter is hosting V as well. V is known to become enriched in P minerals such as apatite, but there is very little P content within these samples, the P is likely located in the organic matter. U and V have similar correlations with P within these cores, both have significant correlations within the SJ, CDW, and MF cores. Comparatively, strong to moderate inverse correlations were observed between V and TIC in the LC, SJ, and CWDs from the whole-rock dataset, which indicates that carbonate is not a host phase.

These findings partially agree with previous studies. Al minerals are a host for V within the CW member. However, the results also show that pyrite is also the primary host phase for V. This was unexpected as pyrite is not widely considered to be a primary host for V (Bennett and Canfield, 2020; Bian et al., 2022; Huang et al., 2015; Shi et al., 2021). The observations between Al and V do mostly align with the redox conditions that were interpreted by Lu et al. (2024). The LC and SJ cores were interpreted as having been deposited in deeper waters that had anoxic conditions. Within these cores, V and Al had significant correlations. However, correlations were also observed in cores deposited under oxic conditions (MF & CWD cores). This also suggests that clay minerals act as host phases for V in both anoxic and oxic conditions.

6.2 Trace Metal-to-Al Ratios as Redox Proxies

As introduced in Chapter 2.3, both Bennett and Canfield (2020) and Kunert and Kendall (2023) used data from modern marine environments to develop Al-normalized trace metal and Re/Mo ranges to identify ancient local redox conditions at the time of

deposition. When the water column is oxygenated, the identified O_2 ranges are suboxic = 0-15 μM ; dysoxic = 15-90 μM ; and oxic > 90 μM (Algeo and Liu, 2020). Anoxic refers to an anoxic but non-sulfidic water column whereas euxinic refers to an anoxic and sulfidic water column. The sedimentary trace metal ratio range for each local redox condition is defined in Table 10 below.

Table 10: Identified ranges for trace metal ratios by Bennett and Canfield (2020) and Kunert and Kendall (2023)

	Euxinic	Anoxic	Suboxic	Dysoxic	Oxic
V/Al	46-23	>46	<23	<23	<23
Mo/Al	>5	>5	<5	<5	<0.4
U/Al	>1	>5	1-5	1-5	<1
Re/Al	>1.3	>1.3	>1.3	>1.3	<1.3
Re/Mo	<2	<2	2-10	>10	>10

The next two sections consider the trace metal /Al and Re/Mo ratios of each core from the RR Member and Collingwood Member.

6.2.1 RR Trace Metal/Al and Re/Mo Ratios

The PS core had V/Al values <23 $\mu\text{g g}^{-1}/\%$ which can indicate suboxic/dysoxic or oxic. The U/Al values were <1 $\mu\text{g g}^{-1}/\%$ and the Re/Al values were <1.3 $\text{ng g}^{-1}/\%$, indicating deposition in oxic conditions. The Mo/Al values were <5 $\mu\text{g g}^{-1}/\%$ which is within the suboxic/dysoxic range. In contrast, the Re/Mo values were <2 which is the only indicator suggesting anoxic/euxinic conditions at this locality. Overall, the RR in this core can be interpreted as having been deposited from oxygenated bottom waters based on the consistent agreement between all trace metal / Al ratios.

The SJ core had Mo/Al values that were all within the suboxic/dysoxic range. U/Al values were within the oxic range, but Re/Al values were >1.3 $\text{ng g}^{-1}/\%$ which can indicate either suboxic/dysoxic, anoxic, or euxinic conditions. The Re/Mo values were mostly within the anoxic/euxinic ranges. The V/Al values of <23 $\mu\text{g g}^{-1}/\%$ could indicate either oxic, suboxic, or dysoxic settings. Combining the results from all metal/Al ratios, it can be interpreted that the RR in this core was more likely deposited in suboxic/dysoxic settings than in oxic or anoxic/euxinic conditions.

The MF core had a majority of V/Al values that landed within the euxinic range ($46\text{--}23\text{ }\mu\text{g g}^{-1}/\%$), with some landing in the suboxic/dysoxic or oxic range ($<23\text{ }\mu\text{g g}^{-1}/\%$). The U/Al values were within the oxic range, the Re/Al values agreed as they were $<1.3\text{ ng g}^{-1}/\%$. The MF core had Mo/Al values within the oxic category. The Re/Mo values were within the anoxic/euxinic category. There was disagreement between some of the proxies but given where most of the values landed, the RR in this core was deposited in an oxic environment.

The PI core had V/Al values mostly within the euxinic range, and the Re/Mo values were within the anoxic or euxinic range as well. Both the U/Al and Mo/Al values all landed within the suboxic/dysoxic range. However, the Re/Al values disagreed as they were $<1.3\text{ ng g}^{-1}/\%$ indicating oxic conditions. There was significant disagreement between the proxies for this core. There was no agreement between any of the proxies, so the redox state is ambiguous.

Overall, the Re/Mo ratios suggested that the cores were deposited in anoxic/euxinic conditions. However, the trace metal/Al ratios typically did not agree and suggested that the cores were deposited in oxic-dysoxic-suboxic conditions. The results partially agree with the interpretations from Lu et al. (2024) that the RR was deposited in oxic-suboxic conditions.

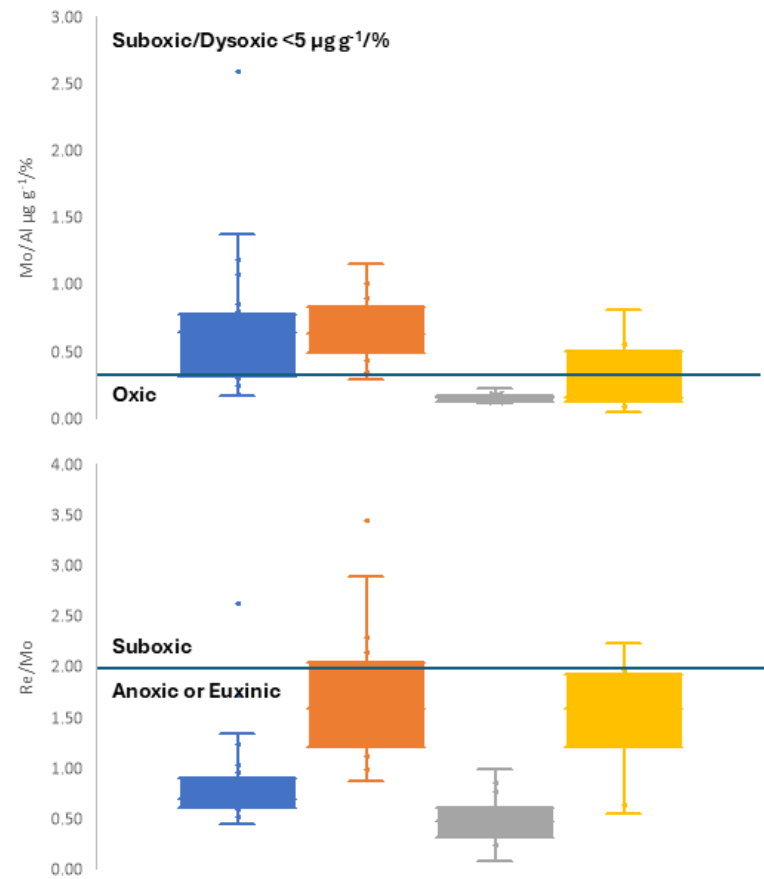
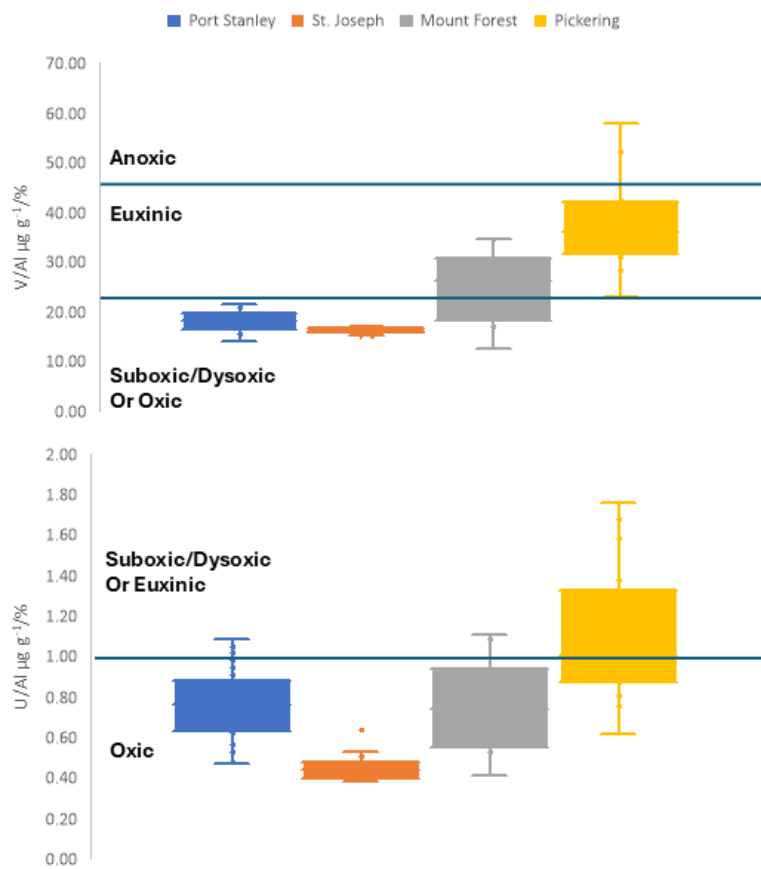


Figure 14: Using trace metal/Al ratios and Re/Mo ratios to determine the redox conditions of the Rouge River Member.

6.2.2 Collingwood Member Trace Metal/Al and Re/Mo Ratios

The LC core had V/Al values that were right in between the euxinic ($23\text{--}46 \mu\text{g g}^{-1}/\%$) and suboxic/dysoxic/oxic ($<23 \mu\text{g g}^{-1}/\%$) fields. The Mo/Al values fell within the suboxic/dysoxic ranges between 0.4 and $5 \mu\text{g g}^{-1}/\%$. The U/Al values were within the suboxic/dysoxic or euxinic range with some values landing within the oxic range. The Re/Al values agreed as they were $>1.3 \text{ ng g}^{-1}/\%$ which can indicate either anoxic, suboxic/dysoxic, or euxinic conditions. The Re/Mo values fell within the euxinic or anoxic range. The redox state is ambiguous based on the proxies and there was not clear agreement among any of them.

The SJ core had V/Al values mostly within the euxinic field but also to a lesser extent within the suboxic/dysoxic or oxic field. The U/Al and Mo/Al values were both within the suboxic/dysoxic range. The Re/Al values were $>1.3 \text{ ng g}^{-1}/\%$, indicating either anoxic, suboxic/dysoxic, or euxinic conditions. The Re/Mo values were largely within the suboxic range. The CW in this core can be interpreted as having been deposited under suboxic/dysoxic conditions.

The MF core had high V/Al values that fell within the anoxic range ($>46 \mu\text{g g}^{-1}/\%$) and some values that landed within the euxinic range. The U/Al fell within the suboxic/dysoxic range. The majority of the Mo/Al values fell within the oxic range with some landing within the suboxic/dysoxic range. The Re/Al values were $>1.3 \text{ ng g}^{-1}/\%$, suggesting suboxic/dysoxic, anoxic, or euxinic conditions, and the Re/Mo values were within the suboxic range, although some samples were also plotted in the anoxic/euxinic field. There was no agreement between the proxies, so the redox state is ambiguous.

The CWC core had V/Al values that were within the suboxic/dysoxic/oxic range. The U/Al values landed mostly within the oxic range with some within the suboxic/dysoxic/euxinic range. Both the Mo/Al ratios are within the suboxic/dysoxic range and the Re/Mo values were within the suboxic range, with some Re/Mo values landing in the oxic/dysoxic range. In contrast to the other cores, the CW member in this core appears to have been deposited in oxic conditions.

Both the trace metal and Re/Mo ratios exhibited little to no agreement with the results from Lu et al. (2024), who suggested that sediments within deeper waters (LC & SJ) were deposited within anoxic conditions and samples deposited within shallow waters (CWD & MF) were deposited under oxic conditions. The LC core proxies did not have clear agreement resulting in an ambiguous redox state. Comparatively, the SJ core was interpreted as having been deposited within suboxic/dysoxic conditions, which does not agree with previous results. The CWC was the only core that agreed with the previous results. The CW member from this core was interpreted as having been deposited in oxic conditions, which agrees with Lu et al. (2024). The proxies from the MF core in the CW member did not have a clear agreement resulting in an ambiguous redox state.

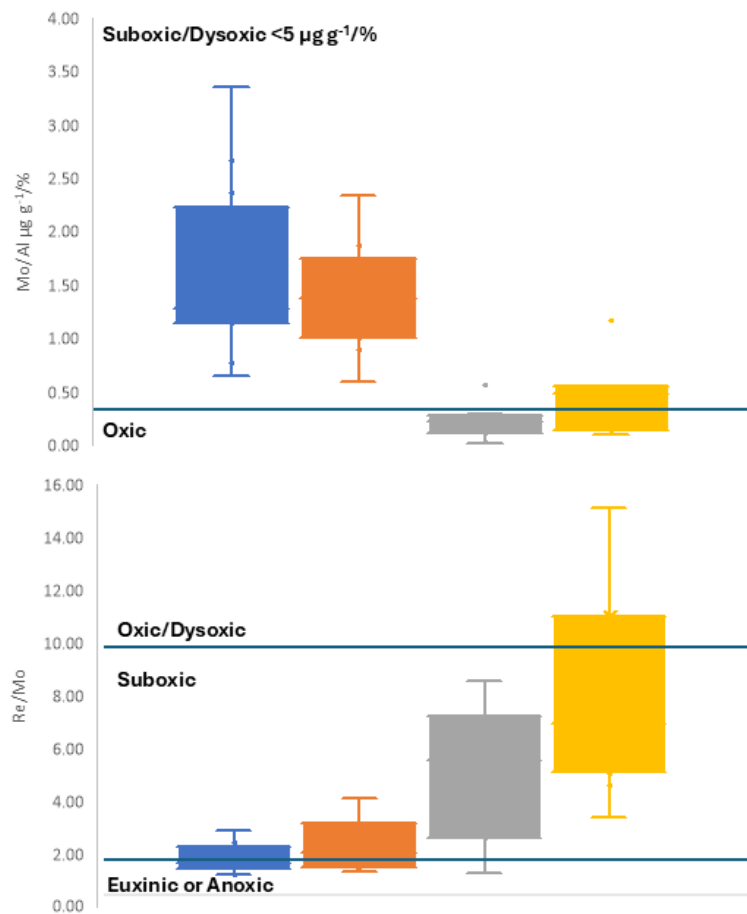
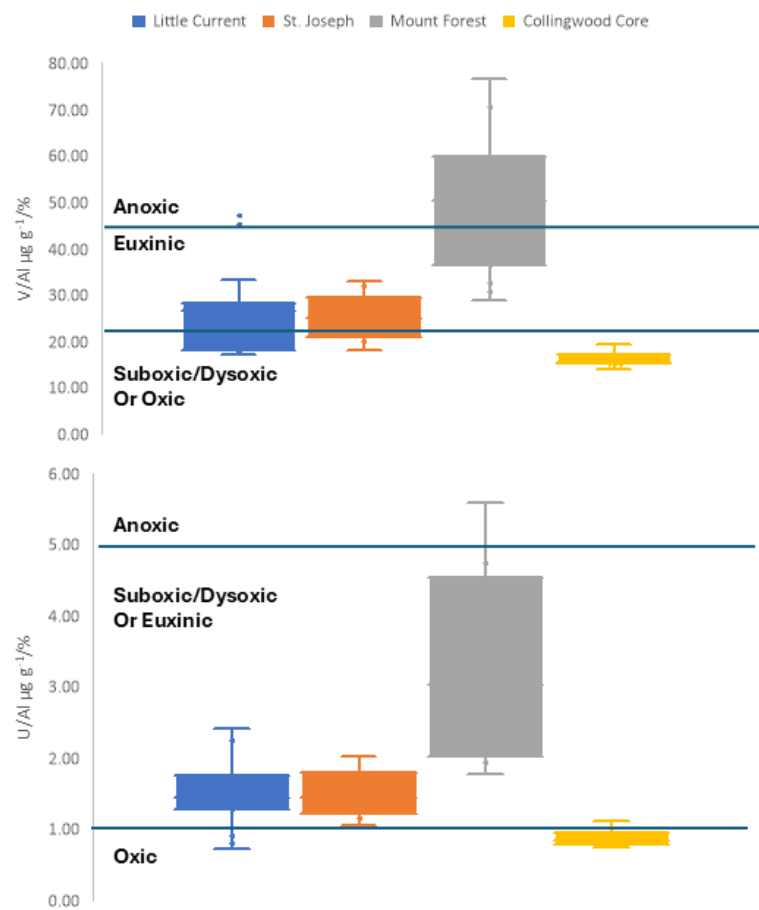


Figure 15: Using trace metal/Al ratios and Re/Mo ratios to determine the redox conditions of the Collingwood Member.

6.2.3 Summary

Overall, the local redox conditions inferred from the trace metal ratios using the classification scheme of Bennett and Canfield (2020) and Kunert and Kendall (2023) do not agree with each other for most cores. All cores had Mo/Al values of $<5 \mu\text{g g}^{-1}\%$ which indicates they were deposited in settings that could have been oxic, suboxic, or dysoxic. However, the V/Al contradicts this interpretation, with multiple cores for both the RR Member and Collingwood Member yielding V/Al ratios suggestive of anoxic and/or euxinic local redox conditions. The U/Al values that are between $1\text{--}5 \mu\text{g g}^{-1}\%$ can indicate either euxinic, suboxic, or dysoxic conditions. Many cores, particularly from the RR Member but also to a lesser extent the Collingwood Member, have Re/Mo ratios pointing to anoxic and/or euxinic conditions. The CWD core for the Collingwood Member was the only example of consistent agreement, oxygenated bottom waters in this case. This is because the Ordovician marine environment of the studied rock units was significantly different from the modern ocean settings on which these parameters were established by Bennett and Canfield (2020) and Kunert and Kendall (2023). The epicontinental settings where the RR Member and CW Member were deposited are not well represented in the modern ocean. There was also a greater extent of ocean anoxia and euxinia during the late Ordovician compared to today's settings (Hammarlund et al., 2012; Pohl et al., 2021; Zou et al., 2018).

An example of the effect of expanded ocean/anoxia on redox proxies is the Re/Mo ratio. Because Re burial in marine sediments is efficient for both anoxic/non-sulfidic and euxinic conditions whereas Mo burial in marine sediments is most efficient for euxinic conditions, the greater extent of ocean anoxia in the Ordovician ocean would reduce the global Re oceanic inventory to a greater extent than the Mo

inventory, resulting in lower seawater Re/Mo ratios (Erickson & Helz, 2000; Morford et al., 2005; Sheen et al., 2018). Consequently, the lower Re/Mo ratios for these late Ordovician samples may represent a false signature of anoxia/euxinia.

Oceans that have expanded anoxia or euxinia would have lower redox-sensitive trace metal contents within their waters which cause the trace metal/Al ratios to be lower. This would cause the trace/metal ranges of each redox category to shift down. The exception would be V/Al where the oxic ranges are the lowest and euxinic/anoxic the highest. Multiple cores had V/Al values within the euxinic range. This could have been influenced by the epicontinental sea environment where these cores were deposited.

It is common for epicontinental seas to have a Fe-Mn particulate shuttle operating if there is a chemocline fluctuating near the sediment-water interface (i.e., intermittently anoxic). This mechanism can transport trace metals that are associated with Fe and Mn oxide phases that form under mildly oxidizing shallower water and are transported to sediments in deeper anoxic/euxinic waters (T. J. Algeo & Tribovillard, 2009; X. Chen et al., 2022). This mechanism can enhance the delivery of certain redox-sensitive trace metals to sediments. Mo and V can all be transported to sediments this way; V is more affected than Mo. Both U and Re are minimally influenced by the shuttle (Kunert et al., 2020; Ostrander et al., 2019). It is plausible that the Fe-Mn particulate shuttle created a false euxinic signature for the RR and CW using the euxinic range of both V/Al from Bennett and Canfield (2020) and Re/Mo from Kunert and Kendall (2023). In conclusion, redox thresholds established by these studies based on modern marine data are not applicable to Ordovician marine environments. More generally, these thresholds probably should not be used to establish the local redox conditions of bottom waters during the Early Paleozoic or Precambrian when paleogeography and global ocean redox states were significantly different from the modern ocean.

Chapter 7: Conclusion

The results from this thesis showed that the 2M nitric acid leach is successful at removing trace metals from some of the samples. The 2M nitric acid leach successfully removed a majority of trace metals from the CW Member, but less from the RR Member. The host phases for trace metals have been an ongoing discussion. This study has successfully identified the host phases of Tl, Re, Mo, U, and V within organic-rich Katian organic-rich sedimentary rocks.

The host phases that were identified were mostly in agreement with previous studies. The prominent host phases for Tl are pyrite and clay minerals, with some hosted in organic matter. Re can be found within organic matter and pyrite but also exhibits the potential to be hosted in certain clay minerals. The host phases for Mo were not as clear cut in the RR Member, but given the overall trends, the results from this study support the previous studies that Mo is found within pyrite and organic matter, but organic matter is the primary host in non-euxinic environments (Zhou et al., 2024). U was found to have been primarily hosted by organic matter and pyrite. The primary host phases for V within these shales are organic matter and clay minerals, which agrees with previous literature (Bennett and Canfield, 2020; Bian et al., 2022; Huang et al., 2015; Shi et al., 2021).

The parameters presented by Bennett and Canfield (2020) are useful for identifying modern local bottom-water redox conditions through trace metal ratios. However, applying these ratios to the Ordovician Ocean which was more anoxic/euxinic than the modern oceans, or to ancient environments, such as epicontinental seas, which are not well-represented in the modern oceans should be done alongside other analytical methods to ensure accuracy. The trace metal ratios only partially agreed with previous redox studies on the RR and CW, but there were discrepancies from core to core. Ordovician marine environments cannot use the redox thresholds determined by these studies using current marine data. In general, these

thresholds are not suitable for determining the local redox conditions of bottom waters in the Early Paleozoic or Precambrian, when global ocean redox states and paleogeography differed greatly from those of the modern ocean.

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Chapter 8

8.1 Appendix A

Table A.1 Mineralogical Data – Rouge River Member

Rouge River Member										Avrg Conc.
Mineral	PS-9	PS-23	PS-35	PS-57	MF-4	MF-7	SJ-3	SJ-10	SJ-19	
Depth (m)	827.27	838.39	845.30	856.26	91.57	84.77	30.35	41.66	34.48	
QUARTZ	32.50	38.60	38.60	33.90	16.40	18.50	28.50	31.60	24.80	29.27
PLAGIOCLASE	2.10	2.80	3.30	2.00	0.00	0.60	0.00	0.00	0.00	1.20
K FELDSPAR	2.00	1.70	1.90	2.20	2.20	3.80	8.00	8.50	8.50	4.31
MUSCOVITE/ILLITE	27.20	31.80	29.20	32.00	12.00	13.50	30.30	31.50	24.40	25.77
CHLORITE	6.70	6.10	5.20	7.10	1.90	3.20	8.10	9.50	4.50	5.81
CALCITE	5.40	2.80	5.70	6.10	47.10	45.80	0.00	1.60	0.00	12.72
DOLOMITE	3.90	3.40	0.30	0.50	8.00	0.80	3.50	0.80	12.50	3.74
Fe DOLOMITE-ANKERITE	6.50	4.80	0.50	0.40	7.70	1.50	1.70	1.10	9.10	3.70
PYRITE	1.70	2.70	2.80	3.60	0.00	0.30	2.00	2.70	2.60	2.04

Table A.2 Mineralogical Data – Collingwood Member

CWD												Avrg Conc.
	MF-18	SJ-21	SJ-24	SJ-30	LC-1	LC-7	LC-13	LC-15	CW-21	CW-27	CW-30	
Depth (m)	485.21	159.18	161.95	168.24	105.73	108.51	111.27	112.12	72.98	76.11	78.79	
QUARTZ	3.00	8.20	10.40	9.70	27.10	9.90	5.70	9.30	17.90	7.50	9.00	10.70
PLAGIOCLASE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.20	0.00	0.00	0.11
K FELDSPAR	0.00	3.50	4.60	8.60	5.70	5.20	3.00	5.70	2.00	0.00	0.00	3.48
MUSCOVITE/ILLITE	1.00	5.00	7.60	7.20	27.60	5.80	1.60	7.00	20.70	2.00	2.50	8.00
CHLORITE	0.30	1.00	1.00	0.00	4.90	1.30	0.00	0.00	3.60	0.60	0.90	1.24
CALCITE	95.50	48.70	43.60	21.10	0.00	36.00	56.50	16.80	3.80	87.60	84.70	44.94
DOLOMITE	0.00	0.30	0.00	17.40	10.50	1.00	4.70	16.90	24.50	0.60	0.80	6.97
Fe DOLOMITE-ANKERITE	0.20	1.30	0.30	15.20	9.00	0.50	4.00	11.80	17.70	1.50	2.10	5.78
PYRITE	0.00	0.50	1.00	0.50	2.50	1.10	0.50	0.50	2.50	0.20	0.00	0.85

8.2 Appendix B: Removal Rate of Trace Metals from Rock Powder by 2M Nitric Acid Leach

Percent of Tl (μg) left behind by the 2M Nitric Acid Leach in the RR

<i>Sample Name</i>	<i>2M-Tl (μg)</i>	<i>Residue Tl (μg)</i>	<i>Total Tl (μg)</i>	<i>% Left in Residue</i>
<i>PS-1</i>	0.02	0.06	0.09	71%
<i>PS-3</i>	0.05	0.07	0.11	57%
<i>PS-5</i>	0.03	0.05	0.07	61%
<i>PS-15</i>	0.04	0.06	0.10	57%
<i>PS-20</i>	0.03	0.04	0.07	53%
<i>PS-25</i>	0.06	0.05	0.11	44%
<i>PS-30</i>	0.07	0.06	0.13	46%
<i>PS-35</i>	0.10	0.06	0.16	37%
<i>PS-40</i>	0.08	0.04	0.12	33%
<i>PS-45</i>	0.18	0.11	0.29	38%
<i>PS-56</i>	0.03	0.06	0.10	65%
<i>SJ-4</i>	0.02	0.05	0.07	74%
<i>SJ-10</i>	0.04	0.07	0.11	62%
<i>P-1</i>	0.04	0.09	0.13	71%
<i>P-12</i>	0.03	0.07	0.10	70%
<i>P-26</i>	0.09	0.06	0.15	40%

Percent of Tl (µg) left behind by the 2M Nitric Acid Leach in the CW

<i>Sample Name</i>	<i>2M- Tl (ug)</i>	<i>Residue Tl (ug)</i>	<i>Total Tl (ug)</i>	<i>% Left in Residue</i>
<i>SJ-20</i>	0.24	0.02	0.26	6%
<i>SJ-25</i>	0.27	0.01	0.28	4%
<i>SJ-30</i>	0.14	0.01	0.15	6%
<i>LC-5</i>	1.02	0.03	1.05	3%
<i>LC-10</i>	0.06	0.01	0.06	11%
<i>LC-15</i>	0.24	0.01	0.25	5%
<i>CW- 21</i>	0.07	0.04	0.11	39%

Percent of Mo (µg) left behind by the 2M Nitric Acid Leach in the RR

<i>Sample Name</i>	<i>2M- Mo (ug)</i>	<i>Residue Mo (ug)</i>	<i>Total Mo (ug)</i>	<i>% Left in Residue</i>
<i>PS-1</i>	0.04	0.17	0.21	81%
<i>PS-3</i>	0.10	0.10	0.20	50%
<i>PS-5</i>	0.04	13.11	13.15	99%
<i>PS-15</i>	0.14	0.12	0.25	46%
<i>PS-20</i>	0.15	0.11	0.27	43%
<i>PS-25</i>	0.40	0.14	0.54	26%
<i>PS-30</i>	0.44	0.24	0.68	35%
<i>PS-35</i>	0.52	0.17	0.69	24%
<i>PS-40</i>	0.40	0.15	0.56	28%
<i>PS-45</i>	0.96	0.39	1.35	29%
<i>PS-56</i>	0.10	0.10	0.20	49%
<i>SJ-4</i>	0.04	0.05	0.09	52%
<i>SJ-10</i>	0.19	0.30	0.48	62%
<i>P-1</i>	0.04	0.09	0.13	71%
<i>P-12</i>	0.03	0.07	0.10	67%
<i>P-26</i>	0.09	0.06	0.15	40%

Percent of Mo (µg) left behind by the 2M Nitric Acid Leach in the CW

<i>Sample Name</i>	<i>2M- Mo (µg)</i>	<i>Residue Mo (µg)</i>	<i>Total Mo (µg)</i>	<i>% Left in Residue</i>
<i>SJ-20</i>	2.20	0.09	2.29	4%
<i>SJ-25</i>	2.02	0.21	2.23	9%
<i>SJ-30</i>	4.52	0.15	4.67	3%
<i>LC-5</i>	4.04	0.16	4.19	4%
<i>LC-10</i>	1.04	0.06	1.10	6%
<i>LC-15</i>	2.92	0.15	3.07	5%
<i>CW-21</i>	0.20	0.05	0.25	21%

Percent of Re (ng) left behind by the 2M Nitric Acid Leach in the RR

<i>Sample Name</i>	<i>2M-Re (ng)</i>	<i>Residue Re (ng)</i>	<i>Total Re (ng)</i>	<i>% Left in Residue</i>
<i>PS-1</i>	9.74E-03	6.16E-06	9.75E-03	0.06%
<i>PS-3</i>	6.94E-03	4.01E-04	7.34E-03	5%
<i>PS-5</i>	5.05E-03	5.02E-04	5.55E-03	9%
<i>PS-15</i>	6.01E-03	7.01E-05	6.08E-03	1%
<i>PS-20</i>	4.14E-03	2.26E-06	4.15E-03	0.05%
<i>PS-25</i>	7.92E-04	1.30E-04	9.21E-04	14%
<i>PS-30</i>	5.64E-04	2.95E-04	8.60E-04	34%
<i>PS-35</i>	8.36E-04	1.09E-04	9.45E-04	11%
<i>PS-40</i>	5.12E-04	1.12E-04	6.24E-04	18%
<i>PS-45</i>	1.70E-03	1.32E-04	1.84E-03	7%
<i>PS-56</i>	1.94E-04	2.03E-05	2.14E-04	9%
<i>SJ-4</i>	2.13E-04	2.52E-04	4.66E-04	54%
<i>SJ-10</i>	3.49E-04	1.39E-04	4.88E-04	28%
<i>P-1</i>	4.24E-04	1.52E-04	5.77E-04	26%
<i>P-12</i>	3.69E-04	2.49E-04	6.18E-04	40%
<i>P-26</i>	6.66E-04	1.32E-04	7.98E-04	16%

Percent of Re (ng) left behind by the 2M Nitric Leach in the CW

<i>Sample Name</i>	<i>2M-Re (ng)</i>	<i>Residue Re (ng)</i>	<i>Total Re (ng)</i>	<i>% Left in Residue</i>
<i>SJ-20</i>	6.89E-03	5.73E-05	6.94E-03	1%
<i>SJ-25</i>	5.85E-03	1.25E-04	5.97E-03	2%
<i>SJ-30</i>	5.16E-03	2.64E-05	5.19E-03	0.5%
<i>LC-5</i>	1.20E-02	2.33E-04	1.23E-02	2%
<i>LC-10</i>	2.04E-03	2.30E-05	2.06E-03	1%
<i>LC-15</i>	4.53E-03	8.72E-05	4.62E-03	2%
<i>CW-21</i>	4.16E-04	8.20E-05	4.98E-04	16%

Percent of U (µg) left behind by the 2M Nitric Leach in the RR

<i>Sample Name</i>	<i>2M-U (ug)</i>	<i>Residue U (ug)</i>	<i>Total U (ug)</i>	<i>% Left in Residue</i>
<i>PS-1</i>	0.07	0.43	0.50	86%
<i>PS-3</i>	0.14	0.32	0.46	69%
<i>PS-5</i>	0.07	0.23	0.30	77%
<i>PS-15</i>	0.16	0.26	0.42	61%
<i>PS-20</i>	0.16	0.18	0.34	53%
<i>PS-25</i>	0.30	0.30	0.60	50%
<i>PS-30</i>	0.29	0.34	0.63	54%
<i>PS-35</i>	0.40	0.32	0.72	44%
<i>PS-40</i>	0.40	0.23	0.62	36%
<i>PS-45</i>	1.02	0.64	1.66	38%
<i>PS-56</i>	0.06	0.10	0.16	63%
<i>SJ-4</i>	0.07	0.23	0.30	77%
<i>SJ-10</i>	0.11	0.30	0.40	74%
<i>P-1</i>	0.37	0.28	0.65	43%
<i>P-12</i>	0.25	0.35	0.59	58%
<i>P-26</i>	0.28	0.29	0.58	50%

Percent of U (µg) left behind by the 2M Nitric Leach in the CW

<i>Sample Name</i>	<i>2M-U (ug)</i>	<i>Residue U (ug)</i>	<i>Total U (ug)</i>	<i>% Left in Residue</i>
<i>SJ-20</i>	1.45	0.12	1.57	8%
<i>SJ-25</i>	2.16	0.14	2.30	6%
<i>SJ-30</i>	1.63	0.11	1.74	6%
<i>LC-5</i>	3.12	0.24	3.36	7%
<i>LC-10</i>	0.85	0.07	0.92	8%
<i>LC-15</i>	1.75	0.13	1.88	7%
<i>CW-21</i>	0.15	0.23	0.38	60%

Percent of V (μg) left behind by the 2M Nitric Leach in the RR

<i>Sample Name</i>	<i>2M-V (μg)</i>	<i>Residue V (μg)</i>	<i>Total V (μg)</i>	<i>% Left in Residue</i>
<i>PS-1</i>	2.99	10.71	13.70	78%
<i>PS-3</i>	2.57	9.12	11.69	78%
<i>PS-5</i>	2.04	6.29	8.33	75%
<i>PS-15</i>	3.82	7.02	10.84	65%
<i>PS-20</i>	3.70	4.66	8.36	56%
<i>PS-25</i>	2.78	8.08	10.86	74%
<i>PS-30</i>	3.47	10.76	14.23	76%
<i>PS-35</i>	5.64	8.56	14.20	60%
<i>PS-40</i>	3.95	6.48	10.42	62%
<i>PS-45</i>	8.38	17.40	25.79	67%
<i>PS-56</i>	2.63	1.96	4.58	43%
<i>SJ-4</i>	2.99	7.31	10.29	71%
<i>SJ-10</i>	3.66	9.56	13.22	72%
<i>P-1</i>	8.30	9.31	17.61	53%
<i>P-12</i>	8.99	11.31	20.30	56%
<i>P-26</i>	6.06	9.68	15.74	62%

Percent of V (µg) left behind by the 2M Nitric Leach in the CW

<i>Sample Name</i>	<i>2M-V (ug)</i>	<i>Residue V (ug)</i>	<i>Total V (ug)</i>	<i>% Left in Residue</i>
<i>SJ-20</i>	2.81	2.26	5.07	45%
<i>SJ-25</i>	20.19	3.21	23.40	14%
<i>SJ-30</i>	23.07	1.45	24.53	6%
<i>LC-5</i>	22.13	5.99	28.12	21%
<i>LC-10</i>	41.03	1.68	42.72	4%
<i>LC-15</i>	8.15	2.78	10.93	25%
<i>CW-21</i>	25.30	4.66	29.96	16%

8.3 Appendix C: P and R Values from Whole Rock & 2M Nitric Acid Trace Metals vs Host Phase Indicators

8.3.1 Rouge River Member

8.3.1.1 Thallium

Al (%) vs Tl (ppm)

Al vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.12	0.39	0.01	0.91
SJ	0.39	0.01	0.29	0.26
MF	-0.33	0.03	0.26	0.47
PI	0.32	0.02	0.09	0.73

TS (%) vs Tl (ppm)

TS vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.72	<0.001	0.37	0.004
SJ	0.14	0.59	-0.07	0.79
MF	0.32	0.36	0.11	0.75
PI	-0.19	0.48	0.50	0.04

TOC (%) vs Tl (ppm)

TOC vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.003	0.85	-0.01	0.93
SJ	-0.15	0.58	0.83	<0.001
MF	0.4	0.25	0.28	0.08
PI	0.17	0.53	0.65	0.007

TIC (%) vs Tl (ppm)

TIC vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.15	0.28	-0.1	0.48
SJ	-0.15	0.58	0.59	0.01
MF	0.07	0.84	-0.11	0.76
PI	0.03	0.92	0.33	0.22

P (%) vs Tl (ppm)

P vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.50	<0.001	0.12	0.36
SJ	0.33	0.19	0.79	<0.001
MF	0.18	0.61	0.96	<0.001
PI	0.23	0.39	0.71	0.002

8.3.1.2 Rhenium

Al (%) vs Re (ppb)

Al vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.36	<0.001	-0.48	<0.001
SJ	-0.48	0.05	0.008	0.73
MF	0.29	0.42	0.50	0.14
PI	-0.29	0.27	0.08	0.78

TS (%) vs Re (ppb)

TS vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.92	<0.001	-0.22	0.10
SJ	0.18	0.48	0.05	0.86
MF	0.45	0.19	0.17	0.64
PI	0.05	0.84	0.008	0.98

TOC (%) vs Re (ppb)

TOC vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.003	0.85	-0.56	<0.001
SJ	-0.15	0.58	0.9	<0.001
MF	0.4	0.25	0.44	0.2
PI	0.17	0.53	0.69	0.003

TIC (%) vs Re (ppb)

TIC vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.25	0.06	0.22	0.11
SJ	0.77	<0.001	0.72	0.001
MF	-0.07	0.85	-0.2	0.58
PI	0.34	0.19	0.19	0.48

P (%) vs Re (ppb)

P vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.86	<0.001	-0.17	0.20
SJ	0.61	0.008	0.75	<0.001
MF	0.11	0.77	-0.02	0.96
PI	0.38	0.14	0.57	0.02

8.3.1.3 Molybdenum

Al (%) vs Mo (ppm)

Al vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.15	0.26	0.47	<0.001
SJ	-0.06	0.83	0.50	0.07
MF	-0.06	0.88	0.10	0.79
PI	-0.33	0.22	0.50	0.05

TS (%) vs Mo (ppm)

TS vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.68	<0.001	0.77	<0.001
SJ	-0.01	0.97	-0.25	0.32
MF	0.29	0.41	0.33	0.35
PI	0.8	<0.001	0.08	0.77

TOC (%) vs Mo (ppm)

TOC vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.57	<0.001	0.48	<0.001
SJ	0.68	<0.001	0.61	0.008
MF	-0.06	0.87	0.22	0.55
PI	0.5	0.05	0.3	0.26

TIC (%) vs Mo (ppm)

TIC vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.07	0.61	0.08	0.56
SJ	0.19	0.47	0.27	0.29
MF	-0.53	0.11	-0.44	0.2
PI	-0.19	0.49	-0.25	0.35

P (%) vs Mo (ppm)

P vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.63	<0.001	0.78	<0.001
SJ	0.65	0.005	0.77	<0.001
MF	-0.04	0.90	0.71	0.02
PI	-0.07	0.80	0.62	0.01

8.3.1.4 Vanadium

Al (%) vs V (ppm)

Al vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.76	<0.001	0.72	<0.001
SJ	0.97	<0.001	0.95	<0.001
MF	0.002	0.99	0.42	0.23
PI	-0.26	0.33	0.95	<0.001

TS (%) vs V (ppm)

TS vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.28	0.04	0.07	0.61
SJ	0.18	0.49	-0.37	0.15
MF	0.10	0.78	0.13	0.73
PI	0.14	0.61	-0.38	0.14

TOC (%) vs V (ppm)

TOC vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.59	<0.001	0.38	0.003
SJ	-0.39	0.12	0.04	0.87
MF	-0.29	0.41	0.3	0.4
PI	0.58	0.02	0.003	0.99

TIC (%) vs V (ppm)

TIC vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.72	<0.001	0.12	0.38
SJ	-0.66	<0.001	-0.04	0.89
MF	-0.74	0.01	-0.21	0.56
PI	-0.17	0.52	-0.07	0.95

P (%) vs V (ppm)

P vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.43	<0.001	0.29	0.03
SJ	0.03	0.92	0.61	0.009
MF	-0.65	0.04	0.85	0.002
PI	0.56	0.02	0.74	0.001

8.3.1.5 Uranium

Al (%) vs U (ppm)

Al vs U	Whole-rock		Leach	
	r value	p value	r value	p value
PS	0.25	<0.001	0.68	<0.001
SJ	0.59	<0.001	0.72	0.001
MF	0.170	0.64	0.24	0.51
PI	-0.25	0.35	-0.48	0.06

TS (%) vs U (ppm)

TS vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.02	0.88	0.08	0.55
SJ	0.20	0.44	-0.29	0.26
MF	0.51	0.13	0.2	0.57
PI	0.21	0.43	0.06	0.83

TOC (%) vs U (ppm)

TOC vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.84	<0.001	0.79	<0.001
SJ	0.25	0.12	0.45	0.07
MF	0.67	0.41	0.23	0.53
PI	0.78	<0.001	0.31	0.24

TIC (%) vs U (ppm)

TIC vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	-0.46	<0.001	-0.2	0.14
SJ	-0.15	0.46	0.2	0.44
MF	-0.22	0.54	-0.2	0.56
PI	-0.25	0.35	0.33	0.22

P (%) vs U (ppm)

P vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
PS	0.002	0.99	0.41	0.002
SJ	0.29	0.25	0.83	<0.001
MF	0.40	0.26	0.96	<0.001
PI	0.60	0.01	0.62	0.01

8.3.2 Collingwood Member

8.3.2.1 Thallium

Al (%) vs Tl (ppm)

Al vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	-0.12	0.39	0.71	0.003
SJ	0.39	0.01	0.16	0.64
CWD	-0.33	0.03	0.75	0.05
MF	0.32	0.02	0.89	<0.001

TS (%) vs Tl (ppm)

TS vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.76	<0.001	0.75	0.001
SJ	0.83	0.001	0.86	<0.001
CWD	0.83	0.02	0.86	0.001
MF	0.8	0.0008	0.85	<0.001

TOC (%) vs Tl (ppm)

TOC vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.05	0.86	0.38	0.16
SJ	0.74	0.01	0.67	0.02
CWD	0.43	0.33	0.50	0.25
MF	0.51	0.07	0.56	0.07

TIC (%) vs Tl (ppm)

TIC vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	-0.9	<0.001	-0.81	<0.001
SJ	-0.95	<0.001	-0.79	<0.001
CWD	-0.82	0.02	-0.82	0.02
MF	-0.54	0.05	0.96	<0.001

P (%) vs Tl (ppm)

P vs Tl	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.52	0.05	0.44	0.10
SJ	0.87	<0.001	0.60	0.05
CWD	0.71	0.07	0.60	0.15
MF	0.61	0.02	0.53	0.05

8.3.2.2 Rhenium

Al (%) vs Re (ppb)

Al vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.53	0.04	0.67	0.006
SJ	0.72	0.01	0.54	0.08
CWD	0.69	0.08	0.27	0.55
MF	0.64	0.02	0.56	0.04

TS (%) vs Re (ppb)

TS vs Re	Whole-rock		Leach	
	r value	p value	r value	p value
LC	0.92	<0.001	0.8	<0.001
SJ	0.18	0.6	0.79	<0.001
CWD	0.44	0.32	0.41	0.24
MF	0.05	0.87	0.84	<0.001

TOC (%) vs Re (ppb)

TOC vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.68	0.005	0.61	<0.001
SJ	0.58	0.06	0.67	0.003
CWD	0.99	<0.001	0.94	<0.001
MF	0.5	0.08	-0.04	0.88

TIC (%) vs Re (ppb)

TIC vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	-0.66	0.007	-0.76	<0.001
SJ	-0.56	0.07	-0.9	<0.001
CWD	-0.77	0.04	-0.75	0.01
MF	-0.45	0.12	-0.46	0.07

P (%) vs Re (ppb)

P vs Re	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.44	0.10	0.61	0.07
SJ	0.33	0.31	0.78	0.004
CWD	0.70	0.08	0.78	0.04
MF	0.43	0.13	0.46	0.09

8.3.2.3 Molybdenum

Al (%) vs Mo (ppm)

Al vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.26	0.35	0.30	0.28
SJ	-0.18	0.59	0.33	0.33
CWD	0.65	0.1	0.39	0.37
MF	0.61	0.03	0.61	0.02

TS (%) vs Mo (ppm)

TS vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.28	0.31	0.56	<0.001
SJ	0.58	0.06	0.33	0.2
CWD	0.62	0.13	0.56	0.09
MF	0.95	<0.001	0.94	<0.01

TOC (%) vs Mo (ppm)

TOC vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.71	<0.001	0.76	<0.001
SJ	0.5	0.04	-0.27	0.3
CWD	0.89	<0.001	0.81	0.004
MF	0.61	0.01	0.61	0.01

TIC (%) vs Mo (ppm)

TIC vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	-0.25	0.37	-0.48	<0.001
SJ	-0.39	0.23	0.005	0.98
CWD	-0.87	0.008	-0.76	0.008
MF	0.87	<0.001	-0.71	0.002

P (%) vs Mo (ppm)

P vs Mo	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.10	0.71	0.41	0.13
SJ	-0.04	0.89	-0.13	0.02
CWD	0.75	0.05	0.67	0.10
MF	0.34	0.23	-0.006	0.83

8.3.2.4 Vanadium

Al (%) vs V (ppm)

Al vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.53	0.04	0.63	0.01
SJ	0.67	0.02	0.89	<0.001
CWD	0.98	<0.001	0.93	<0.001
MF	0.93	<0.001	0.58	0.03

TS (%) vs V (ppm)

TS vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.61	0.05	0.61	<0.001
SJ	0.79	0.003	0.49	0.15
CWD	0.86	0.009	0.73	0.01
MF	0.65	0.01	0.4	0.14

TOC (%) vs V (ppm)

TOC vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.55	0.03	0.5	<0.001
SJ	0.78	0.004	0.23	0.37
CWD	0.6	0.14	0.26	0.46
MF	0.48	0.09	0.43	0.09

TIC (%) vs V (ppm)

TIC vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	-0.67	0.006	-0.67	<0.001
SJ	-0.88	<0.001	-0.88	0.89
CWD	-0.91	0.003	-0.81	0.56
MF	0.83	<0.001	0.7	0.95

P (%) vs V (ppm)

P vs V	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.32	0.24	0.41	0.13
SJ	0.35	0.28	0.64	0.03
CWD	0.83	0.02	0.84	0.02
MF	0.76	0.001	0.59	0.03

8.3.2.5 Uranium

Al (%) vs U (ppm)

Al vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.37	0.17	0.25	0.36
SJ	0.66	0.02	0.48	0.14
CWD	0.98	<0.001	0.62	0.14
MF	0.72	0.01	0.42	0.14

TS (%) vs U (ppm)

TS vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.67	0.01	0.61	<0.001
SJ	0.78	0.004	0.87	<0.001
CWD	0.79	0.03	0.66	0.04
MF	0.77	0.002	0.47	0.07

TOC (%) vs U (ppm)

TOC vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.79	<0.001	0.89	<0.001
SJ	0.84	0.001	-0.27	0.79
CWD	0.76	0.04	0.81	0.004
MF	0.38	0.2	0.12	0.65

TIC (%) vs U (ppm)

TIC vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	-0.58	0.02	-0.5	<0.001
SJ	-0.78	0.004	-0.88	<0.001
CWD	-0.94	0.001	-0.82	0.003
MF	0.82	<0.001	0.47	0.06

P(%) vs U (ppm)

P vs U	Whole-rock		Leach	
	r-value	p-value	r-value	p-value
LC	0.49	0.06	0.49	0.06
SJ	0.47	0.15	0.60	0.06
CWD	0.90	0.005	0.84	0.02
MF	0.57	0.03	0.42	0.14

8.4 Appendix D: Trace Metal & Bulk Major Elemental Data

TABLE D.1

ROUGE RIVER MEMBER- LEACH DATA												
Sample	Tl	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	Tl (WR)	V (WR)
	ppm	ppm	ppm	ppb	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
PS2	0.22	0.82	1.23	79.48	21.56	1.41	1.40	2.22	1.36	0.15	0.60	131.14
PS3	0.36	0.81	1.12	55.04	20.42	1.35	1.33	2.13	1.38	0.16	0.90	127.96
PS4	0.39	0.38	0.72	55.93	25.49	1.71	1.30	1.25	0.97	0.10	0.54	129.89
PS5	0.28	0.44	0.65	49.30	19.94	1.34	1.28	1.76	1.11	0.12	0.65	129.75
PS6	0.28	0.76	1.73	79.24	30.47	0.85	1.38	2.35	0.94	0.17	0.61	133.10
PS7	0.37	0.86	0.87	67.64	21.52	1.08	0.85	2.40	4.83	0.17	0.48	94.27
PS8	0.37	0.52	1.19	59.54	28.59	0.85	0.85	2.21	4.34	0.14	1.22	102.84
PS9	0.31	0.64	1.15	60.93	18.90	1.22	1.24	2.52	1.19	0.16	0.69	133.80
PS10	0.41	1.15	1.29	57.88	28.21	0.79	1.15	2.29	3.31	0.16	0.52	108.77
PS11	0.36	1.08	1.13	63.08	29.67	1.06	1.30	2.21	1.99	0.18	0.68	123.97
PS12	0.32	1.05	1.08	52.24	18.24	1.11	1.26	2.48	1.13	0.17	0.63	135.46
PS13	0.50	0.79	0.99	59.88	20.14	1.12	1.23	2.42	1.20	0.18	0.63	134.63
PS14	0.37	1.46	1.29	52.97	20.25	0.98	1.53	2.88	1.08	0.15	0.67	135.80
PS15	0.42	1.13	1.36	50.25	31.94	0.96	1.16	2.44	2.76	0.16	0.62	114.52
PS16	0.37	1.99	1.40	60.56	21.15	1.07	1.60	3.40	0.67	0.18	0.79	131.25
PS17	0.46	1.01	1.25	51.96	29.57	1.05	1.12	3.19	1.54	0.17	0.78	121.98
PS18	0.38	2.67	1.99	58.15	19.09	1.08	1.50	3.98	0.60	0.16	0.71	141.10

PS19	0.47	2.89	2.30	65.04	22.38	1.34	1.52	3.76	0.75	0.14	0.44	91.24
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TABLE D.1 CONTINUED

Sample	TI	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	TI (WR)	V (WR)
	ppm	ppm	ppm	ppb	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
PS20	0.47	1.41	1.46	38.31	34.23	0.81	1.02	2.08	5.35	0.14	0.41	92.66
PS21	0.31	1.78	1.20	17.65	18.69	0.82	1.51	2.74	1.03	0.14	0.67	136.17
PS22	0.43	5.05	2.46	7.81	20.55	1.07	1.61	4.37	0.40	0.17	0.79	161.38
PS23	0.66	5.11	2.63	7.67	36.45	1.25	1.74	3.48	1.56	0.16	0.67	144.82
PS24	0.51	3.67	2.52	8.26	33.24	1.11	1.63	3.66	1.56	0.17	1.08	142.87
PS25	0.54	3.78	2.80	7.49	26.27	1.34	1.56	3.96	0.95	0.16	1.84	154.50
PS26	0.56	4.12	2.00	7.84	26.95	1.26	1.76	3.85	1.01	0.11	1.04	154.91
PS27	0.54	3.72	2.29	3.20	24.93	1.19	1.47	4.11	1.18	0.14	0.73	165.67
PS28	0.61	3.66	2.31	8.12	35.05	1.82	1.46	3.49	1.19	0.17	1.36	159.69
PS29	0.65	3.76	2.06	2.57	32.58	1.51	1.74	3.90	0.49	0.14	0.84	173.73
PS30	0.56	3.76	2.49	4.86	29.89	1.49	1.74	4.78	0.89	0.13	0.90	169.69
PS31	0.60	4.08	2.88	10.71	44.73	2.01	1.63	4.86	0.71	0.19	0.66	150.89
PS32	0.72	4.49	2.91	6.95	42.42	1.84	1.65	4.17	1.24	0.18	0.94	158.66
PS33	0.68	3.39	2.29	2.51	62.70	1.66	1.39	3.45	3.38	0.17	0.55	137.66
PS34	0.63	2.04	1.50	3.83	19.57	0.79	1.60	4.00	1.01	0.10	0.50	142.55
PS35	0.32	5.07	3.92	8.12	54.77	3.01	2.19	4.36	0.77	0.23	0.72	142.99
PS36	0.95	3.67	2.75	3.92	48.25	2.45	2.13	3.82	0.89	0.20	1.70	140.22
PS37	0.65	3.34	2.39	3.93	36.49	1.96	1.62	3.59	0.80	0.14	0.84	166.01
PS38	0.62	3.26	3.18	5.16	33.45	1.67	1.30	4.26	1.77	0.18	0.65	144.79
PS39	0.60	4.65	3.37	6.73	41.95	2.18	1.58	3.68	1.14	0.23	0.65	138.78

TABLE D.1 CONTINUED

Sample	TI	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	TI (WR)	V (WR)
	ppm	ppm	ppm	ppb	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
PS40	0.77	4.00	3.93	5.07	39.06	2.02	1.27	4.45	1.49	0.23	0.70	144.27
PS41	0.81	3.18	2.96	4.95	37.57	1.94	1.13	4.07	0.99	0.15	0.89	154.59
PS42	0.56	3.25	2.76	3.14	42.19	2.41	1.23	3.03	1.23	0.21	0.69	144.01
PS43	0.68	3.61	3.12	5.39	36.61	1.99	1.33	3.74	1.46	0.25	0.80	140.01
PS44	0.64	3.55	3.37	3.74	29.09	1.51	1.13	4.47	1.72	0.20	0.64	151.12
PS45	0.56	4.85	5.15	8.62	42.40	2.28	1.34	4.15	1.40	0.19	0.54	137.09
PS46	0.55	2.89	2.44	3.23	26.81	1.43	1.52	3.81	1.36	0.19	0.88	151.30
PS47	0.60	4.49	3.42	6.36	33.33	1.78	1.68	3.99	1.57	0.24	0.82	145.44
PS48	0.65	2.97	2.76	3.12	32.42	1.83	1.18	3.48	1.28	0.23	0.49	132.96
PS49	0.64	2.40	2.24	1.89	18.13	1.00	1.22	3.80	1.38	0.14	1.62	144.16
PS50	0.36	12.16	2.02	20.98	34.16	1.76	6.41	2.11	5.55	0.57	2.60	65.33
PS51	6.76	5.89	1.72	8.70	24.66	1.45	3.93	2.73	0.88	0.23	2.26	133.64
PS52	2.13	2.15	1.70	5.42	22.21	1.25	1.42	3.08	1.36	0.14	0.87	156.37
PS53	0.46	4.91	2.66	5.12	27.26	1.39	2.34	3.89	1.35	0.30	0.94	135.60
PS54	1.15	3.28	1.99	6.43	21.33	1.29	2.84	2.56	1.25	0.20	1.02	120.31
PS55	1.64	0.93	0.92	4.01	15.91	1.01	1.67	2.51	2.34	0.11	1.56	122.22
PS56	0.59	0.99	0.60	1.93	26.18	1.61	1.09	1.00	0.88	0.05	0.41	134.10
PS57	0.34	1.75	1.42	3.42	24.03	1.54	2.03	2.38	1.00	0.18	0.81	141.62
SJ3	0.48	2.33	1.12	3.58	33.39	1.97	1.20	1.77	0.60	0.12	0.75	117.61
SJ4	0.16	0.37	0.60	1.85	25.96	1.54	1.11	0.90	1.48	0.07	0.42	110.01

TABLE D.1 CONTINUED

Sample	Tl	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	Tl (WR)	V (WR)
	ppm	ppm	ppm	ppb	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
SJ5	0.21	0.50	0.64	1.71	26.42	1.63	1.29	1.06	1.11	0.07	0.47	122.82
SJ6	0.30	0.82	0.86	2.77	32.49	2.05	1.43	1.01	0.56	0.07	0.65	148.05
SJ7	0.26	0.87	0.79	1.26	32.54	2.07	1.23	0.96	0.37	0.06	0.55	126.63
SJ8	0.08	0.27	0.23	0.81	10.37	0.68	1.33	1.29	0.51	0.03	0.54	135.84
SJ9	0.31	1.23	0.85	2.96	27.34	1.77	1.24	1.34	0.51	0.08	0.41	114.22
SJ10	0.33	1.51	0.87	2.85	29.92	1.90	1.40	1.40	0.50	0.08	0.63	139.24
SJ11	0.26	1.16	0.75	2.89	25.05	1.57	1.33	1.50	0.54	0.08	0.49	128.57
SJ12	0.68	3.07	1.74	5.43	50.76	2.93	1.13	1.35	0.47	0.11	0.66	140.63
SJ13	0.35	1.63	0.89	2.17	31.14	1.88	1.29	1.29	0.51	0.07	0.94	146.47
SJ14	0.38	1.72	0.85	3.41	26.98	1.62	1.22	1.56	0.58	0.06	0.60	125.46
SJ15	0.37	1.48	0.88	3.30	23.08	1.46	1.27	1.67	0.68	0.09	0.76	131.81
SJ16	0.40	1.34	0.85	3.57	27.08	1.64	1.42	1.87	0.76	0.08	0.63	112.26
SJ17	0.34	1.02	0.70	3.50	27.28	1.62	1.31	1.09	1.16	0.07	0.40	88.94
SJ18	0.55	2.75	1.11	3.70	35.20	1.93	1.20	1.91	1.24	0.08	0.53	101.94
SJ19	1.00	2.86	1.33	10.39	29.66	1.27	1.34	4.38	2.80	0.12	0.66	98.70
MF2	1.07	2.35	1.68	10.94	74.54	0.76	1.47	1.07	0.85	0.25	0.65	129.95
MF4	1.36	2.77	2.63	4.11	109.28	1.20	1.44	1.36	1.09	0.46	0.59	125.19
MF5	1.79	2.61	2.23	2.94	76.06	0.56	1.65	1.79	1.45	0.42	1.71	123.38
MF6	1.67	2.56	1.19	1.92	61.93	0.43	1.65	1.67	1.35	0.12	0.48	126.03
MF7	1.96	4.97	4.35	6.61	163.90	0.93	1.29	1.96	1.33	0.77	0.73	124.80

TABLE D.1 CONTINUED

Sample	Tl	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	Tl (WR)	V (WR)
	ppm	ppm	ppm	ppb	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
MF8	1.44	3.40	3.23	3.28	103.03	0.50	2.39	1.44	1.31	0.65	0.80	122.54
MF10	0.57	1.38	1.71	2.96	62.78	0.70	0.51	0.57	2.02	0.36	0.45	117.95
MF13	1.96	1.34	1.58	2.60	60.55	0.42	1.41	1.96	1.41	0.33	0.66	128.36
MF14	1.39	2.91	2.81	1.32	100.82	0.25	1.29	1.39	0.79	0.58	0.73	122.95
MF16	0.79	3.81	2.67	3.19	89.10	0.20	1.44	0.79	0.45	0.48	0.62	154.46
P1	0.34	5.99	3.54	3.93	76.89	4.35	2.76	2.00	0.11	0.14	0.70	170.11
P8	0.25	2.00	2.32	2.89	79.63	4.83	0.31	0.54	0.60	0.12	1.00	171.30
P9	0.53	17.77	1.88	3.47	114.31	6.68	0.37	0.54	0.52	0.21	0.76	153.36
P10	0.25	1.99	3.97	2.68	73.83	5.04	0.37	0.57	0.49	0.09	0.57	156.68
P11	0.21	1.50	4.13	1.74	67.43	4.71	0.37	1.30	1.61	0.12	0.56	160.42
P12	0.30	13.44	1.29	3.27	79.67	4.47	2.53	2.13	0.18	0.12	1.15	180.94
P13	0.21	1.29	2.26	1.63	47.51	3.10	1.60	0.47	0.34	0.09	0.44	161.82
P14	0.25	8.06	2.88	2.72	72.56	4.43	2.92	0.46	0.44	0.12	0.48	163.50
P15	0.15	1.58	4.82	1.53	43.19	2.70	2.35	0.52	0.33	0.06	0.40	156.69
P16	0.32	6.97	3.05	3.37	75.50	4.62	3.86	0.70	0.46	0.10	0.56	152.36
P17	0.23	2.51	1.99	3.50	76.40	4.94	0.43	0.58	0.52	0.10	0.70	143.58
P18	0.24	2.20	1.34	2.73	76.65	4.75	2.11	0.49	0.43	0.15	0.59	166.15
P25	0.16	2.99	2.79	2.45	53.13	3.66	6.15	0.41	0.50	0.07	0.51	155.08
P26	0.87	5.54	5.32	6.66	60.56	3.33	1.74	2.59	1.27	0.17	1.08	174.51
P27	0.22	2.40	4.47	2.12	72.50	4.27	1.66	0.59	0.44	0.12	2.40	176.55
P28	0.23	1.33	1.68	2.54	74.29	4.93	0.23	0.41	1.02	0.11	1.04	139.41

*Data previously published in Lu, (2022). Tl(WR) & V(WR) – Thallium and Vanadium from the whole-rock data

TABLE D.2

Sample	Tl	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	Tl (WR)	V (WR)
	ppm	ppm	ppm	ppb	Ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
LC1	9.25	26.15	14.76	71.69	249.78	11.08	1.34	3.59	2.54	0.99	0.80	101.29
LC2	8.54	21.77	11.92	75.42	197.11	6.29	1.35	2.86	5.56	1.50	0.46	84.90
LC3	7.86	23.06	14.02	89.48	258.85	9.07	1.36	4.66	5.34	1.36	0.62	85.62
LC4	4.20	39.00	21.39	81.17	220.49	8.40	1.93	5.95	5.19	4.68	0.32	66.08
LC5	9.11	36.00	27.87	107.21	354.04	8.90	1.64	8.41	3.95	2.91	0.53	107.06
LC6	11.24	43.51	33.48	105.92	304.68	7.94	2.52	8.41	3.05	4.15	0.70	125.00
LC7	12.64	67.03	35.73	118.33	375.87	4.94	1.30	8.31	5.76	0.86	0.28	158.91
LC8	4.48	36.21	24.02	63.52	326.62	4.19	0.96	6.46	6.29	0.94	0.13	96.26
LC9	5.78	36.62	30.83	87.86	175.30	3.01	1.12	8.18	6.44	1.51	0.32	85.28
LC10	0.49	8.96	7.30	17.56	75.65	1.51	0.52	3.53	8.71	0.35	0.10	51.87
LC11	2.22	22.63	14.86	41.55	182.27	2.71	0.59	4.75	8.13	0.47	0.09	64.98
LC12	1.86	20.54	13.27	37.62	149.55	2.05	0.70	5.33	7.40	0.54	0.11	56.41
LC13	0.44	11.79	7.79	20.28	73.72	1.40	0.57	3.77	8.35	0.35	0.08	33.64
LC14	3.39	32.88	21.33	57.49	136.02	2.21	0.94	8.63	6.09	0.82	0.13	72.09
LC15	2.23	27.11	16.23	42.10	216.94	4.11	0.74	5.50	7.07	0.47	0.13	60.10
SJ20	2.17	19.85	13.03	62.04	189.56	6.37	0.66	5.69	7.19	1.28	0.10	52.48
SJ21	3.63	25.46	14.41	76.27	163.46	3.96	0.77	6.67	7.15	0.89	0.13	61.69
SJ22	1.80	7.27	12.39	46.08	106.26	3.27	0.72	5.60	7.41	1.86	0.13	47.20
SJ23	4.79	23.29	25.35	107.58	309.16	8.49	1.12	8.06	5.91	3.29	0.25	73.11
SJ24	11.08	49.66	37.77	130.21	246.43	4.59	1.35	8.99	5.79	2.19	0.24	102.36
SJ25	2.47	18.97	20.27	54.89	194.05	4.30	1.00	8.02	6.44	1.51	0.17	77.31
SJ26	0.52	7.03	5.08	18.48	58.82	1.31	0.71	5.77	7.65	0.29	0.09	59.99

TABLE D.2 CONTINUED

Sample	Tl	Mo	U	Re	V	Al	TS*	TOC*	TIC*	P	Tl (WR)	V (WR)
	ppm	ppm	ppm	ppb	Ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm
SJ27	1.81	91.58	12.38	36.86	183.64	4.96	0.91	4.17	7.73	0.70	0.08	40.22
SJ28	2.09	24.64	15.81	40.29	85.09	2.20	0.81	8.05	7.66	0.52	0.11	54.19
SJ29	3.39	55.24	26.07	68.31	367.84	7.17	0.85	6.47	6.77	0.91	0.14	74.80
SJ30	1.27	38.01	13.70	43.43	197.44	5.66	0.72	4.59	7.30	0.63	0.13	55.77
CW21	0.56	1.71	1.31	3.57	25.30	1.20	1.23	1.67	5.56	0.13	0.48	61.10
CW22	0.47	4.08	1.97	15.23	20.03	0.92	0.86	9.29	4.97	0.19	0.35	20.51
CW23	0.21	1.36	1.18	8.36	11.96	0.72	0.82	7.98	5.43	0.14	0.22	21.03
CW27	0.06	0.59	0.75	2.35	11.48	0.74	0.28	0.62	9.58	0.07	0.06	56.11
CW28	0.04	0.59	0.39	1.48	7.84	0.46	0.27	1.26	7.96	0.05	0.03	16.27
CW29	0.08	0.37	0.85	3.76	15.17	0.98	0.24	1.36	7.60	0.16	0.20	40.86
CW30	0.05	0.34	0.64	1.97	10.41	0.64	0.70	0.40	8.51	0.10	0.09	31.95
MF-4	0.09	0.44	1.63	10.94	20.47	1.20	0.21	1.20	6.66	0.26	0.19	12.26
MF-5	0.05	0.27	0.96	4.11	9.52	0.56	0.13	2.13	7.42	0.03	0.06	7.69
MF-6	0.04	0.33	0.54	2.94	8.16	0.43	0.24	0.96	7.17	0.09	0.06	14.36
MF-7	0.12	0.77	0.45	1.92	12.70	0.93	0.51	4.11	5.25	0.07	0.24	9.35
MF-8	0.04	0.24	1.10	6.61	9.21	0.50	0.15	2.30	7.51	0.11	0.04	16.27
MF-10	0.06	0.39	0.75	3.28	10.48	0.70	0.18	2.67	6.61	0.13	0.15	40.86
MF-11	0.09	0.55	0.74	2.96	10.18	0.76	0.34	1.47	8.09	0.10	0.18	31.95
MF-13	0.04	0.28	0.68	5.14	7.80	0.42	0.17	3.15	6.42	0.03	0.03	12.26
MF-14	0.02	0.21	0.30	2.60	4.30	0.25	0.14	0.72	8.05	0.02	0.03	7.69
MF-16	0.03	0.16	1.55	1.32	5.19	0.20	0.16	0.67	7.78	0.08	0.04	14.36
MF-17	0.02	0.14	0.62		3.96	0.19	0.12	0.91	8.19	0.06	0.04	9.35

*Data previously published in Lu (2022). Tl (WR) & V (WR) – Whole-rock Thallium and Vanadium