NATURALLY-OCCURRING CHROMIUM AND VANADIUM IN CHARLOTTE TERRANE ROCKS: A SOURCE OF TRACE ELEMENTS TO GROUNDWATER?

by

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ABSTRACT

JACEY JEAN VAIL. Naturally-occurring chromium and vanadium in Charlotte Terrane rocks: A source of trace elements to groundwater? (Under the direction of DR. DAVID VINSON)

Vanadium (V) and chromium (Cr) contamination has become a rising concern in North Carolina due to a coal ash spill in February 2014. Coal ash is known to contain these trace elements, but V and Cr are also naturally occurring. Cr and V above health advisory guidelines has been identified in groundwater areas in the vicinity of coal ash sites, but the contamination source is still unknown. This coal ash spill occurred within the geologic region of the Charlotte Terrane rocks where the abundance of naturally occurring V and Cr is unknown. In this study, 46 samples were collected from five map scale units ranging from mafic to felsic rock compositions. Studies surrounding the behaviour of Cr and V have shown these elements tend to be associated with oxides, especially Fe and Mn. It was hypothesized that mafic Charlotte Terrane rocks would contain higher amounts of total Cr and V compared to intermediate/felsic rocks. A three-step sequential extraction was performed on each rock sample to quantify the amount of Cr and V that could potentially be released into groundwater. The third extraction, hydroxylamine hydrochloride, targeted oxides. It was hypothesized most Cr and V would be extracted in this step and more would be extracted from mafic rocks than intermediate/felsic rocks.

After XRF analysis, it was determined that mafic rocks contain, on average, higher amounts of total Cr and V than intermediate/felsic rocks. For mafic rocks, the average total Cr was 356 µg/g and the average total V was 247 µg/g. For intermediate/felsic rocks, the average total Cr was 58 µg/g and the average total V was 85 µg/g. It should be noted that total Cr and V for intermediate/felsic rocks are semiquantitative because most of the XRF results for these rocks were near the detection limit. As for the hydroxylamine hydrochloride, the confirmed intermediate/felsic rocks, on average, had higher extraction concentrations of Cr (but not V) compared to the mafic rocks. On average, the hydroxylamine-extractable Cr was 23.1 µg/g in intermediate/felsic rocks and 13.2 µg/g for mafic rocks. When hydroxylamine-extractable Cr is compared to total Cr about 40.4% of total Cr was extracted from felsic/intermediate rocks and about 3.7% from mafic rocks. On average, the hydroxylamine-extractable V for intermediate/felsic rocks was 3 µg/g and 3.7 µg/g for mafic rocks. When hydroxylamine-extractable V is compared to total V about 3.5% of total V was extracted from felsic/intermediate rocks and about 1.5% was extracted from mafic rocks. Overall, rock type does seem to be a factor in Cr and V occurrence while leachability of Cr and V is less clear. A higher proportion of total Cr and V was leachable in felsic/intermediate which may imply that Cr and V in intermediate/felsic rocks are held in more leachable sites than in mafic rocks.

In conclusion, total Cr and V can be associated with specific rock type. Mafic rocks have higher total Cr and V, but felsic/intermediate rock had higher hydroxylamine-extractable Cr compared to mafic rocks. A larger proportion of total Cr and V were extracted from the felsic rock than the mafic rocks. The results do not support mafic rocks as the main source of Cr and V into groundwater, but the results do support Charlotte Terrane rocks being a potential natural source of Cr and V to groundwater.

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1 Introduction

Vanadium (V) and chromium (Cr) contamination is a significant concern surrounding coal ash storage sites in North Carolina. Hundreds of private well owners near coal ash disposal ponds were issued letters from the NC Department of Environmental Quality (NCDEQ) advising them to not drink their well water due to this contamination (Henderson, 2015; NC Department of Environmental Quality, 2015c). These letters were later rescinded over controversy about the acceptable levels on Cr and V in groundwater and dispute over the sources of Cr and V (Henderson, 2016a). It is known that coal ash contains V and Cr, but the source of the contamination for these private well owners and residents is not fully understood. It might be inferred that the contamination is due to the coal ash, but these elements occur naturally in area lithologies. Vengosh et al. (2016) found Cr and V in NC Piedmont groundwater far from coal ash sites, suggesting (1) Cr and V has a naturally occurring source (Dwivedi et al., 2017; Regan et al., 2017) and (2) Cr and V may occur throughout regional groundwater and not only close to coal ash sites. This study seeks to investigate the naturally-occurring V and Cr content in select Charlotte Terrane rock types and the degree to which these elements could be leached into groundwater.

1.1 Geologic setting

This study will utilize the “terrane” nomenclature of Hibbard et al. (2002) instead of the older “belt” terminology. The Charlotte Terrane is a band of Piedmont rocks that occurs from Georgia to central North Carolina (Figure 1) and is thought to be Neoproterozoic to mid-Paleozoic in age. The protoliths are from a volcanic arc system and are therefore primarily volcanic and intrusive (Hibbard et al., 2002). According to Goldsmith et al. (1988), the rocks are divided into pre-, syn- and post-tectonic suites. The most abundant suite in the Charlotte Terrane rocks is pre-tectonic (Neoproterozoic to early Paleozoic). This study focuses on the pre-tectonic suite (Figure 2).

The pre-tectonic suite is a metamorphosed volcanic-plutonic complex ranging in composition from ultramafic and mafic (i.e. basalt and gabbro) to felsic and ranging in texture from coarse-grained plutonic rocks through porphyritic hypabyssal rocks, which include extrusive volcanic flows and tuffs (Figure 3; Goldsmith et al., 1988). Metamorphic grade ranges from upper greenschist to lower amphibolite facies (Dennis and Shervais, 1996). Although these rocks have undergone metamorphism, the metaintrusives commonly do not show foliation. Instead, they show their degree of metamorphism through mineralogical changes (Wilson and Jones, 1986). Metamorphic minerals include chlorite, serpentine, albite, and epidote (Dennis and Shervais, 1996). The main mafic rock types in the pre-tectonic suite are metagabbro, metadiabase, metavolcanics and a metamorphic mafic complex, which includes metamorphosed equivalents of gabbroic and ultramafic intrusives, hypabyssal and possible extrusive basalts. The main felsic to intermediate rocks include meta-quartz diorite and metavolcanics (Goldsmith et al., 1988).

Goldsmith et al. (1988) mapped large areas in the Charlotte Terrane as metavolcanic. At the map scale, the metavolcanic rocks are typically described as undivided felsic to mafic rocks and are commonly interbedded (mv) (Goldsmith et al., 1988). Overall, the Charlotte Terrane has abundant mafic and felsic material that is intrusive, metavolcanic, and a higher metamorphic grade (upper greenschist to lowermost amphibolite facies) than the rocks to the east in the Carolina Terrane and to the west in the Kings Mountain belt.

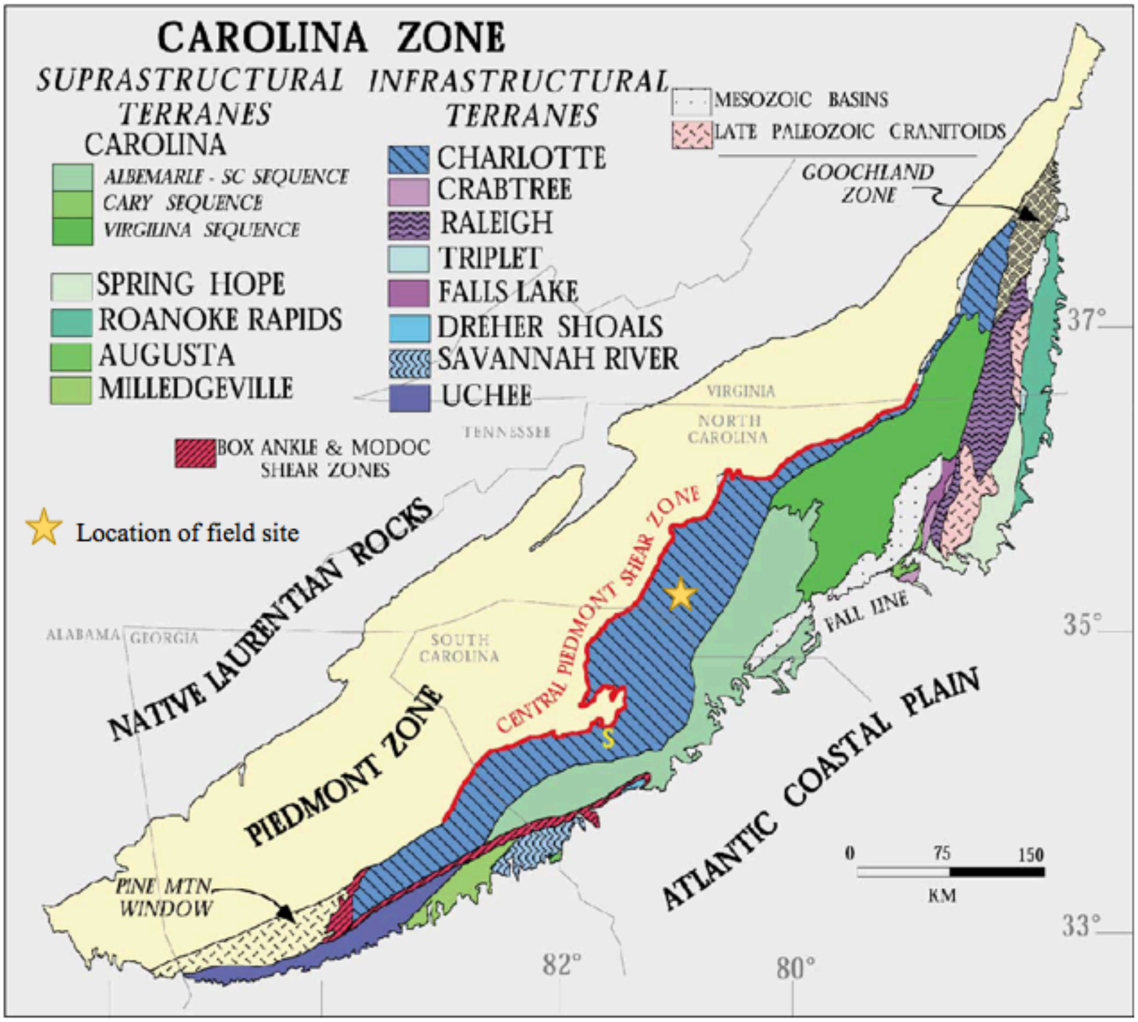


Figure 1: The distribution of terranes in the Carolina Zone modified from Hibbard et al. (2002). The yellow star represents the field study area within the Charlotte Terrane in the Charlotte, North Carolina metro area.

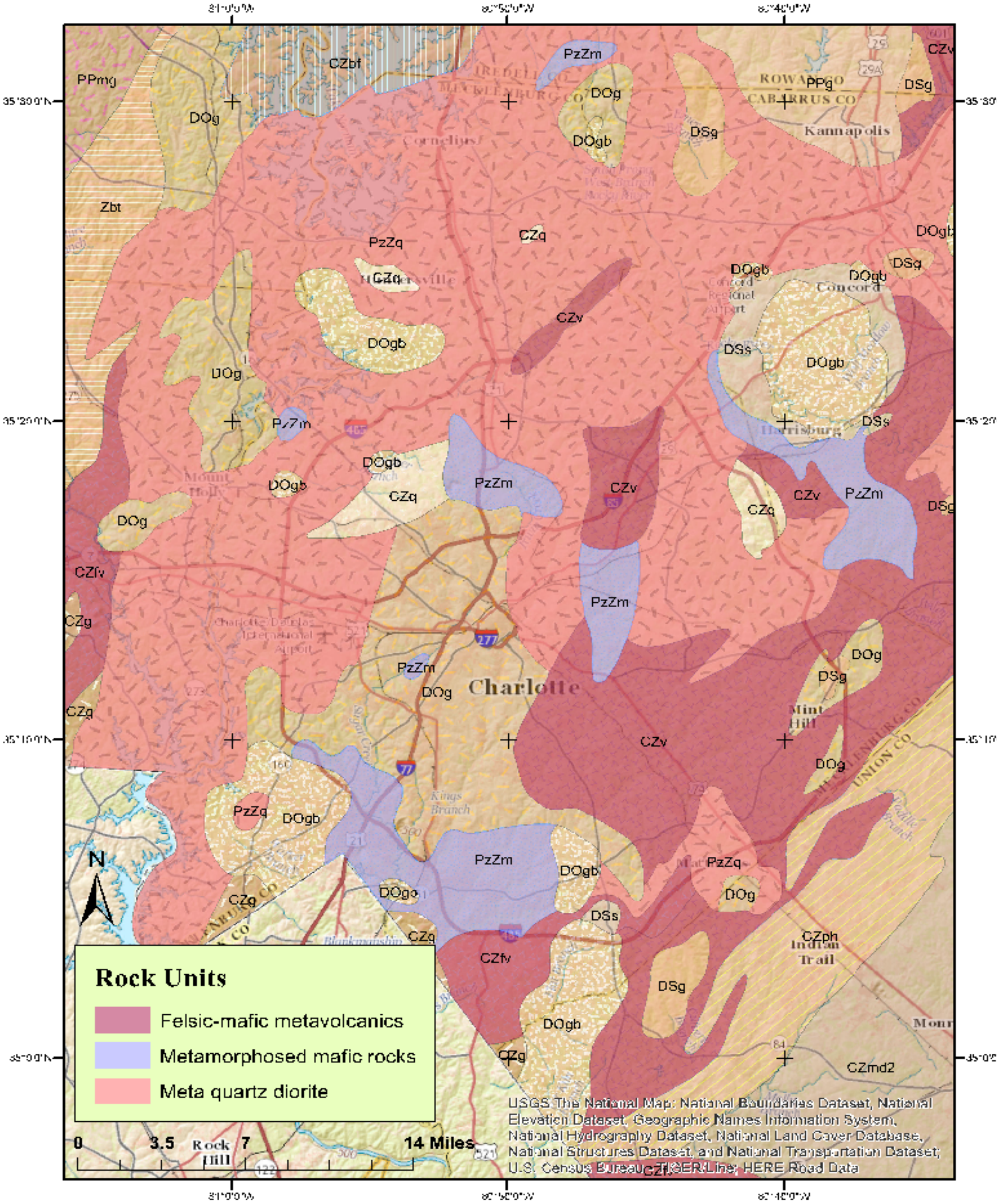


Figure 2: Bedrock geologic map of Charlotte Terrane rocks in the Charlotte area. The red, violet, and pink rock units are the targeted pre-tectonic rock types for this project. Shapefile data are based on North Carolina Geological Survey (1985) and the base map was obtained from ArcGIS Online.

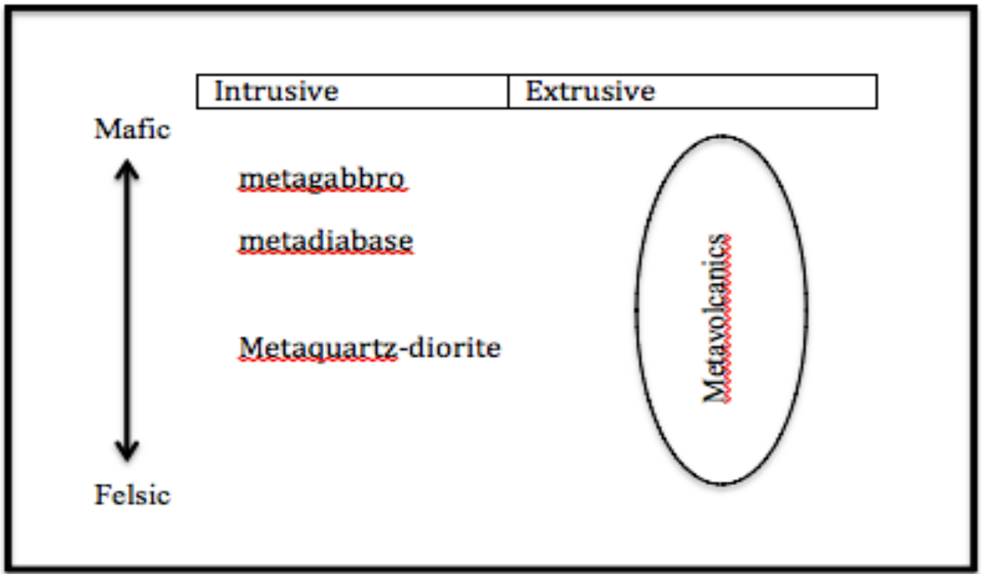


Figure 3: Simplified distribution of rock types in the pre-tectonic suite in the study area sorted by composition ranging from mafic to felsic rock types (Goldsmith et al., 1988). Younger rock types have been omitted from this study.

1.2 Local geology

This study was provided with bedrock cores that were collected at the Langtree Peninsula research station, located on the Davidson College Lake Campus on Lake Norman in Iredell County, North Carolina. This location is in the central region of the Charlotte Terrane near its north-western edge. These cores were collected during a 5 year study of the regolith-fractured bedrock groundwater system by the NC Department of Environment and Natural Resources, Division of Water Quality (Pippin et al., 2008). The cores used in this study were CH-6 and CH-7. The location of CH-6 is 35° 31’ 48.25” N and 80° 52’ 46.79” W. Samples were taken from CH-6 at depths of 22.6’ to 48’ below land surface. The location of CH-7 is 35° 31 51.57 N and 80° 52 45.82 W. Samples were taken from CH-7 at depths of 26’ to 52’ below the land surface (Figure 4Figure 5,Figure 6,Figure 7,Figure 8, and 9). In CH-7, the hornblende biotite gneiss rock type dominated the bedrock samples from 26’ to 31’ (Figure 7). From 31’to 43’ hornblende biotite gneiss and quartz diorite are present (Figure 7, Figure 8). From 43’to 53’ quartz diorite is the dominant rock type (Figure 8, Figure 9) (Pippin et al., 2008). The meta quartz diorite in the core is likely part of the metamorphosed quartz diorite and tonalite (mqd) rock unit from Goldsmith et al., (1988) (Figure 10). This rock type is likely part of the "Older Plutonic Complex", or pre-tectonic suite, as Goldsmith et al. (1988) described, which are late Proterozoic to early Paleozoic in age (Figure 11). The rock is gray to grayish-green, fine- to medium-grained, generally (weakly) foliated to massive, with an increase in foliation with depth. Pippen et al. (2008) described both fine- and medium-grained units as quartz diorite (Figure 9). The major minerals found are quartz, biotite, hornblende, and plagioclase feldspar. Minor minerals found are pyrite, epidote, and chlorite with the latter two commonly replacing hornblende. The hornblende biotite gneiss could correlate with 2-3 different rock units from Goldsmith et al. (1988) that are all thought to be older than the mqd unit (Figure 10):

1. Fine-grained biotite gneiss (bgf) – the Langtree cores are collected from this unit (Figure 12)
2. Metavolcanic rocks (mv) – this unit is broad enough to include mvm and Zbvm. This unit is described to include commonly interbedded felsic, intermediate, and mafic metavolcanics (mvm). The mvm unit includes metavolcanics with basaltic, andesitic and dacitic composition. It is mostly tuffs, but could also have hypabyssal intrusives. This unit correlates with the Battleground Formation (Zbvm) which is primarily medium to dark-gray, fine- to medium-grained hornblende gneiss and epidote amphibolite of basaltic to andesitic composition.

To properly identify the meta quartz diorite and the hornblende biotite gneiss from Pippin et al. (2008) to Goldsmith et al. (1988), the relationships between the rock units needs to be understood. In the text from Pippin et al. (2008), the dominant rock type of the cores was described as quartz diorite with some occurrence of biotite hornblende gneiss. The relationship between the two rock types were not mentioned in the text. However, in the appendices of Pippin et al. (2008) the geologic core descriptions describe a relationship between the two rock types. The core descriptions describe the biotite hornblende gneiss rocks as xenoliths within the meta quartz diorite in CH-6 and CH-7. If the biotite hornblende gneiss is a xenolith as Pippin et al. (2008) describes, these “gneiss” layers would be older than the quartz diorite.

Possible evidence in the cores suggest that the “gneiss” layers are older than the quartz diorite. For example, the “gneiss” layers appear to have undergone more metamorphism and are more foliated than the quartz diorite. If the quartz diorite was older then it too would have the same degree of foliation. Also, in the “gneiss” a halo (recrystallized area) can be seen along the edges of the intrusion (in the country rock), which is common for contact metamorphism, meaning the gneiss is older. Another piece of evidence could be the slight change in grain size (a smaller grain size) in the quartz diorite along the contact between the quartz diorite and the “gneiss” rock type. This shows the faster cooling rate of the quartz diorite when it came into contact with the cooler country rock. On the campus of UNCC surface outcrops provide evidence of inclusions of the dark, fine-grained rocks within the quartz diorite rocks. With the outcrops, the cores, and the map of Goldsmith et al. (1988) it would seem that the dark, fine-grained rock types is intruded by the quartz diorite.

Another explanation could be that there are two generations of fine grained mafic rock, one older than the meta quartz diorite, and one younger. The older (possibly the mafic component of the Langtree cores) would be the metavolcanics and the younger would be the metadiabase. In the future, further research on each rock unit’s mineralogy could help address the uncertainty or age relationship.

Figure 4: Core CH-7 showing the soil and saprolite from depth 0-9.5 ft. The core is 2.5 inches in diameter and each core sleeve is about 28.5 inches long. No samples were taken from this section.

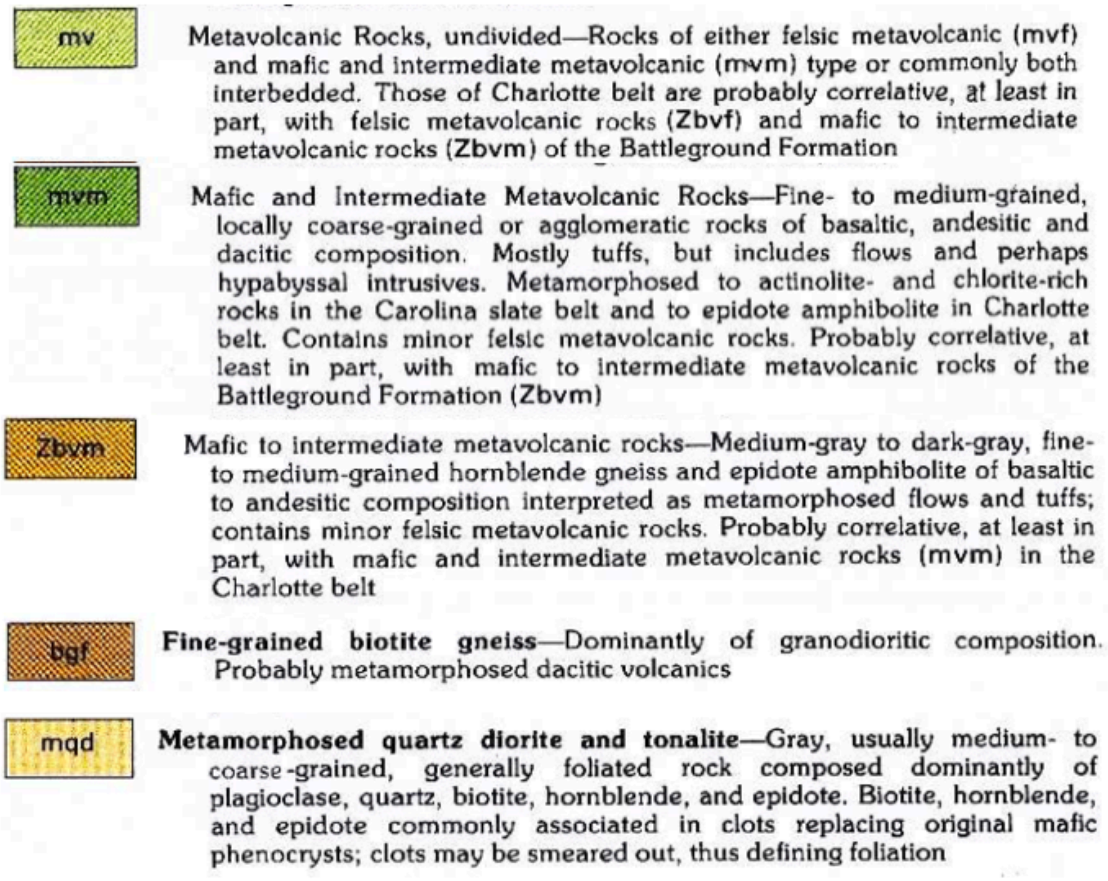
Figure 5: Core CH-7 9.5' – 18.5' showing saprolite. No samples were taken from this section.

Figure 6: Core CH-7 18.5' – 28', showing the saprolite-to-bedrock transition. Samples were taken from 24' and 26'.

Figure 7: Core CH-7 28’ – 38’. Samples were taken from 29.7’, 29.8’, and 32.6’.

Figure 8: Core CH-7 38’ – 46’ showing the typical size of bedrock samples. A sample was taken at 38’ and 38.5’.

Figure 9: Core CH-7 46' – 53'. Samples were taken from 47', 50.3', and 52'.



mv	Metavolcanic Rocks, undivided—Rocks of either felsic metavolcanic (mvf) and mafic and intermediate metavolcanic (mvm) type or commonly both interbedded. Those of Charlotte belt are probably correlative, at least in part, with felsic metavolcanic rocks (Zbvf) and mafic to intermediate metavolcanic rocks (Zbvm) of the Battleground Formation
mvm	Mafic and Intermediate Metavolcanic Rocks—Fine- to medium-grained, locally coarse-grained or agglomeratic rocks of basaltic, andesitic and dacitic composition. Mostly tuffs, but includes flows and perhaps hypabyssal intrusives. Metamorphosed to actinolite- and chlorite-rich rocks in the Carolina slate belt and to epidote amphibolite in Charlotte belt. Contains minor felsic metavolcanic rocks. Probably correlative, at least in part, with mafic to intermediate metavolcanic rocks of the Battleground Formation (Zbvm)
Zbvm	Mafic to intermediate metavolcanic rocks—Medium-gray to dark-gray, fine- to medium-grained hornblende gneiss and epidote amphibolite of basaltic to andesitic composition interpreted as metamorphosed flows and tuffs; contains minor felsic metavolcanic rocks. Probably correlative, at least in part, with mafic and intermediate metavolcanic rocks (mvm) in the Charlotte belt
bgf	**Fine-grained biotite gneiss**—Dominantly of granodioritic composition. Probably metamorphosed dacitic volcanics
mqd	**Metamorphosed quartz diorite and tonalite**—Gray, usually medium- to coarse-grained, generally foliated rock composed dominantly of plagioclase, quartz, biotite, hornblende, and epidote. Biotite, hornblende, and epidote commonly associated in clots replacing original mafic phenocrysts; clots may be smeared out, thus defining foliation

Figure 10: Rock type descriptions of rock types that may occur in the Davidson Langtree cores modified from Goldsmith et al. (1988).

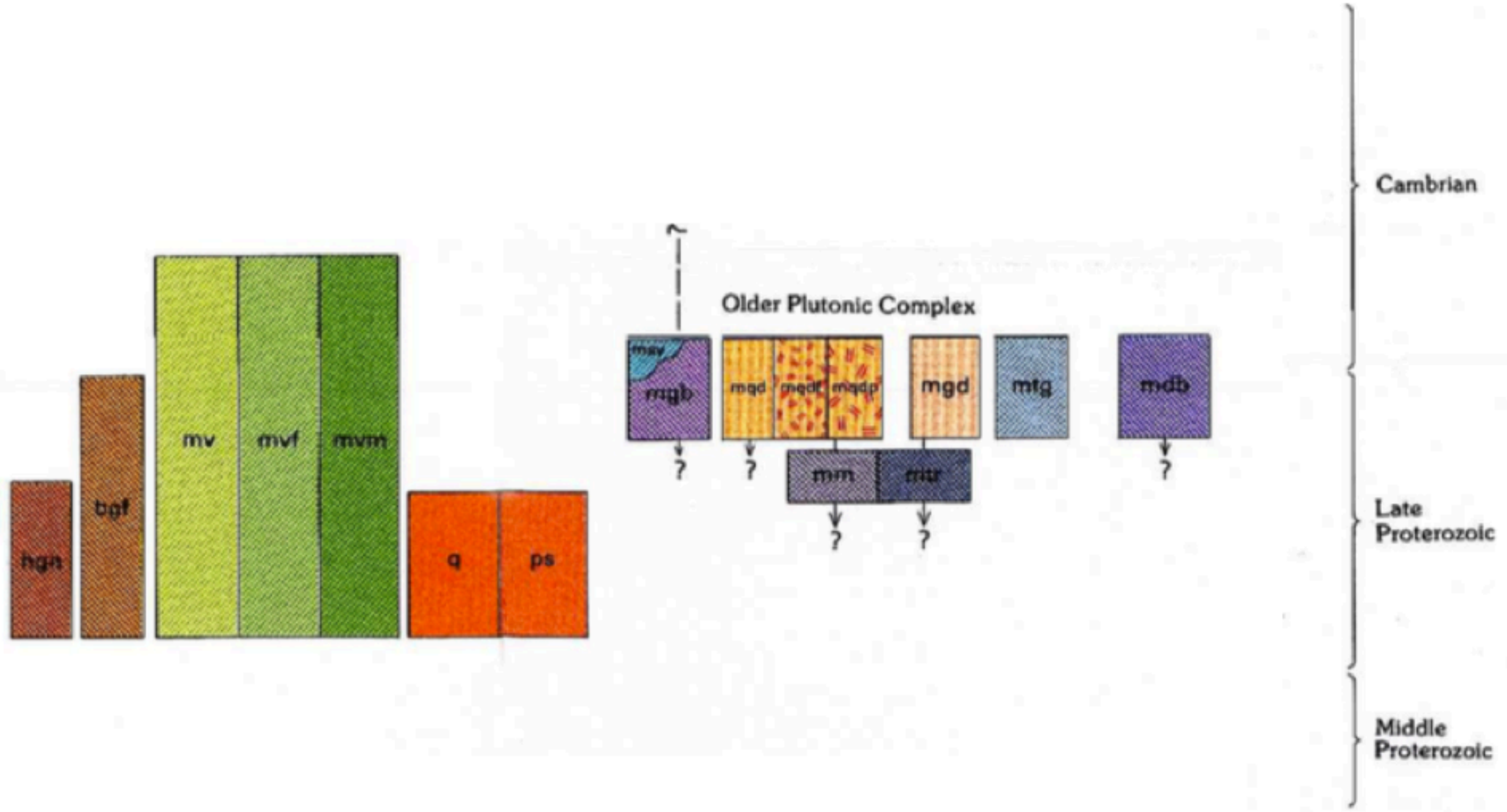


Figure 11: Age relationships among Charlotte Terrane rock types. (Modified from Goldsmith et al. (1988)).

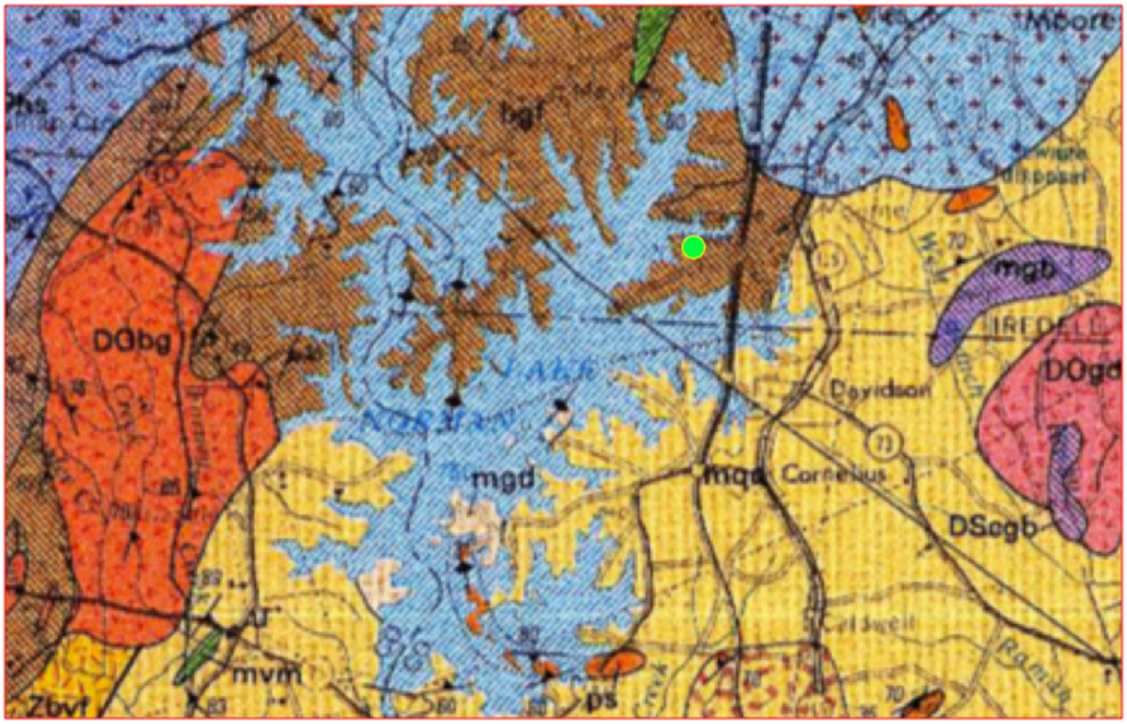


Figure 12: Modified geologic map from Goldsmith et al., (1988) showing the Langtree cores (neon green dot). These samples were taken from the unit labelled bgf (fine-grained biotite gneiss).

1.3 Occurrence of vanadium and chromium

Vanadium and chromium are relatively abundant in mafic rocks in Earth's crust. The average abundance of V in the Earth's crust is about 120 ppm (120 µg/g) and Cr is about 100 ppm (100 µg/g) (Izbicki et al., 2008; Sracek et al., 2014). The average V level in mafic rocks is about 250 ppm (Nriagu, 1998; Pohl, 2011) and Cr ranges from 200 – 2400 ppm in ultramafic rocks and about 100 - 200 ppm in mafic rocks (Ball and Izbicki, 2004; Izbicki et al., 2008; Nriagu, 1988). In felsic rocks (e.g. granitic rocks), Cr concentrations are much lower, averaging 10 ppm (Izbicki et al., 2008; Nriagu, 1988) and V is about 20 ppm (Nriagu, 1998; Pohl, 2011). Diorite has a V average of 148 ppm and the abundance of V in US coal ranges from 15 ppm (Western coal), to 30 ppm (Eastern coal) and 34 ppm (Interior coal) (Nriagu, 1998). The difference in abundances of Cr and V are due to the chemical composition of each rock type and substitutional arrangement in minerals. Felsic rocks have relatively high silica content (> 66%, intermediate with 52 – 66% silica) correlating with low levels of Cr and V in groundwater e.g. (Vinson et al., 2011). Felsic rocks have a lower concentrations of oxides (such as Fe and Mg), which result in lower abundances of Cr and V. Depending on setting, oceanic crust is composed of mafic rocks (~45-52% silica) such as basalts, which usually contain higher amounts of pyroxenes and are more likely to contain high Cr (Albarède, 2003). Higher amounts of V can also be expected in mafic rocks because V can be readily substituted for Fe and Mg (Kuck, 1983; Nriagu, 1998; Sracek et al., 2014; Wright et al., 2014). Also, V behaves similarly to Cr and is hypothesized to co-occur in similar circumstances (Winter, 2010).

Cr and V are incompatible elements that fractionate due to chemical affinity and tend to stay in melts rather than entering mineral structures. Depending on melt elemental composition, Cr and V can behave as compatible elements. For example, in basaltic and andesitic rocks Cr is incompatible in olivine and plagioclase (Winter, 2010). Although not heavily studied, this is due to the structure of the silicates. Cr is unable to "fit" into the atomic structure. Cr is however compatible in orthopyroxene (opx), clinopyroxene (cpx), and especially the oxide mineral magnetite in basaltic and andesitic rocks (Winter, 2010). Therefore, Cr occurs more in oxides rather than silicates.

It should be noted that Cr and V occur in different oxidation states. For V, it can exist in multiple oxidation states from -2 to +5, but the most common forms found in the Earth surface environment (and mineral form) are V(V), V(IV) and V(III) (Breit and Wanty, 1991; Crans et al., 1998; Rehder, 2008; Sracek et al., 2014; Wright et al., 2014; Xiao et al., 2015). The most mobile form of V is V(V) in the common pH ranges for surface water. Vanadium(IV) is often formed when V(V) is in a reducing environment in aqueous solutions. Vanadium(III), in nature, exists in very reducing environments. Any V(III) containing minerals are immediately oxidized when leached from soil (Crans, 1998). Therefore, the leachability of V in the environment is highly dependent on chemical reactions with mineral surfaces, oxide coatings and further dependent on groundwater pH and redox state (Crans et al., 1998; Ortiz-Bernad et al., 2004; Wanty et al., 1990; Wright et al., 2014). Determination of V oxidation state in the environment is complex and vanadium will be referenced simply as V in this study.

The two main oxidation states for Cr are trivalent [Cr(III)] (most commonly found in Cr-containing minerals and referenced in this paper simply as Cr) and hexavalent [Cr(VI)] (Ball and Izbicki, 2004). Cr tends to be slightly soluble in natural water and usually immobile, but Cr(VI) tends to be highly soluble in water and much more mobile (Ball and Izbicki, 2004; Gonzalez et al., 2005; Vengosh et al., 2016). The form most common for Cr to occur and dominate groundwater in NC is the hexavalent form (Vengosh et al., 2016).

Both V and Cr contamination are associated with naturally occurring sources and anthropogenic sources (Hope, 1997; Izbicki et al., 2008; Ortiz-Bernad et al., 2004; Xiao et al., 2015). Multiple studies have identified and researched Cr contamination due to industrial activities and natural sources (Ball and Izbicki, 2004; Barnhart, 1997; Blowes, 2002; Dwivedi et al., 2017; Gonzalez et al., 2005; Izbicki et al., 2008, 2015; Linos et al., 2011; McNeill et al., 2012; Novak et al., 2014; Oze et al., 2007). In the United States, Cr contamination, specifically Cr(VI), has been reported in Hinkley, CA, the Mojave Desert, and in North Carolina. Hinkley, CA has contamination due specifically to anthropogenic sources (Ball and Izbicki, 2004; Bullen, 2012; Saha and Orvig, 2010). Other industries, such as electroplating, leather tanning, pigment in paint, smelting, and industries using Cr as an anticorrosion agent have been found to have caused extensive Cr contamination in surface water and groundwater (Ellis et al., 2004; Novak et al., 2017; Regan et al., 2017; Wanner et al., 2012; Vengosh et al., 2016). In addition to the confirmed Cr spill at an industrial site in Hinkley, CA, research in the Mojave Desert is focused on the natural source of contamination, specifically ultramafic rocks (Ball and Izbicki, 2004; Izbicki et al., 2008). Since a coal ash spill in 2014, Cr contamination has been an issue in North Carolina. There is ongoing research to determine if this contamination is due to coal ash or if it is naturally occurring (e.g. Vengosh et al., 2016). As mentioned earlier, Cr contamination from naturally occurring sources tend to be associated with ultramafic, mafic, and basaltic rock types, aquifers, and sediment.

Limited data exist on the Cr and V content of Charlotte Terrane rocks. A study of whole-rock trace elements, including Cr and V, was conducted by Dennis and Shervais (1996) in Charlotte Terrane rocks in South Carolina. In general, most of the ultramafic and mafic rocks are high in Cr, ranging from 300-1,400 ppm, and are lower in V (160-550 ppm) than Cr (Table 1).

Table 1: Average Cr and V abundances (range in parentheses) of metaintrusive and metavolcanic rocks in the Charlotte Terrane (Dennis and Sherais, 1996).

Rock Type	Average whole-rock Cr (ppm)	Average whole-rock V (ppm)
Mafic metaintrusive	540 (24 – 1296)	274 (64 – 619)
Felsic metaintrusive	72 (30 – 121)	230 (111 – 381)
Mafic metavolcanic	131 (28 – 1444)	285 (282 – 522)
Felsic metavolcanic	25 (14 – 62)	100 (19 – 324)

The exception to high Cr levels in the mafic rocks is the metagabbros. The metagabbros range from 24 – 583 ppm and average 213 ppm for Cr, which is higher than the felsic rocks, but low for the mafic rocks in this study. The most abundant felsic to intermediate rock type is metamorphosed quartz diorite, which is locally intruded by metadiabase, especially in the Charlotte area. The diorite is lower in Cr (30-121 ppm. 72 ppm average) than the mafic rocks (24-1296 ppm. 540 average), and slightly lower in V (111-381 ppm, 230 ppm average) than the mafic rocks (64-619 ppm, 274 ppm average; Dennis and Shervais, 1996).

In addition to regional reconnaissance geological mapping, limited groundwater research has been conducted within the Charlotte Terrane. A recent (2015) NCDEQ website reproduced a groundwater map, derived from the 1970s-era National Uranium Resource Evaluation (NURE), showing the Charlotte Terrane having the highest overall V concentrations in North Carolina (NC Department of Environmental Quality, 2015a). However, in the Charlotte Terrane, no detailed geochemical study has examined the fraction of Cr and V that is easily leachable into groundwater.

1.4 Societal significance

Coal combustion products (referred to here as coal ash) include bottom ash and fly ash, which are materials that did not volatilize during coal combustion. For decades, these have been captured and disposed of on-site because their production greatly exceeds the potential for re-use. Since the highly-visible failures of coal ash ponds in Tennessee and North Carolina in 2008 and 2014, much attention has turned to the potential environmental effects of the largely unlined ponds in which coal ash is stored.

Coal ash contains elevated levels of naturally-occurring trace elements, some of which are of health interest. In North Carolina, these trace elements became a serious concern when residents living near ash ponds were notified that coal ash leaching. This could lead to possible migration of affected groundwater into the bedrock fracture network could affect their private domestic wells. In North Carolina, one main producer, Duke Energy, has sites of potential concern for coal ash handling. Duke Energy operates 14 coal-fired power plants with unlined ponds, and groundwater contamination has been found at some plants (Henderson, 2014).

Public water systems (PWSs) are regulated at the federal and state level. According to the North Carolina Department of Environment and Natural Resources (DENR), the Risk Explanation Frequently Asked Questions 2015 document (NC Department of Environmental Quality, 2015a) states the federal drinking water standard for total Cr is 100 parts per billion (μg/L), with no specific standards or guidance on the Cr(VI) species, also known as hexavalent chromium. North Carolina's groundwater quality standard is 10 μg/L based on the assumption that all Cr occurs as the more toxic Cr(VI). In NC, PWSs are only required to meet federal standards, and private domestic wells are only subject to voluntary advisories with no binding federal or state water quality regulations. As for V, there is no federal standard, but NC has established an Interim Maximum Allowable Concentration (IMAC) of 0.3 μg/L. An IMAC is a non-binding recommendation for groundwater.

In spring 2015, the North Carolina Division of Environmental Quality (NCDEQ) issued letters to hundreds of private well owners near coal ash disposal ponds in the Charlotte region, advising them that their well water was unsafe for drinking and cooking. While some cosmetic or aesthetic factors were noted (e.g. pH, iron), the primary concern was the elevated levels of V and Cr, which exceeded a one-in-one million lifetime cancer risk as recommended by the North Carolina Department of Health and Human Services (DHHS) (Henderson, 2015; NC Department of Environmental Quality, 2015c). The NC Department of Health and Human Services (DHHS) updated health risk evaluations (HRE) to well owners, public and private, near 11 plants or stations in NC as of August 20, 2015. Well owners near 7 of these 11 facilities received "Do Not Drink" HREs for V and Cr(VI), or Cr and other metals. Owners near 2 out of the 11 facilities received "Do Not Drink" HREs for V and other metals (NC Department of Environmental Quality, 2015b). Subsequently, in 2016, the previous advisory was rescinded, along with the letter advising homeowners not to drink their well water (Henderson, 2016b). With this modified advice, homeowners were instructed that the concentrations of Cr and V in their wells are safe to drink.

The debate on the source of Cr(VI) and V has grown with the drinking advisory being rescinded. It has been suggested that coal ash is not the source, but the director of the Division of Public Health stated the natural contribution is currently unclear (Henderson, 2016a). If these contaminants are naturally occurring, it can still be a health concern but occurs over a larger area than the vicinity of coal ash facilities. The Catawba Riverkeeper organization compiled data revealing 20 times higher Cr(VI) levels in private wells near two Duke plants than the averages of 11 public systems (Henderson, 2016a). One shortcoming of the Riverkeeper analysis is that it compares groundwater samples to river and lake water (Henderson, 2016a) which would be expected to have different Cr and V levels. While recent events have drawn attention to Cr and V levels in groundwater, the naturally-occurring aspect of this problem has not been thoroughly examined in the Charlotte Terrane, where several Duke facilities are located. To my knowledge, regional elemental research has not been performed on the Charlotte Terrane rock to examine the naturally-occurring aspect of this problem. It should be emphasized that the natural occurrence of Cr and V is best evaluated away from the Duke Energy facilities. The proposed research will provide initial information as to how much, if any, Cr and V is coming from a natural source rather than from ash, and will provide crucial information to identify potential mineral sources of Cr and V.

2 Objectives and hypothesis

The objective of this study is to examine naturally-occurring and easily-leachable Cr and V in selected rock types of the Charlotte Terrane, in the Charlotte area. I hypothesize that the mafic rocks will contain higher levels of overall V and Cr than the felsic rocks. I also hypothesize higher levels of easily-leachable V and Cr in the mafic rocks, which are therefore a possible source these elements to wells drilled into mafic rocks. If supported, this hypothesis could have important implications for water quality. If the Cr and V are naturally-occurring, the intensively-studied coal ash ponds (that is, point sources) are not the only possible sources of Cr and V to groundwater, but rather the elements of concern could occur throughout the region (non-point sources).

3 Methods

3.1 Field sample collection

Samples were collected generally in the Charlotte metro area (Figure 13) with the guidance of the USGS Geologic Map of the Charlotte 1x2 Quadrangle, North Carolina (Goldsmith et al., 1988). Samples were collected from field occurrences that are *quasi* in place at the scale of the 1:250,000 Charlotte Quadrangle map. It should be noted that the 1:250,000 scale map by Goldsmith et al. (1988) was reconnaissance due to its scale. Therefore, at the outcrop scale, observed lithologies were likely to be more complex than mapped by Goldsmith et al. (1988). For example, outcrops along Alumni Way and near the UNC Charlotte soccer stadium appear to be a felsic intrusive rock intruding a fairly high volume of fine-grained dark rocks. This dark fine-grained rock might be different than sub-map-scale intrusive relationship that was noted in the descriptive text of Goldsmith et al. (1988). Goldsmith et al. (1988) described a mafic rock (metadiabase (mbd)) as being prominent, usually as unmapped dikes, within map-scale metaquartz diorite in the Charlotte area. Again, Goldsmith has determined metavolcanics (mv) and metamorphosed mafic complexes (mm) to be older than the meta quartz diorite and other mafic units, such as the metadiabase, to be younger than the meta quartz diorite. This study did not focus on rock ages, but on the rock composition. Therefore, the idea of having two generations of fine-grained mafic rocks is important for context because they may have genetic differences affecting trace elements.

While massive mafic rock bodies were expected to be poorly exposed compared to felsic rocks, due to the faster chemical weathering of mafic minerals, the mafic rocks did seem to be reasonably well preserved as intrusions within the felsic rocks (especially in the bedrock cores). Therefore, these outcrop-scale mafic dike occurrences, and the bedrock cores, were a viable way to ensure that sufficient mafic rock samples were obtained for this study.

Selected map-scale lithologies in the pre-tectonic suite were examined to test the mafic vs. felsic hypothesis as a control on Cr and V occurrence. Suitable sampling sites included natural outcrops, cores, road cuts, stream beds, residual boulders and boulders exposed by construction activities (Figure 14 and Figure 15). Features indicating whether a rock is *quasi* in place were noted. For example, spheroidal weathering is evidence that a boulder is a residual boulder from the natural environment and not transported from a quarry. Exactly 46 representative samples were collected. Once a site was determined, the collection methods were:

1. Record GPS coordinates
2. Photograph and describe sample occurrence
3. Collect a sample that is 8 x 8 x 5 cm to ensure that at least 50 grams of rock was collected

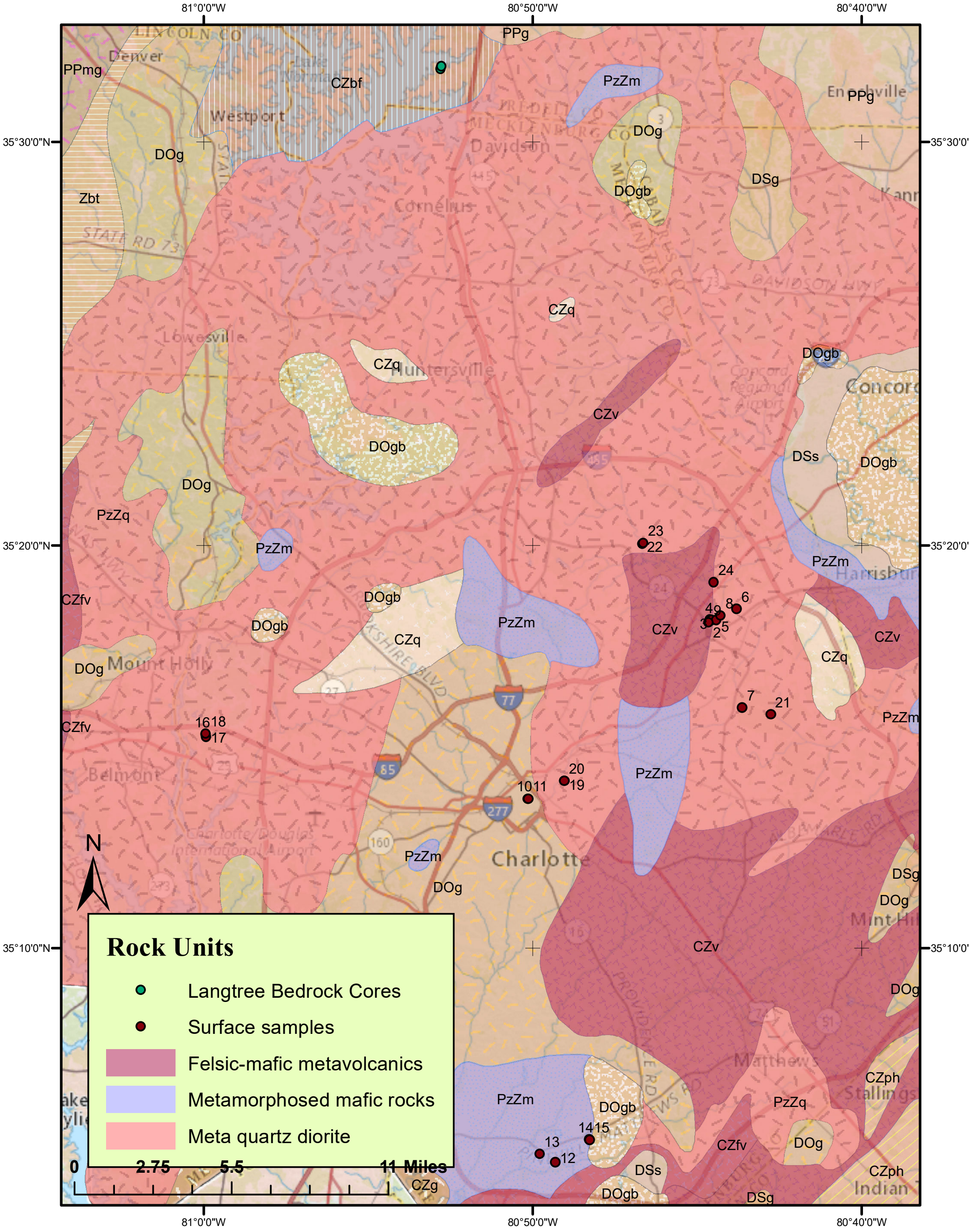


Figure 13: Bedrock geologic map of Charlotte Terrane rocks in the Charlotte area showing sample locations. The red, violet, and pink rock units are the targeted pre-tectonic rock types for this project. Shapefile data are based on North Carolina Geological Survey (1985) and the base map was obtained from ArcGIS Online.

Figure 14: Site 3 located on the UNCC campus was a natural outcrop with residual boulders.

Figure 15: Site 20 is a representative bedrock sample located in a stream bed. This location was within Cordelia Park in Charlotte, NC.

3.2 Laboratory methods

Most rock samples were cut down to the freshest, least-weathered sample of appropriate mass to conduct the needed analyses. Others included weathered surfaces and fracture surfaces. While the objective was to seek the least weathered portion of each hand sample, weathered samples were not disqualified from this study because drilled wells in the Piedmont can intercept and pull water across weathered surface coatings that line groundwater-bearing fractures. Rock samples were cut or hammered to collect ~ 30 g of sample (Figure 16). Samples were further crushed to a flour-like consistency and transferred to a clean, new zip-lock bag. One gram from every sample was collected by shaking up the zip-lock bag, to avoid bias, for sequential extraction, to determine the leachability of Cr and V in simulated groundwater solutions. This one gram was then crushed to just pass through a 100-mesh sieve (2.75 Φ or 0.177mm) for size consistency. Twenty-four crushed samples were chosen, based on mafic vs intermediate/felsic hand sample identification, to analyze the bulk chemical compositions by X-ray fluorescence (XRF) (Figure 16). For these samples, 3-4 g of crushed samples were transferred to a clean, new centrifuge tube as extra crushed sample, and the remaining ~23-25g of sample was sent to Virginia Tech for XRF analysis. Only 24 samples were chosen for XRF analysis due to budgetary reasons.

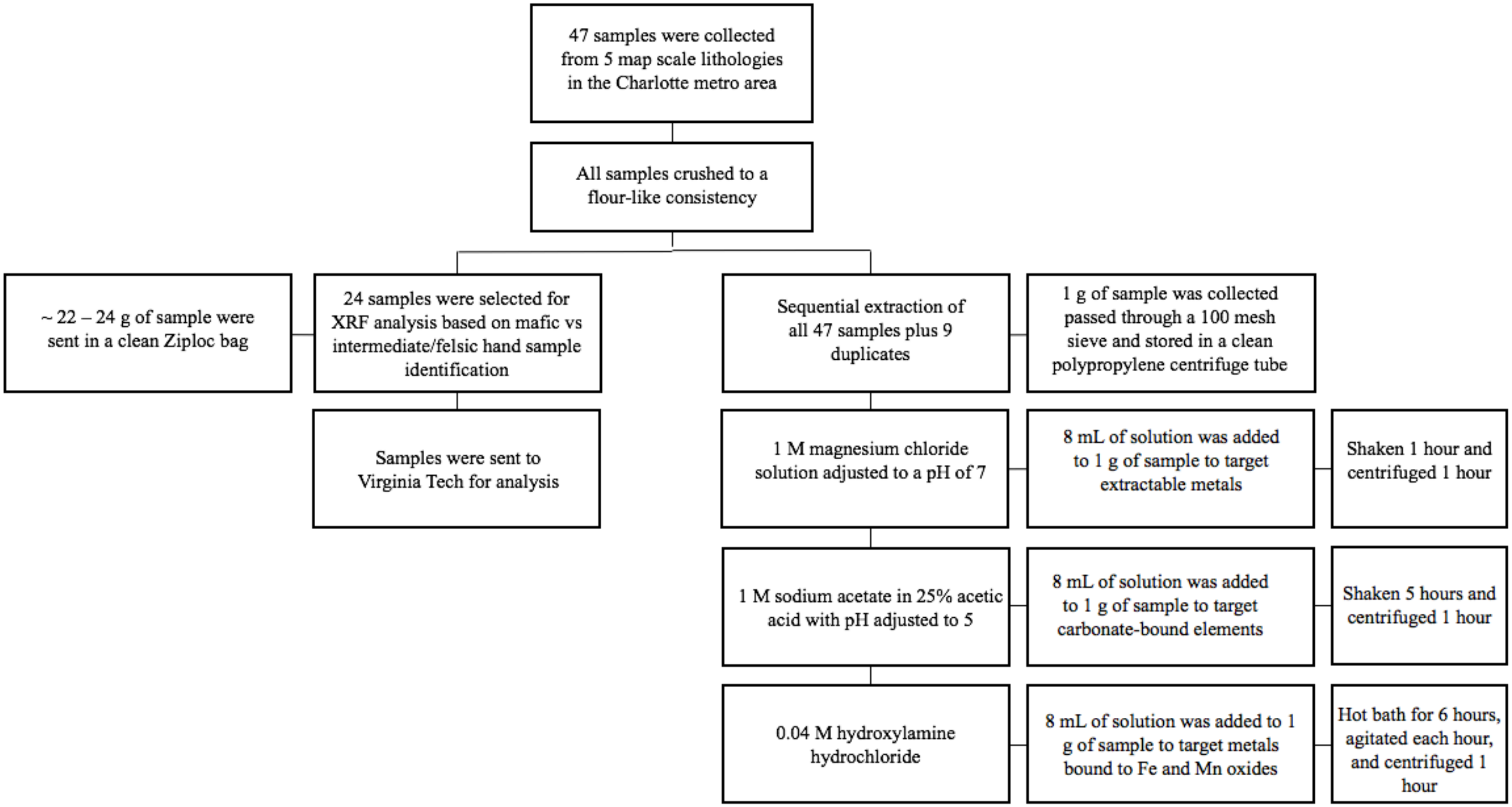


Figure 16: Flow chart explain the step-by-step process for XRF and sequential extraction modified from Tessier et al., 1979; Stewart et al., 2015.

3.2.1 X-ray fluorescence spectroscopy

X-ray fluorescence spectroscopy (XRF) was used to determine major element abundances (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) in the rock samples and to assign mafic vs. intermediate/felsic composition. Trace element analysis was also completed by XRF for selected elements (Cr and V). Known USGS standards were used. For budgetary reasons, 24 representative samples underwent XRF analysis. The samples were sent to the laboratory of Dr. Esteban Gazel at Virginia Tech. About 23-25 grams of crushed sample was used for the XRF analysis.

3.2.2 Sequential extraction

One gram of crushed and sieved rock samples as described above underwent sequential extraction using a procedure modified from Tessier et al. (1979) to identify the ease of leachability and general type of phase(s) in which V and Cr occur. Extraction in magnesium chloride (step 1 below) will liberate easily-extractable metals that might be leached from the rocks by simple groundwater flow or salinity changes. Acetic acid (step 2 below) attacks any carbonate-bound elements that may be present (Tessier et al., 1979; Stewart et al., 2015). Hydroxylamine hydrochloride (step 3 below) was used to target trace metals bound to iron and manganese oxides (Tessier et al., 1979). This will help infer how easily V and Cr could be leached from the minerals in mafic and felsic rocks into the groundwater. A total of 46 samples, plus 9 duplicates, underwent 3 extraction steps. All reagents were prepared, and rinses conducted, with distilled deionized water having a specific conductance of at least 18 MΩ/cm.

1. Step 1: 1 M magnesium chloride solution adjusted to a pH of 7 extraction: Following Tessier et al. (1979), a 1 M magnesium chloride solution was prepared using reagent grade magnesium chloride and adjusted to pH 7. In this method, 8 mL of the solution was added to 1 g of sample in a clean polyethylene centrifuge tube and transferred to a shaker

table for 1 hour at 275 rpm. At the end of 1 hour of shaking the samples were then centrifuged for one hour at 2,000 rpm. The supernatant was poured into a new polyethylene centrifuge tube with one drop of optima grade acetic acid preservative. Samples were rinsed for the second extraction step by adding distilled deionized water and centrifuging for one hour at 2,000 rpm. The supernatant water was discarded.

2. Step 2: 1 M sodium acetate in 25% acetic acid with pH adjusted to 5 extraction: Following Tessier et al. (1979), a 1 M sodium acetate solution was prepared using reagent grade sodium acetate in a matrix of 25% high-purity acetic acid. In this method, 8 mL of the solution was added to the pre-rinsed sample from step 1 and transferred to a shaker table for 5 hours at 275 rpm. At the end of the 5-hour shaker table process, samples were then centrifuged for one hour at 2,000 rpm. The supernatant was poured into a new polyethylene centrifuge tube with one drop of Fisher Optima grade acetic acid preservative. Subsequently, samples were rinsed as described as above to be prepared for the third step of extraction.
3. Step 3: 0.04 M hydroxylamine hydrochloride extraction: Following Tessier et al. (1979), a 0.04 M hydroxylamine hydrochloride solution was prepared using reagent grade hydroxylamine hydrochloride (Sigma-Aldrich) in a matrix of 25% high-purity acetic acid (Sigma-Aldrich). In this method, 8 mL of the solution was added to the pre-rinsed sample from step 2 and transferred to a hot water bath at a normal temperature of 96°C ± 2°C for 6 hours. In the hot water bath, temperature measurements were checked hourly and samples were vigorously hand-shaken 2-3 times per hour. The temperature was monitored using an identical water-filled centrifuge tube placed in the bath. Due to the limitations of the equipment in use, a temperature of 89°C ± 2°C was attained for the water bath and a temperature of 79°C ± 2°C was attained in the identical water-filled centrifuge tube in the bath. At the end of the 6-hour hot water bath, samples were cooled

in a cold-water bath for ~10 minutes then centrifuged for one hour at 2,000 rpm. The supernatant was poured into a new polyethylene centrifuge tube without additional preservative. Subsequently, samples were rinsed as described above in the event that the samples were needed again.

4 Results

4.1 Total element determinations by XRF and rock type assignment

For the XRF analysis, 25 samples were tested of which 24 produced usable results (Table 3). Major elements were analyzed and were quantified with good to high confidence. The SiO_2% data were the determining factor to assign a mafic or felsic/intermediate composition. Other major element data, such as Fe_2O_3, MnO, and CaO helped support the SiO_2 data. This data also gave the total concentration of Cr and V (ppm) for each sample. The average value of %SiO_2 was 55.82% and ranged from 47.32% to 76.69%. The average value of %Fe_2O_3 was 8.97% and ranged from 0.72% to 13.01%. %MgO had an average value of 5.37% and ranged from 0.05% to 11.02%. %CaO had an average value of 8.20% and ranged from 0.42% to 11.95%. The average value of %Na_2O was 3.01% and ranged from 1.57% to 6.49%.

SiO_2 content was used as an indicator of a rock's mafic or felsic classification. A mafic rock contains 45 – 52 wt.% of $SiO_{2,}$ is high in Fe Mg, Ca, and low in K and Na. An intermediate rock contains 52 – 66 wt.% of SiO_2 and is intermediate in Fe, Mg, Ca, Na, and K. A felsic rock contains >66 wt.% SiO_2 and is low in Fe, Mg, Ca, and high in K, and Na (Raymond, 1995; Winter, 2010). Based on this classification, 15-16 of the samples were mafic, 4-5 were intermediate, and 4 were felsic.

Table 2: Comparison of mapped rock type, preliminary (hand sample) classification, and XRF classification of mafic (M), intermediate (I), and felsic (F) rock types. Under rock names, if there is a foot measurement it is below the surface, and (fs) means the sample was a fracture surface in the Langtree core.

Rock Name	Latitude (N)	Longitude (W)	Mapped rock type (Goldsmith et al., 1988 and NC Geological Survey,1985)	Preliminary rock type (M/I/F)	XRF determined rock type (M/I/F)
Site 1	35.30244	80.74358	F/M metavolcanic	M	M
Site 5	35.30235	80.74020	meta quartz diorite	M	I
Site 6 dark	35.30691	80.72998	meta quartz diorite	M	M
Site 8a	35.30422	80.73801	meta quartz diorite	M	M
Site 8c	35.30422	80.73801	meta quartz diorite	M	M
Site 13	35.08121	80.82974	meta quartz diorite	M	M

Rock Name	Latitude (N)	Longitude (W)	Mapped rock type (Goldsmith et al., 1988 and NC Geological Survey,1985)	Preliminary rock type (M/I/F)	XRF determined rock type (M/I/F)
Site 16	35.25491	80.99885	meta quartz diorite	M	M
Site 17	35.25413	80.99868	meta quartz diorite	M	M
CH-6 46’	35.53006	80.87966	metamorphic fine-grained biotite gneiss	M	M
CH-6 plug 1 (~48’)	35.53006	80.87966	metamorphic fine-grained biotite gneiss	M	M
CH-7 29.7’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	M	M
CH-7 plug 4 (38.5’)	35.53099	80.87939	metamorphic fine-grained biotite gneiss	M	M
CH-7 38.7’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	M	M
Site 3	35.30233	80.74258	F/M metavolcanic	I/F	I
Site 6 light	35.30691	80.72998	meta quartz diorite	F	F
Site 8b light	35.30422	80.73801	meta quartz diorite	I/F	I
Site 9	35.30131	80.7441	F/M metavolcanic	I/F	F
Site 12	35.07788	80.82175	metamorphosed mafic	I/F	M
Site 14	35.08728	80.80453	metamorphosed mafic	I/F	M
Site 15	35.08712	80.8045	metamorphosed mafic	F	F
Site 20	35.23582	80.81718	meta quartz diorite	F	F
CH-6 plug 6 (38.5’)	35.53006	80.87966	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-6 43.0’ (fs)	35.53006	80.87966	metamorphic fine-grained biotite gneiss	I/F	M
CH-6 plug 2 (47’)	35.53006	80.87966	metamorphic fine-grained biotite gneiss	I/F	M/I
CH-7 34.5’ (fs)	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	I
Site 2	35.30248	80.74349	F/M metavolcanic	M	n/a
Site 4	35.30229	80.74256	F/M metavolcanic	M	n/a
Site 7	35.2661	80.7272	meta quartz diorite	I/F	n/a
Site 18a	35.25531	80.99889	meta quartz diorite	I/F	n/a
Site 18b	35.25531	80.99889	meta quartz diorite	I/F	n/a
Site 19	35.23568	80.81725	meta quartz diorite	I/F	n/a
Site 21	35.26324	80.71271	meta quartz diorite	I/F	n/a

Rock Name	Latitude (N)	Longitude (W)	Mapped rock type (Goldsmith et al., 1988 and NC Geological Survey,1985)	Preliminary rock type (M/I/F)	XRF determined rock type (M/I/F)
Site 22	35.3337	80.77765	meta quartz diorite	M	n/a
Site 23	35.33416	80.77723	meta quartz diorite	M	n/a
Site 24	35.31799	80.74145	meta quartz diorite	M	n/a
CH-6 22.6’	35.53006	80.87966	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 26’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 29.8’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	M	n/a
CH-7 32.6’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 45.5’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 47’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 50.3’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 52’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-7 plug 3, 38’	35.53099	80.87939	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-6 plug 5, 38’	35.53006	80.87966	metamorphic fine-grained biotite gneiss	I/F	n/a
CH-6 plug 7, 27.5’	35.53006	80.87966	metamorphic fine-grained biotite gneiss	I/F	n/a

The XRF analysis included Cr and V (Table 3). Detection limits were not available for these analyses, so non-detectable or negative abundances were given values of zero for plotting and statistical analysis. SiO_2 was negatively correlated with total Cr (r= -0.91) and with total V (r= -0.61). Therefore, the highest levels of total Cr and total V occurred in the mafic rocks.

Table 3: XRF analysis of 24 selected samples. Samples were analyzed for bulk chemical composition, Cr and V. Modified from table provided by Esteban Gazel, PhD, of Virginia Tech Department of Geosciences.

Sample	**SiO_2 (wt%)**	**Rock Type**	**Fe_2O_3 (wt%)**	**MnO (wt%)**	**Cr (mg/kg)**	**V (mg/kg)**
JV-1	50.03	Mafic	11.06	0.20	599	259
JV-2	65.29	Intermediate/Felsic	5.37	0.09	18	61
JV-3	51.26	Mafic	10.02	0.21	71	274
JV-4	49.88	Mafic	10.76	0.26	557	248
JV-5	47.32	Mafic	13.01	0.18	71	239
JV-6	50.93	Mafic	10.86	0.18	90	183
JV-7	49.57	Mafic	11.64	0.20	304	276
JV-8	49.09	Mafic	12.64	0.20	726	340
JV-9	48.48	Mafic	11.80	0.24	415	276
JV-10	48.45	Mafic	11.83	0.23	388	269
JV-11	48.40	Mafic	11.90	0.21	109	259
JV-12	49.65	Mafic	10.25	0.21	675	228
JV-13	49.37	Mafic	10.36	0.21	708	227
JV-14	63.99	Intermediate	6.60	0.14	74	121
JV-15	73.45	Felsic	1.89	0.03	<LOD	37
JV-16	62.56	Intermediate	7.87	0.14	122	184
JV-17	69.89	Felsic	6.23	0.11	70	133
JV-18	51.65	Mafic	9.38	0.16	110	172
JV-19	51.17	Mafic	9.94	0.17	397	217
JV-20	76.69	Felsic	0.72	0.02	<LOD	27
JV-21	74.65	Felsic	1.45	0.06	<LOD	32
JV-23	52.01	Mafic	10.21	0.18	198	272
JV-24	51.55	Mafic	10.06	0.18	279	240
JV-25	54.28	Mafic/intermediate	9.46	0.16	182	225

4.2 Sequential extractions

Sequential extraction results are presented in Table 4, Table 5, and Table 6. These results are presented in units of μg element/kg rock which is equivalent to parts per billion. These were derived from the sequential extractions by the following equation:

$$\frac{\mu g\ of\ element}{L\ liquid} \times \frac{mL\ liquid}{gram\ of\ sample\ used} = \frac{\mu g\ of\ element\ extracted}{kg\ of\ sample}$$

In general, hydroxylamine hydrochloride extracted the largest quantity of trace elements (Cr, V, Fe, Mn, As, Se) while $MgCl_2$ extracted the smallest quantity.

Table 4: Sequential extractions of V and Cr. Sample ID* means that duplicate extraction was performed and the average of the duplicates is reported here. <LOD represents values below the detection limit, and <LOD* represents samples that had one duplicate below detection limit and the other above the detection limit.

Sample ID	Sample weight (g)	$MgCl_2$ V (µg/kg)	Na Acetate V (µg/kg)	Hydrox. Hydro V (µg/kg)	$MgCl_2$ Cr (µg/kg)	Na Acetate Cr (µg/kg)	Hydrox. Hydro Cr (µg/kg)
site 1	0.9984	<LOD	56	2800	33	466	24495
site 2	1.0263	<LOD	61	3266	<LOD	315	14740
site 3	0.9696	<LOD	35	3656	<LOD	150	28630
site 4*	0.9050	<LOD	103	4496	<LOD*	601	10366
site 5	1.0225	<LOD	50	2533	<LOD	1648	17400
site 6 light	0.9942	<LOD	<LOD	1724	17	<LOD	18805
site 6 dark	1.0392	<LOD	<LOD	4073	<LOD	<LOD	6154
site 7	0.9998	<LOD	<LOD	928	<LOD	<LOD	25669
site 8a	0.9878	<LOD	132	3091	<LOD	1011	14189
site 8b	1.0004	<LOD	113	4854	23	1778	17329
site 8c*	1.0010	<LOD	156	4083	<LOD	651	14881
site 9*	0.9760	<LOD	61	5219	12	<LOD	12216
site 12	0.9714	<LOD	<LOD	3299	<LOD	<LOD	9240
site 13	0.9883	<LOD	63	3659	<LOD	<LOD	6770
site 14*	1.0116	<LOD	<LOD	2257	<LOD	<LOD	9275
site 15	0.9992	<LOD	<LOD	1461	<LOD	<LOD	32306
site 16	1.0080	<LOD	<LOD	3024	<LOD	242	14444
site 17	0.9886	<LOD	<LOD	3874	17	465	14485
site 18a	0.9838	<LOD	<LOD	4402	<LOD	<LOD	15442
site 18b	0.9943	<LOD	<LOD	3231	<LOD	<LOD	4469
site 19*	1.0043	<LOD	<LOD	960	27	<LOD*	50121

Sample ID	Sample weight (g)	$MgCl_2$ V (µg/kg)	Na Acetate V (µg/kg)	Hydrox. Hydro V (µg/kg)	$MgCl_2$ Cr (µg/kg)	Na Acetate Cr (µg/kg)	Hydrox. Hydro Cr (µg/kg)
site 20	1.0017	<LOD	<LOD	1596	14	114	46665
site 21	1.0015	<LOD	20	4207	<LOD	543	24763
site 22*	1.0002	<LOD	91	3842	11	812	12053
site 23*	1.0004	<LOD	30	3144	23	1421	15248
site 24	1.0032	<LOD	177	2727	<LOD	1715	9242
CH-6 22.6	0.9581	<LOD	14	17401	<LOD	<LOD	835
CH-6 43.0' (fs)	0.9888	<LOD	89	3806	<LOD	189	14984
CH-6 46.0'	1.0009	<LOD	178	2009	<LOD	864	10271
CH-7 26'*	1.0026	<LOD	112	5108	<LOD*	109	8340
CH-7 29.7'	1.0147	<LOD	<LOD	9287	26	247	17550
CH-7 29.8'	1.0093	<LOD	32	6812	<LOD	181	8806
CH-7 32.6'	1.0084	<LOD	69	3165	41	633	16946
CH-7 34.5'	1.0037	<LOD	109	4461	<LOD	501	11788
CH-7 38.7'	1.0124	<LOD	40	3573	41	621	12675
CH-7 45.5'	1.0041	<LOD	92	4295	29	621	15688
CH-7 47'	1.0079	<LOD	92	3455	14	647	10533
CH-7 50.3'	1.0039	<LOD	<LOD	5836	122	297	18886
CH-7 52.0'	1.0125	<LOD	103	4272	19	547	15518
CH-6 PLUG 1	1.0080	<LOD	323	2769	<LOD	4345	9595
CH-6 PLUG 2	1.0017	<LOD	319	3169	25	3448	18968
CH-7 PLUG 3	1.0015	<LOD	316	2944	<LOD	4471	15001
CH-7 PLUG 4	1.0079	<LOD	207	3640	18	2480	13041
CH-6 PLUG 5	1.0007	<LOD	438	2825	15	6616	7769

Sample ID	**Sample weight (g)**	**$MgCl_2$ V (µg/kg)**	**Na Acetate V (µg/kg)**	**Hydrox. Hydro V (µg/kg)**	**$MgCl_2$ Cr (µg/kg)**	**Na Acetate Cr (µg/kg)**	**Hydrox. Hydro Cr (µg/kg)**
CH-6 PLUG 6	1.0011	<LOD	211	3308	24	869	13705
CH-6 PLUG 7*	1.0013	<LOD	126	2940	67	2011	24102
Detection Limit (ppb)		135	9.6	4.902	12	15.1	61.21

Table 5: Sequential extractions of Mn and Fe. Sample ID* means that duplicate extraction was performed and the average of the duplicates is reported here. <LOD represents values below the detection limit, and <LOD* represents samples that had one duplicate below detection limit and the other above the detection limit.

Sample ID	Sample weight (g)	$MgCl_2$ Mn (µg/kg)	Na Acetate Mn (µg/kg)	Hydrox. Hydro. Mn (µg/kg)	$MgCl_2$ Fe (µg/kg)	Na Acetate Fe (µg/kg)	Hydrox. Hydro Fe (µg/kg)
site 1	0.9984	897	2116	13950	4112	81250	2088141
site 2	1.0263	2342	6984	18825	<LOD	84108	1501315
site 3	0.9696	6639	25338	42186	<LOD	74752	2693069
site 4*	0.9050	2502	6150	20821	9336	154953	1716381
site 5	1.0225	1108	2947	32289	1779	121350	1808117
site 6 light	0.9942	2270	14943	31141	401	16552	1454033
site 6 dark	1.0392	3132	26798	74911	<LOD	23226	1080831
site 7	0.9998	640	523	28822	<LOD	8162	1599520
site 8a	0.9878	1424	3150	21519	3640	137599	1347641
site 8b	1.0004	851	2024	25814	3533	160416	1867253
site 8c*	1.0010	3695	16771	19724	3203	208032	1910889
site 9*	0.9760	3574	9398	30963	3151	51462	1910530
site 12	0.9714	460	1021	15195	<LOD	7237	908380
site 13	0.9883	3394	12369	32241	5519	93413	2260042
site 14*	1.0116	911	2229	30984	310	16229	731843
site 15	0.9992	493	567	8583	<LOD	36765	1162530
site 16	1.0080	3299	14913	31690	4117	80794	1522222
site 17	0.9886	1605	5016	23678	3128	72029	1437993
site 18a	0.9838	11994	5687	157674	1935	<LOD	2831470
site 18b	0.9943	328	264	6886	<LOD	<LOD	1050790
site 19*	1.0043	10883	8007	57954	706	16506	1452769

Sample ID	**Sample weight (g)**	**$MgCl_2$ Mn (µg/kg)**	**Na Acetate Mn (µg/kg)**	**Hydrox. Hydro. Mn (µg/kg)**	**$MgCl_2$ Fe (µg/kg)**	**Na Acetate Fe (µg/kg)**	**Hydrox. Hydro Fe (µg/kg)**
site 20	1.0017	14775	20286	282959	580	13928	1677149
site 21	1.0015	6092	10249	32711	678	36353	1297254
site 22*	1.0002	2233	6279	22802	11123	214553	1541334
site 23*	1.0004	2768	11736	96204	13765	298544	6745106
site 24	1.0032	4274	8485	11491	2704	191786	1155502
CH-6 22.6	0.9581	21810	17752	375911	306	<LOD	2323766
CH-6 43.0' (fs)	0.9888	5590	32411	23592	1091	69159	1324434
CH-6 46.0'	1.0009	660	2556	12181	<LOD	81766	806474
CH-7 26'*	1.0026	1537	6113	17416	2667	84715	2021551
CH-7 29.7'	1.0147	4313	10265	28911	5216	55914	3302651
CH-7 29.8'	1.0093	2607	8006	26577	2244	53724	2250272
CH-7 32.6'	1.0084	1141	5617	16176	2843	78072	1408171
CH-7 34.5'	1.0037	2893	17631	22445	1164	84408	1522367
CH-7 38.7'	1.0124	1971	10004	18823	2695	48479	1309364
CH-7 45.5'	1.0041	1111	5780	17767	3771	101902	1849218
CH-7 47'	1.0079	812	3719	15795	2299	80087	1323147
CH-7 50.3'	1.0039	3992	10870	24457	11435	43725	2478334
CH-7 52.0'	1.0125	3187	20962	20836	1726	81620	1648988
CH-6 PLUG 1	1.0080	1213	4875	16714	1922	292222	1050794
CH-6 PLUG 2	1.0017	2025	6695	16764	3053	296696	1401617
CH-7 PLUG 3	1.0015	925	3563	14195	1280	293160	1210984
CH-7 PLUG 4	1.0079	2056	10009	18303	1533	158349	1254093
CH-6 PLUG 5	1.0007	1062	5339	18843	2912	455361	1256720

Sample ID	**Sample weight (g)**	**$MgCl_2$ Mn (µg/kg)**	**Na Acetate Mn (µg/kg)**	**Hydrox. Hydro. Mn (µg/kg)**	**$MgCl_2$ Fe (µg/kg)**	**Na Acetate Fe (µg/kg)**	**Hydrox. Hydro Fe (µg/kg)**
CH-6 PLUG 6	1.0011	1641	4252	18540	5256	250844	1508740
CH-6 PLUG 7*	1.0013	1981	6476	14868	6976	181639	1769827
Detection Limit (ppb)		1.44	3.40	0.2428	237	110.0	15.1444

Table 6: Sequential extractions of As and Se. Sample ID* means that duplicate extraction was performed and the average of the duplicates is reported here. <LOD represents values below the detection limit, and <LOD* represents samples that had one duplicate below detection limit and the other above the detection limit.

	Sample weight (g)	**$MgCl_2$ As (µg/kg)**	**Na Acetate As (µg/kg)**	**Hydrox. Hydro As (µg/kg)**	**$MgCl_2$ Se (µg/kg)**	**Na Acetate Se (µg/kg)**	**Hydrox. Hydro Se (µg/kg)**
site 1	0.9984	<LOD	<LOD	20	<LOD	<LOD	<LOD
site 2	1.0263	<LOD	<LOD	29	<LOD	<LOD	<LOD
site 3	0.9696	<LOD	<LOD	18	<LOD	<LOD	<LOD
site 4*	0.9050	<LOD	<LOD	55	<LOD	<LOD	<LOD
site 5	1.0225	<LOD	<LOD	93	<LOD	<LOD	5.9
site 6 light	0.9942	<LOD	<LOD	30	<LOD	<LOD	<LOD
site 6 dark	1.0392	<LOD	<LOD	34	<LOD	<LOD	<LOD
site 7	0.9998	<LOD	<LOD	171	<LOD	<LOD	<LOD
site 8a	0.9878	<LOD	<LOD	48	<LOD	<LOD	<LOD
site 8b	1.0004	<LOD	<LOD	47	<LOD	<LOD	<LOD
site 8c*	1.0010	<LOD	<LOD	24	<LOD	<LOD	<LOD
site 9*	0.9760	<LOD	<LOD	20	<LOD	<LOD	<LOD
site 12	0.9714	<LOD	<LOD	29	<LOD	<LOD	<LOD
site 13	0.9883	<LOD	<LOD	14	<LOD	<LOD	<LOD
site 14*	1.0116	<LOD	<LOD	26	<LOD	<LOD	<LOD
site 15	0.9992	<LOD	<LOD	62	<LOD	<LOD	2.5
site 16	1.0080	<LOD	<LOD	71	<LOD	<LOD	3.5
site 17	0.9886	<LOD	<LOD	40	<LOD	<LOD	<LOD
site 18a	0.9838	<LOD	<LOD	9	<LOD	<LOD	4.2
site 18b	0.9943	<LOD	<LOD	16	<LOD	<LOD	3.0
site 19*	1.0043	<LOD	<LOD	29	<LOD	<LOD	6.7

	Sample weight (g)	$MgCl_2$ As (µg/kg)	Na Acetate As (µg/kg)	Hydrox. Hydro As (µg/kg)	$MgCl_2$ Se (µg/kg)	Na Acetate Se (µg/kg)	Hydrox. Hydro Se (µg/kg)
site 20	1.0017	<LOD	<LOD	73	<LOD	<LOD	<LOD
site 21	1.0015	<LOD	<LOD	39	<LOD	<LOD	<LOD
site 22*	1.0002	<LOD	<LOD	25	<LOD	<LOD	<LOD
site 23*	1.0004	<LOD	<LOD	26	<LOD	<LOD	<LOD
site 24	1.0032	<LOD	<LOD	31	<LOD	<LOD	<LOD
CH-6 22.6	0.9581	<LOD	<LOD	10	<LOD	<LOD	<LOD
CH-6 43.0' (fs)	0.9888	<LOD	<LOD	92	<LOD	<LOD	13.3
CH-6 46.0'	1.0009	<LOD	<LOD	25	<LOD	<LOD	<LOD
CH-7 26'*	1.0026	<LOD	<LOD	12	<LOD	<LOD	193.2
CH-7 29.7'	1.0147	<LOD	<LOD	11	<LOD	<LOD	37.5
CH-7 29.8'	1.0093	<LOD	<LOD	11	<LOD	<LOD	45.8
CH-7 32.6'	1.0084	<LOD	<LOD	25	<LOD	<LOD	<LOD
CH-7 34.5'	1.0037	<LOD	<LOD	25	<LOD	<LOD	<LOD
CH-7 38.7'	1.0124	<LOD	<LOD	11	<LOD	<LOD	<LOD
CH-7 45.5'	1.0041	<LOD	<LOD	35	<LOD	<LOD	18.3
CH-7 47'	1.0079	<LOD	<LOD	46	<LOD	<LOD	10.8
CH-7 50.3'	1.0039	<LOD	<LOD	17	<LOD	<LOD	<LOD
CH-7 52.0'	1.0125	<LOD	<LOD	33	<LOD	<LOD	8.4
CH-6 PLUG 1	1.0080	<LOD	<LOD	24	<LOD	<LOD	<LOD
CH-6 PLUG 2	1.0017	<LOD	<LOD	37	<LOD	<LOD	<LOD
CH-7 PLUG 3	1.0015	<LOD	<LOD	38	<LOD	<LOD	<LOD
CH-7 PLUG 4	1.0079	<LOD	<LOD	11	<LOD	<LOD	<LOD
CH-6 PLUG 5	1.0007	<LOD	<LOD	38	<LOD	<LOD	<LOD

	Sample weight (g)	**$MgCl_2$ As (µg/kg)**	**Na Acetate As (µg/kg)**	**Hydrox. Hydro As (µg/kg)**	**$MgCl_2$ Se (µg/kg)**	**Na Acetate Se (µg/kg)**	**Hydrox. Hydro Se (µg/kg)**
CH-6 PLUG 6	1.0011	<LOD	<LOD	71	<LOD	<LOD	10.1
CH-6 PLUG 7*	1.0013	<LOD	<LOD	62	<LOD	<LOD	<LOD
Detection Limit (ppb)		164	4	0.8	44	9	2.2

4.2.1 Detection limits and precision

A total of 55 sequential extractions were analyzed by ICP-MS in three matrix solutions each for six elements each (Table 4, Table 5, Table 6). The elements analyzed by ICP-MS were V, Cr, Mn, Fe, As, and Se. Nine of the 55 samples underwent duplicate extractions which were also analyzed. These are considered total procedural duplicates, incorporating the reproducibility of sample preparation, extraction, and chemical analysis. The limit of detection (LOD) for each sequential extraction step was calculated by multiplying the standard deviation of the matrix blank solution by 3 (Table 7). Therefore, the detection limit is specific to each element and matrix solution. Results below the detection limit are represented by <LOD in Table 4Table 6. Results below detection are treated as one-half the detection limit for plots and statistical tests.

Table 7: Detection limits for sequential extractions.

Analytical detection Limit (ppb as analyzed)	**$MgCl_2$**	**Sodium Acetate**	**Hydrox. Hydrochloride**
51V	1.69	0.12	0.61
52Cr	0.15	0.19	7.65
55Mn	0.02	0.04	0.03
56Fe	2.96	1.38	1.89
75As	2.06	0.05	0.10
82Se	0.55	0.11	0.27

Vial detection limit (ppb as extracted, corrected for dilutions made after extraction)	**$MgCl_2$**	**Sodium Acetate**	**Hydrox. Hydrochloride**
51V	16.94	1.20	0.61
52Cr	1.51	1.88	7.65
55Mn	0.18	0.43	0.03
56Fe	29.61	13.76	1.89
75As	20.55	0.50	0.10
82Se	5.49	1.12	0.27

method detection limit (ug per kg sediment)	**$MgCl_2$**	**Sodium Acetate**	**Hydrox. Hydrochloride**
51V	135.51	9.56	4.90
52Cr	12.11	15.07	61.21
55Mn	1.44	3.40	0.24
56Fe	236.87	110.05	15.14
75As	164.42	3.96	0.80
82Se	43.95	8.99	2.20

Percent relative standard deviation (%RSD) was calculated using a mid-range standard solution to calculate precision (reproducibility) of the extraction method (Table 8).

$$100 * \left(\frac{Standard\ deviation\ of\ STD\ 4}{Average\ of\ the\ 3\ runs\ of\ STD\ 4}\right) = \%RSD$$

A lower value of relative standard deviation indicates better precision. All of the matrix solutions produced a %RSD below 5% except Fe in $MgCl_2$ (negative value) and Fe in Sodium Acetate, As in $MgCl_2$, and Se in all three extractions. Duplicate extractions were analyzed to show reproducibility of sample crushing and weighing, how well the samples were homogenized, and analytical reproducibility (Table 9). Therefore, the duplicates represent total procedural duplication, and not only analytical precision. Summary statistics were also calculated to see the mean, median, and mode of each element in the different extraction steps (Table 11).

Table 8: Analytical precision for each element mass within each matrix solution, calculated from triplicate analysis of a mid-range standard solution. % RSD represents percent relative standard deviation.

$MgCl_2$

Standard 4	**51V**	**52Cr**	**55Mn**	**56Fe**	**75As**	**82Se**
run 1:	12.61	4.549	4.579	-0.815	1.827	1.109
run 2:	12.32	4.397	4.482	-1.686	1.914	0.805
run 3:	11.79	4.316	4.445	-1.681	1.639	0.622
Standard deviation	0.42	0.118	0.070	0.501	0.141	0.246
Average	12.24	4.421	4.502	-1.394	1.793	0.8453
%RSD	**3.40%**	**2.676%**	**1.537%**	**-35.971%**	**7.838%**	**29.100%**

Sodium Acetate

Standard 4	**51V**	**52Cr**	**55Mn**	**56Fe**	**75As**	**82Se**
run 1:	12.06	4.69	4.832	2.138	4.809	1.396
run 2:	12.01	4.805	4.861	0.517	4.651	1.304
run 3:	12.01	4.495	4.842	1.434	4.687	1.23
Standard deviation	0.03	0.157	0.015	0.813	0.083	0.08
Average	12.03	4.663	4.845	1.363	4.716	1.31
%RSD	**0.24%**	**3.360%**	**0.304%**	**59.635%**	**1.756%**	**6.35%**

Hydrox. Hydro.

Standard 4	**51V**	**52Cr**	**55Mn**	**56Fe**	**75As**	**82Se**
run 1:	129.1	46.03	52.08	49.52	50.94	12.93
run 2:	123.8	43.29	50.23	47.92	49.65	12.77
run 3:	122.2	42.62	49.26	46.87	49.07	11.46
Standard deviation	3.6	1.81	1.43	1.33	0.96	0.81
Average	125.0	43.98	50.52	48.10	49.89	12.39
%RSD	**2.9%**	**4.11%**	**2.83%**	**2.77%**	**1.92%**	**6.51%**

Table 9: Sequential extraction data for V, Cr, and Mn for duplicate samples.

Sample ID	$MgCl_2$ V (ppb)	Na Acetate V (ppb)	Hydrox. Hydro V (ppb)	$MgCl_2$ Cr (ppb)	Na Acetate Cr (ppb)	Hydrox. Hydro Cr (ppb)	$MgCl_2$ Mn (ppb)	Na Acetate Mn (ppb)	Hydrox. Hydro. Mn (ppb)
Site 4	<LOD	113	4679	25	406	11819	4065	8502	21993
Site 4 D*	<LOD	93	4313	<LOD	796	8914	940	3797	19648
site 8c	<LOD	164	4094	<LOD	845	14529	3636	17015	19636
site 8c D*	<LOD	149	4073	<LOD	456	15233	3754	16527	19812
site 9	<LOD	43	5186	<LOD	<LOD	12664	2993	9664	30533
site 9 D*	<LOD	78	5252	14	<LOD	11768	4156	9132	31394
site 14	<LOD	<LOD	2335	<LOD	<LOD	9585	921	1910	32036
site 14 D*	<LOD	<LOD	2179	<LOD	<LOD	8964	902	2548	29932
site 19	<LOD	<LOD	951	48	<LOD	49435	11272	6797	59066
site 19 D*	<LOD	<LOD	970	<LOD	83	50806	10494	9216	56842
site 22	<LOD	81	3771	18	750	12254	2289	6416	22755
site 22 D*	<LOD	100	3913	<LOD	874	11852	2177	6141	22849
site 23	<LOD	<LOD	3270	22	1133	15794	2765	10852	98681
site 23 D*	<LOD	54	3018	25	1709	14701	2770	12619	93728
CH-7 26'	<LOD	94	5321	<LOD	68	8745	1567	6654	18296
CH-7 26' D*	<LOD	131	4895	13	150	7935	1507	5571	16536
CH-6 PLUG 7	<LOD	125	2931	58	2021	23426	1952	6302	14597
CH-6 PLUG 7 D*	<LOD	127	2949	77	2001	24778	2011	6651	15139

Table 10: Duplicate extraction data for Fe, As, and Se for duplicate samples.

Sample ID	$MgCl_2$ Fe (ppb)	Na Acetate Fe (ppb)	Hydrox. Hydro Fe (ppb)	$MgCl_2$ As (ppb)	Na Acetate As (ppb)	Hydrox. Hydro As (ppb)	$MgCl_2$ Se (ppb)	Na Acetate Se (ppb)	Hydrox. Hydro Se (ppb)
Site 4	16778	146122	1813923	<LOD	<LOD	57	<LOD	<LOD	<LOD
Site 4 D*	1894	163784	1618840	<LOD	<LOD	53	<LOD	<LOD	<LOD
site 8c	2700	222178	1898901	<LOD	<LOD	24	<LOD	<LOD	<LOD
site 8c D*	3707	193886	1922877	<LOD	<LOD	24	<LOD	<LOD	<LOD
site 9	2093	41451	1888525	<LOD	<LOD	20	<LOD	<LOD	<LOD
site 9 D*	4209	61474	1932535	<LOD	<LOD	17	<LOD	<LOD	<LOD
site 14	491	12250	773191	<LOD	<LOD	27	<LOD	<LOD	<LOD
site 14 D*	<LOD	20208	690495	<LOD	<LOD	26	<LOD	<LOD	<LOD
site 19	923	9089	1450563	<LOD	<LOD	29	<LOD	<LOD	7
site 19 D*	490	23923	1454976	<LOD	<LOD	28	<LOD	<LOD	6
site 22	12733	210518	1538892	<LOD	<LOD	26	<LOD	<LOD	<LOD
site 22 D*	9512	218588	1543776	<LOD	<LOD	23	<LOD	<LOD	<LOD
site 23	13339	264134	6933227	<LOD	<LOD	27	<LOD	<LOD	<LOD
site 23 D*	14191	332954	6556985	<LOD	<LOD	26	<LOD	<LOD	<LOD
CH-7 26'	1330	73513	2105725	<LOD	<LOD	13	<LOD	<LOD	181
CH-7 26' D*	4005	95918	1937376	<LOD	<LOD	12	<LOD	<LOD	206
CH-6 PLUG 7	6360	178887	1732947	<LOD	<LOD	62	<LOD	<LOD	<LOD
CH-6 PLUG 7 D*	7593	184390	1806707	<LOD	<LOD	62	<LOD	<LOD	<LOD

Table 11: Summary statistics for sequential extraction data. Highlighted numbers are half of the detection limit which was used when results were at or below detection limit.

	$MgCl_2$ V (ppb)	**Na Acetate V (ppb)**	**Hydrox. Hydro V (ppb)**	**$MgCl_2$ Cr (ppb)**	**Na Acetate Cr (ppb)**	**Hydrox. Hydro Cr (ppb)**	**$MgCl_2$ Mn (ppb)**	**Na Acetate Mn (ppb)**	**Hydrox. Hydro. Mn (ppb)**
Mean	67.76	88.73	3858.37	16.84	889.39	15965.17	3371.86	9068.28	41546.34
Median	67.76	60.71	3381.73	6.06	465.87	14612.73	2144.44	6585.74	21981.74
Range	67.76	5-438	928-17400	6-122	8-6620	835-50100	328-21800	264-32400	6890-376000

	$MgCl_2$ Fe (ppb)	**Na Acetate Fe (ppb)**	**Hydrox. Hydro Fe (ppb)**	**$MgCl_2$ As (ppb)**	**Na Acetate As (ppb)**	**Hydrox. Hydro As (ppb)**	**$MgCl_2$ Se (ppb)**	**Na Acetate Se (ppb)**	**Hydrox. Hydro Se (ppb)**
Mean	2936.09	108521.92	1734209.12	82.21	1.98	37.20	21.97	4.49	8.66
Median	2271.68	81021.83	1515481.30	82.21	1.98	29.16	21.97	4.49	1.10
Range	118-13700	55-455000	732000-675000	82	2	9-171	22	4	1-193

4.2.2 Chromium

From the samples, 18 out of 46 yielded $MgCl_2$-extractable Cr above the detection limit of 12 μg/kg, with a median of 6 μg/kg, a maximum of 122 μg/kg, and an average of 17 μg/kg. Also, 34 out of 46 samples yielded acetate-extractable Cr above the detection limit of 15 μg/kg, with a median of 484 μg/kg, a maximum of 6620 μg/kg, and an average of 907 μg/kg. All of the samples yielded hydroxylamine-extractable Cr above the detection limit of 61 μg/kg, with a median of 14,600 μg/kg, a maximum of 50,120 μg/kg, and an average of 15,970 μg/kg.

$MgCl_2$-extractable and acetate-extractable Cr were essentially uncorrelated with the total silica content of the rock samples analyzed (r = -0.1 and -0.25, respectively) (Figure 17). Therefore, $MgCl_2$-extractable and acetate-extractable Cr were significantly higher (on average) in the mafic rocks than in the felsic rocks. Hydroxylamine-extractable Cr was positively correlated with total SiO_2 (r=0.66). Therefore, the highest value of hydroxylamine-extractable Cr occurred in felsic rocks, in contrast to the hypothesis.

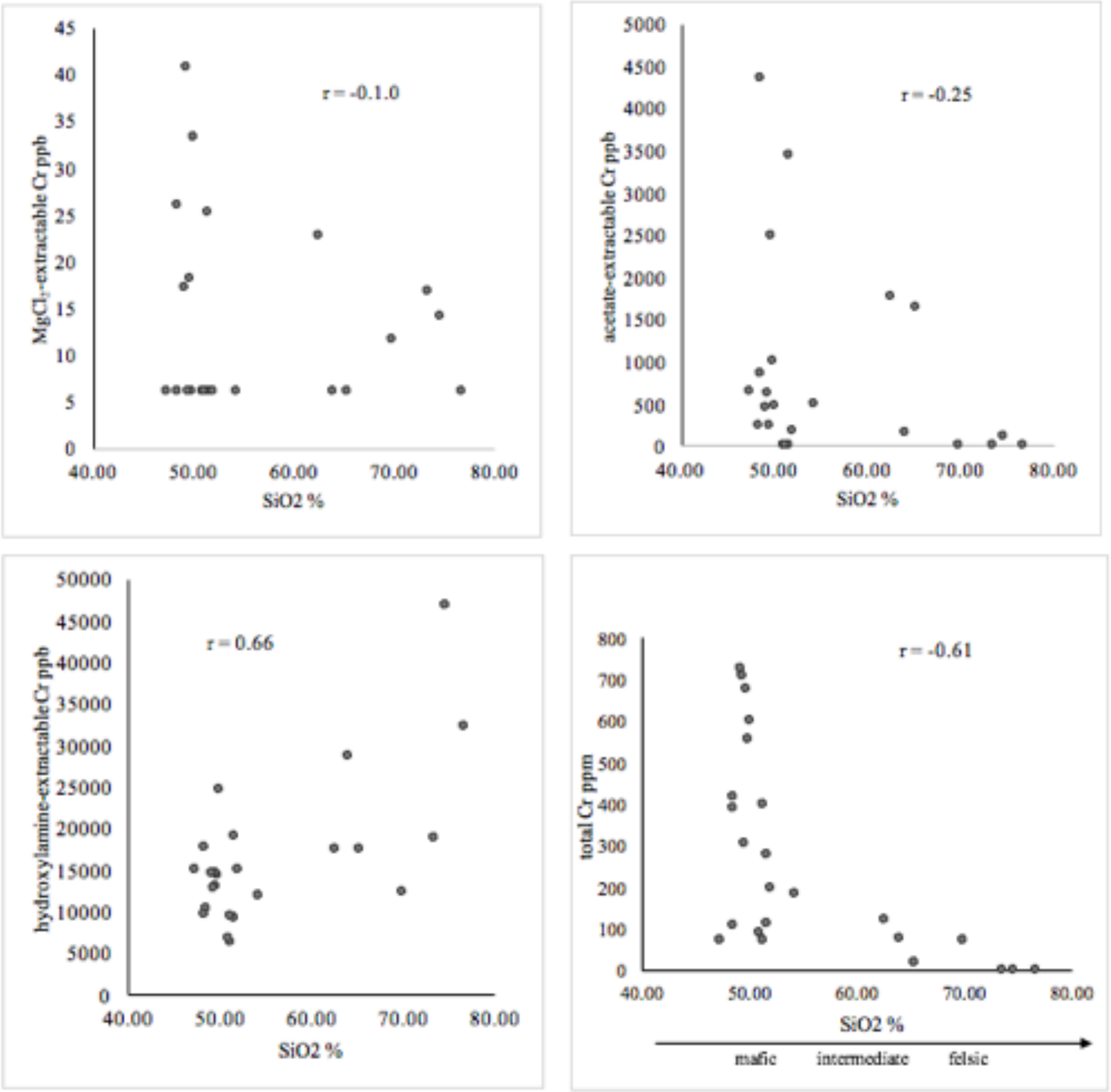


Figure 17: SiO_2% vs $MgCl_2$ - extractable Cr, acetate - extractable Cr, hydroxylamine - extractable Cr, and total Cr.

4.2.3 Vanadium

All of the samples (46 with averaging the duplicate results) yielded $MgCl_2$-extractable V below the detection limit of 135 µg/kg. 13 out of 46 samples yielded acetate-extractable V above the detection limit of 9 µg/kg, with a median value of 61 µg/kg, a maximum value of 438 µg/kg, and an average value of 89 µg/kg. All of the samples yielded hydroxylamine-extractable V above the detection limit of 5 µg/kg, with a median value of 3,380 µg/kg, a maximum value of 17,400 µg/kg, and an average value of 3,860 µg/kg.

Acetate-extractable and hydroxylamine-extractable V were weakly negatively correlated with the total silica content of the rock samples analyzed (*r* = -0.35 and -0.31, respectively). Therefore, acetate-extractable and hydroxylamine-extractable V were highest (on average) in the mafic rocks (Figure 18).

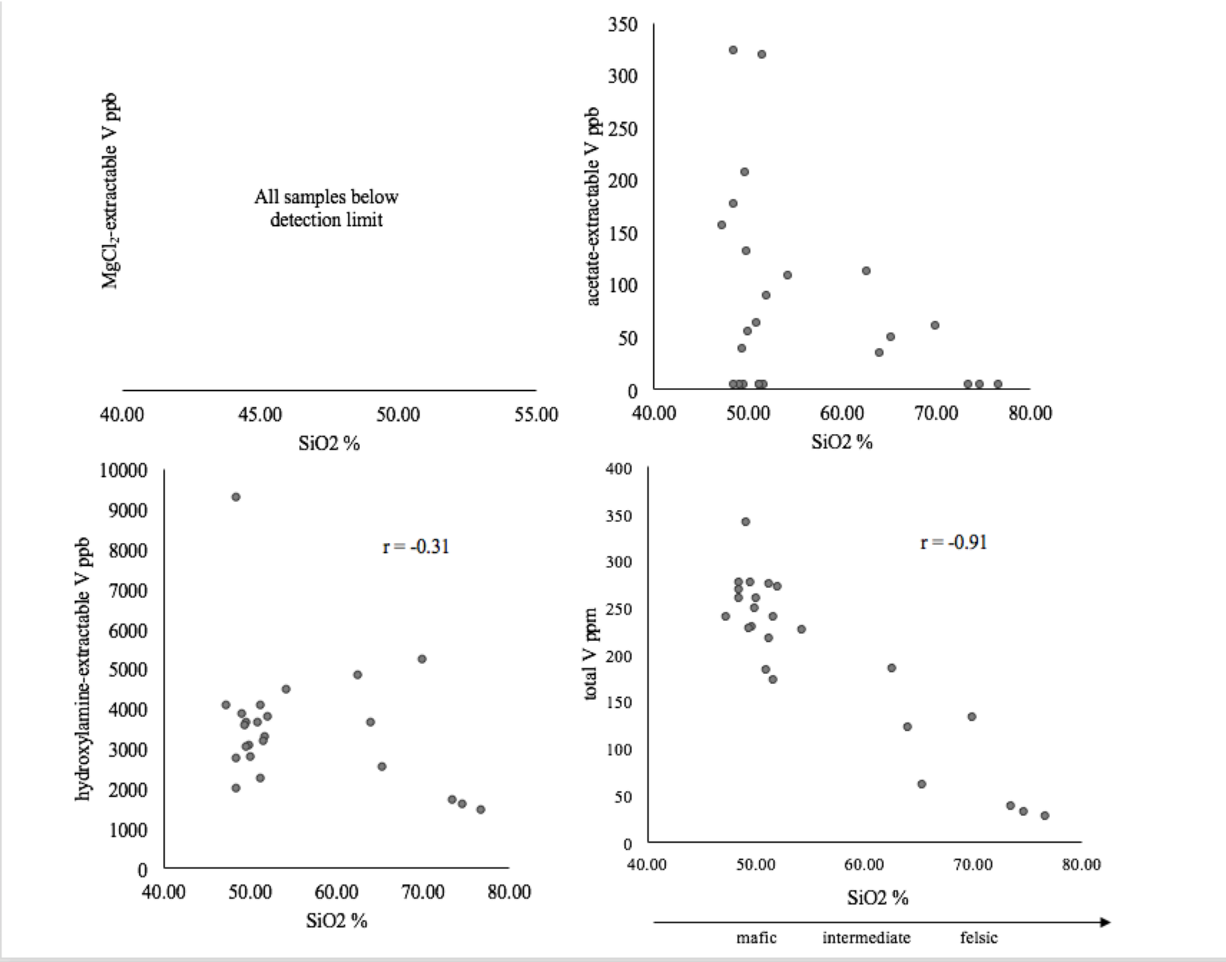


Figure 18: SiO_2% vs $MgCl_2$ - extractable V, acetate - extractable V, hydroxylamine - extractable V, and total V.

4.2.4 Relationship between Cr and V extractions

Acetate-extractable Cr and V were essentially uncorrelated (r = -0.13), likely reflecting the large number of acetate extractions that were near or below detection limits. However, hydroxylamine-extractable Cr and V were positively correlated (r = 0.52) indicating that hydroxylamine-extractable V and Cr co-occur in many samples. Correlation coefficients were not attempted for the $MgCl_2$ extracts because of the large number of non-detects.

4.2.5 Iron, manganese, arsenic, and selenium

The majority of samples yielded detectable $MgCl_2$-extractable, acetate-extractable, and hydroxylamine-extractable Fe and Mn. Only three samples were below the detection limit (110 µg/kg) for acetate-extractable Fe. The average values of $MgCl_2$-extractable Fe were 2,940 µg/kg, 109,000 µg/kg for acetate-extractable Fe, and 1,730,000 µg/kg for hydroxylamine-extractable Fe. $MgCl_2$-extractable and acetate-extractable Fe were weakly negatively correlated with the total silica content of the rock samples (r = -0.37 and -0.34, respectively). Hydroxylamine-extractable Fe was essentially uncorrelated with SiO_2 (r = 0.11). Therefore, $MgCl_2$-extractable and acetate-extractable Fe were highest (on average) in mafic rocks (Figure 19).

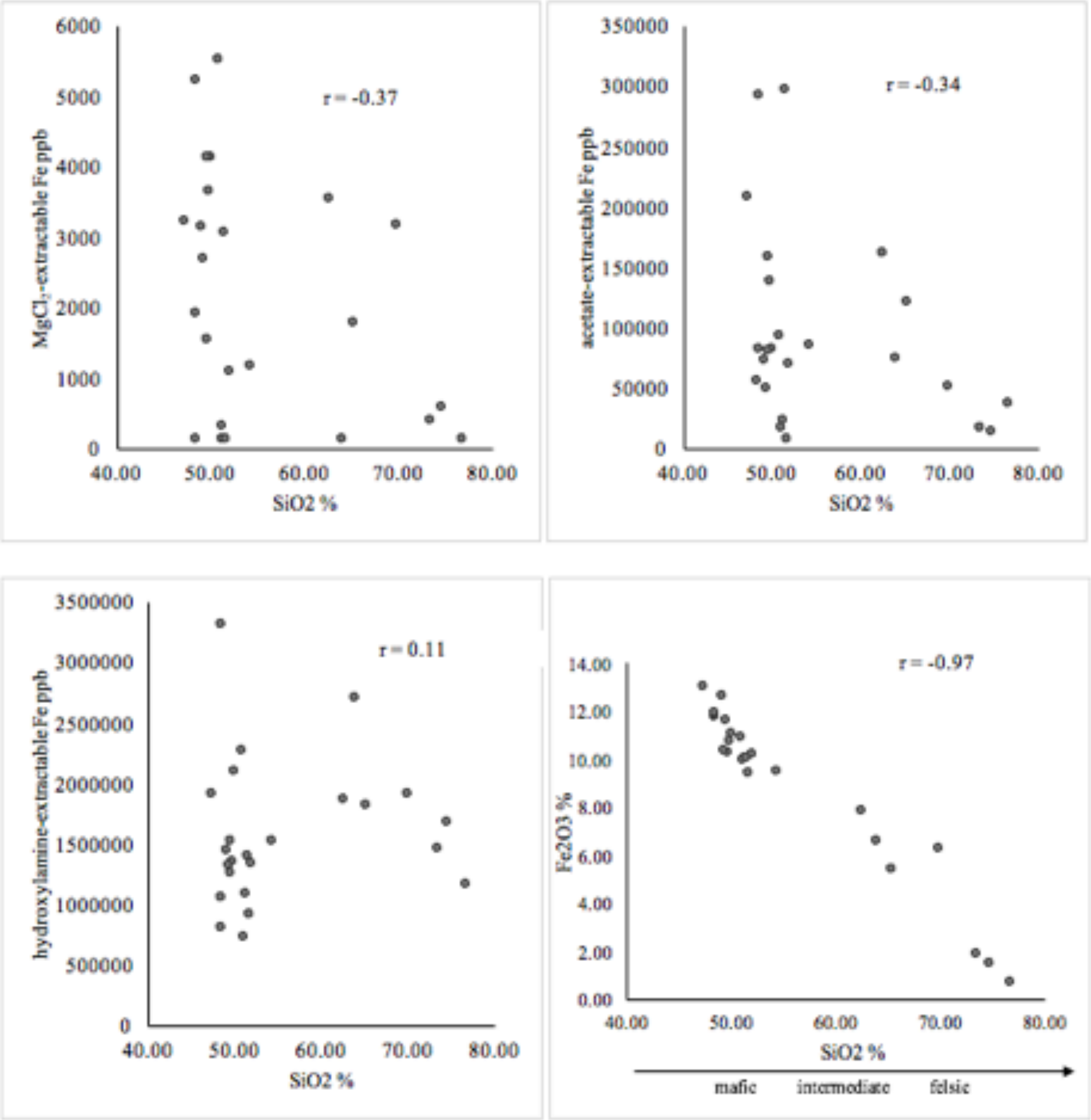


Figure 19: SiO_2% vs iron: $MgCl_2$ - extractable Fe, acetate - extractable Fe, hydroxylamine - extractable Fe, and total Fe.

The average levels of $MgCl_2$-extractable Mn were 3,370 µg/kg, 9,070 µg/kg for acetate-extractable Mn, and 41,500 µg/kg for hydroxylamine-extractable Mn. Mn extractions were weakly positively correlated with the total silica content of the rock samples (*r* = 0.35, 0.05, and 0.42, respectively for $MgCl_2$, acetate, and hydroxylamine-extractable Mn). Therefore, extractable

Mn overall was highest (on average) in intermediate/felsic rocks (Figure 20).

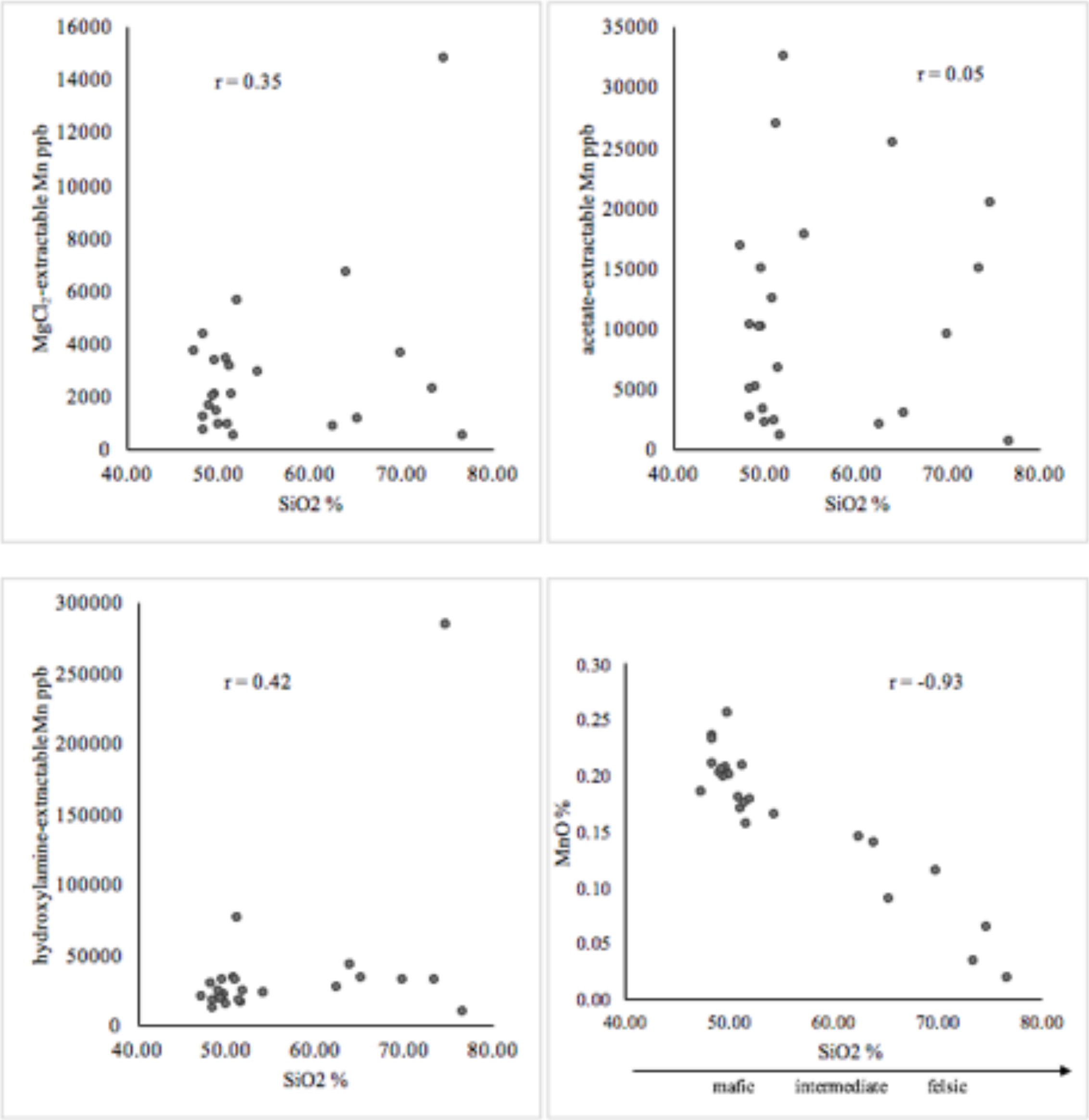


Figure 20: SiO_2% vs manganese: $MgCl_2$ - extractable Mn, acetate - extractable Mn, hydroxylamine - extractable Mn, and total Mn.

Arsenic and selenium were uniformly below detection limits in $MgCl_2$ and acetate extracts. All samples yielded hydroxylamine-extractable As with an average of 37 µg/kg. 14 out of 46 samples yielded hydroxylamine-extractable Se with an average of 9 µg/kg.

5 Discussion

5.1 Rock classification

The results of XRF analysis were used to test the preliminary rock type assignments from hand sample identification. Based on hand sample examination, 13 rocks were initially classified as "mafic" and 12 were "felsic" (Table 2). Using XRF-analyzed SiO_2 content, one sample of the "mafic" hand identified group was actually intermediate/felsic and the remaining 12 were correctly identified as mafic. XRF analysis revealed that the "intermediate/felsic" preliminary group actually contained 2 intermediate, 4 felsic, and 5 mafic samples. The SiO_2 content for the mafic rocks in the preliminary "mafic" hand sample group was uniformly below 50% (except 2). The SiO_2 content for the XRF identified mafic rocks in the preliminary "intermediate/felsic" hand sample group were around 51%, which is higher than the percentage for the XRF confirmed mafic rocks in the hand sample "mafic" category. Ultimately, 4 of the hand samples with a preliminary assignment of intermediate were chemically defined as mafic.

Most samples with a preliminary assignment of intermediate/felsic, based on hand sample analysis, were considered to be a quartz diorite. A quartz diorite has a higher percentage of quartz than diorite. Quartz diorite has 5-20% quartz and a diorite has 0-5% quartz content (Winter, 2010). Both quartz diorite and diorite are a plutonic igneous rock associated with an intermediate composition between mafic and felsic rocks with a granular texture (Jackson, 1997). A quartz diorite tends to be more felsic than a diorite and both form due to partial melting of primary magmas, hybrid magmas, or by fractionation of tholeiitic (containing little or no olivine and a Ca-poor pyroxene) basalt magmas generated in the mantle (Raymond, 1995). The SiO_2 % range for a diorite (intermediate rock) is 52% - 66% (Raymond, 1995; Winter, 2010). Most of the XRF classified "intermediate" rocks with a preliminary assignment of quartz diorite had an SiO_2 % content that fell within the (intermediate) range assigned by Raymond (1995) and Winter (2010). The lowest SiO_2 % for the XRF determined intermediate rocks was borderline mafic/intermediate with a value of 52.01%. The second lowest SiO_2 % value was 54.28% and all other results fell in the range 62.56% - 65.29%. The most surprising sample was “site 5”. The preliminary assignment for this sample was mafic (Figure 21) based on hand sample analysis. The data revealed the SiO_2 content for this particular sample was 65.29% making it an intermediate and almost felsic rock.

Figure 21: Hand sample of site 5 that was collected from an area Goldsmith et al., (1988) mapped as quartz diorite. Preliminary hand sample identification was "mafic" but XRF identification revealed it to be intermediate with 65.29% SiO_2.

When comparing XRF results to the rock classification from Goldsmith et al (1988), it can be seen that map scale rock classification is not the most accurate (Table 11). Many samples, especially the XRF-confirmed mafic samples, were collected from areas mapped as quartz diorite by Goldsmith et al. (1988). In areas mapped as metamorphosed mafic, a few XRF confirmed intermediate rocks were collected (sites 12, 14 and 15). The uncertainty in the Goldsmith et al. (1988) map scale units is due to the scale 1:250,000 and the complexity of the geology. The map explanation of Goldsmith et al (1988) mentions that the metamorphosed quartz diorite unit contains intruding mafic dikes. The mafic dikes are sub-map scale mapped as metadiabase and common throughout the Charlotte area (Goldsmith et al., 1988). Within the mapping location evidence was found to support the idea of some mafic rocks intruding the quartz diorite. This is based on examination of bedrock cores from Davidson, NC and a boulder patch on the UNC-Charlotte campus. Again, there could be two generations of fine grained, dark mafic rocks in the study area. One unit older than met- quartz diorite and one unit younger than the meta-quartz diorite. The question of identifying the country rock was not the main objective of this study but evidence of the "quartz diorite" apparently intruding the mafic rock was observed during field work. Ultimately, the samples collected in this study show that solely relying on map-scale geologic contacts and geologic descriptions are not the most reliable form of rock classification in the Charlotte Terrane.

5.2 Total Cr and V and its relationship to rock type

The reported average value of V in mafic rocks is about 250 ppm (Pohl, 2011). The Charlotte Terrane rocks classified as mafic based on XRF analysis have an average Cr concentration of ~350 ppm and ~250 ppm for V. The V concentration fits the average proposed by Pohl (2011) for mafic rocks. The Cr concentrations are consistent with the ultramafic range of Ball and Izbicki (2004), but the XRF data show that based on SiO_2 content, the most mafic Charlotte Terrane rocks sampled are mafic not ultramafic. It should be noted that most of the total Cr concentrations in the felsic rocks were at or below detection limit. Therefore, such values are interpreted semi-quantitatively. The low numbers do prove lower Cr and V than mafic rocks even if the values aren't quantitatively reliable.

As mentioned earlier, the XRF-analyzed mafic rocks had Cr levels that were in the Cr range associated with ultramafic rocks instead of mafic rocks. What could cause this higher than average total Cr than expected for mafic rocks? The past studies did not specify if the averages were for un-weathered bedrock, surficial samples, or both. Weathering could cause differences in mineral abundances creating a bias in the bulk chemical composition. Weathering would more likely preserve the felsic minerals rather than mafic, which, might yield lower Cr content in the weathered mafic samples compared to the residual un-weathered samples. When total Cr of mafic surface rocks was compared to mafic core samples, there seems to be no correlation between total Cr concentrations vs. sample depth (Figure 22). Since V is proposed to behave similar to Cr, weathered mafic rocks would be expected to have lower V content compared to the residual un-weathered samples as well. As with Cr, V does not seem to be affected by sample depth (Figure 23). In fact, both surface and bedrock samples seem to contain about the same average of total V (~250 ppm).

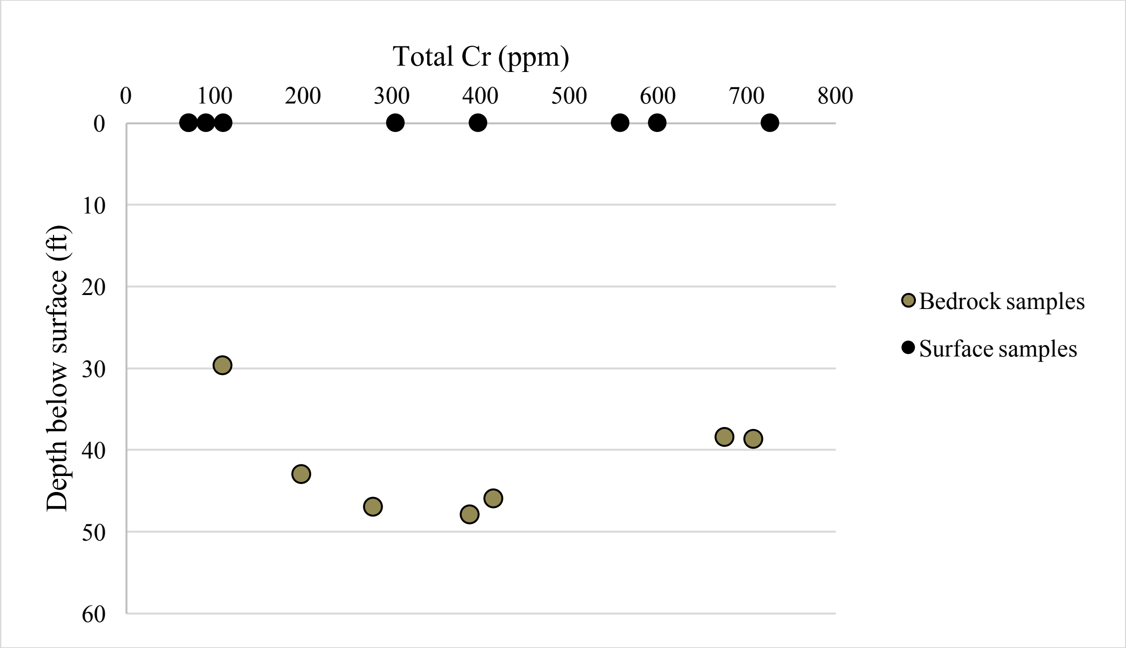


Figure 22: Total Cr (ppm) vs. sample depth (below land surface) for Charlotte Terrane mafic rocks.

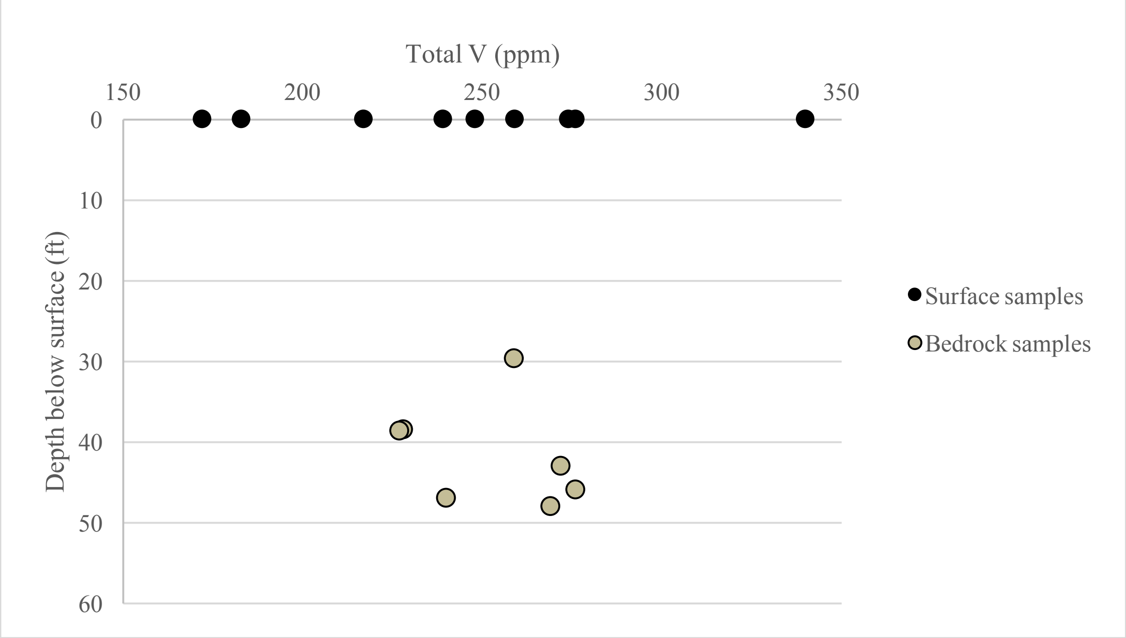


Figure 23: Total V (ppm) vs samples depth (depth below land surface) for the Charlotte Terrane mafic rocks.

From Figure 22 and Figure 23, weathering is most likely not the main mechanism responsible for the Charlotte Terrane rocks to have Cr higher than expected for mafic rocks. It is possible, but not proven, that the mafic minerals present in the Charlotte Terrane rocks contain more Cr than mafic rocks in other settings. How trace elements (Cr and V, specifically) "fit" into mineral structures still isn't fully understood. It could be the minerals present were the best host for Cr, which has Cr levels more typical of ultramafic rocks, or the melts contained more Cr, or metamorphism caused it. Mineral identification would be useful in understanding why Cr concentrations are so high in Charlotte Terrane rocks. Thin section analysis and(or) x-ray diffraction (XRD) analysis would be appropriate to provide mineral identification and abundances. These two methods were not part of this study but could be useful in future studies.

5.2.1 Total Cr and V compared to coal and coal ash

As mentioned earlier, the importance of this research is to fill a knowledge gap about naturally occurring Cr and V in the Charlotte Terrane rocks. This topic is significant due to coal ash spills near Charlotte, NC. The Cr and V values of Charlotte Terrane rocks can be compared to coal and coal ash values from past studies. The range of total Cr in coal ash is 29 - 200 ppm and 10-20 ppm for coal. The range of total V in coal ash is 230 – 260 ppm and 10 – 40 ppm for coal. (Goodarzi and Huggins, 2001; Lachas et al., 1999; von Lehmden et al., 1974; Nriagu, 1988; Ondov et al., 1975; Singh et al., 2010). The Charlotte Terrane rocks seem to have higher total Cr and total V concentrations compared to coal (Figure 24 and Figure 25). On average, total Cr concentrations for the mafic Charlotte Terrane rocks also tend to be higher than coal ash Cr (Figure 26). For V, the coal ash concentrations seem to be in the same average range as the Charlotte Terrane rocks (Figure 27). Based on total Cr and V and without considering the ease of leaching, it seems that mafic Charlotte Terrane rocks are as good, or better candidates for releasing Cr and V to groundwater as is coal ash.

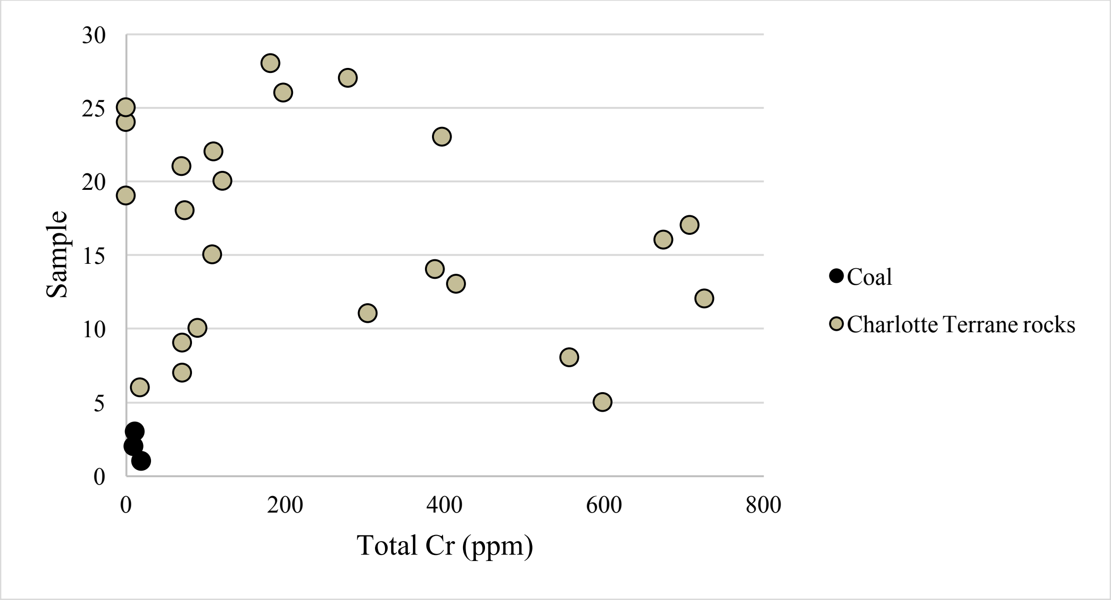


Figure 24: Total Cr (ppm) of coal vs Total Cr (ppm) of Charlotte Terrane rocks. The coal values are from Goodarzi and Huggins (2001); Nriagu (1988); Ondov et al. (1975)

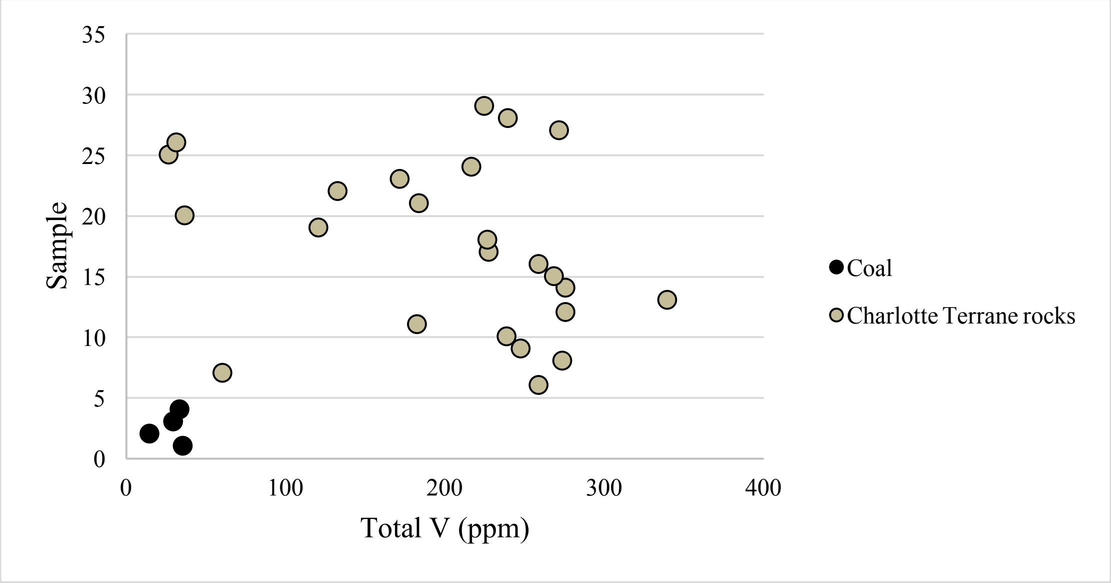


Figure 25: Total V (ppm) of coal vs Total V (ppm) of Charlotte Terrane rocks. The coal values are from Nriagu (1998); Ondov et al. (1975)

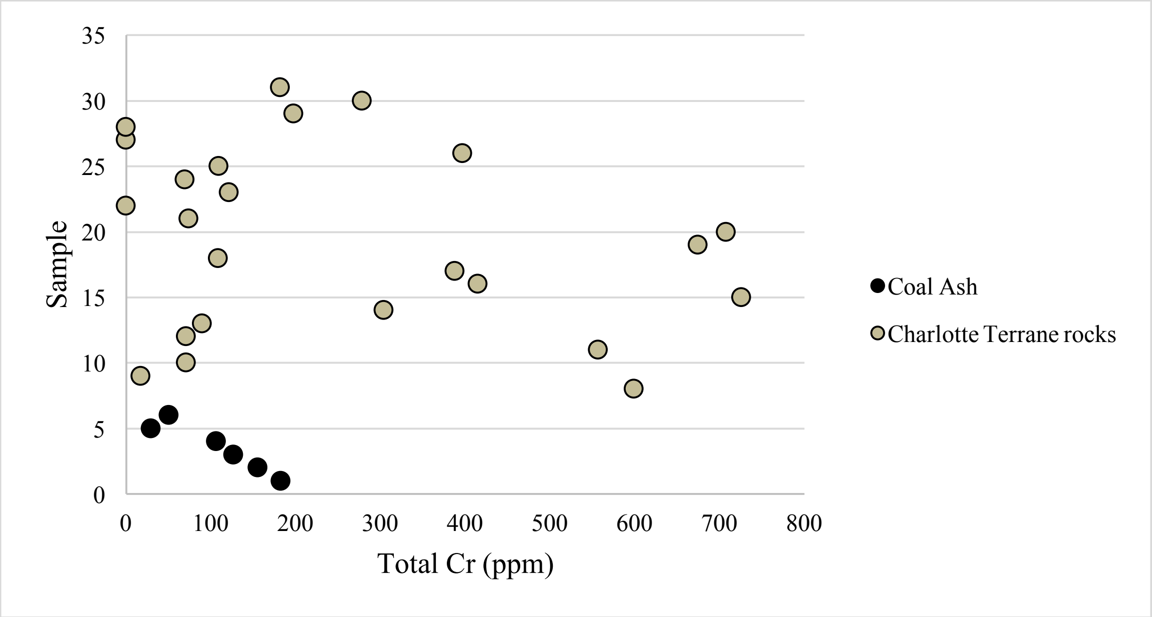


Figure 26: Total Cr (ppm) of coal ash vs total Cr (ppm) of Charlotte Terrane rocks. The coal ash values are from Goodarzi and Huggins (2001); Lachas et al. (1999); von Lehmden et al. (1974); Ondov et al. (1975); Singh et al. (2010)

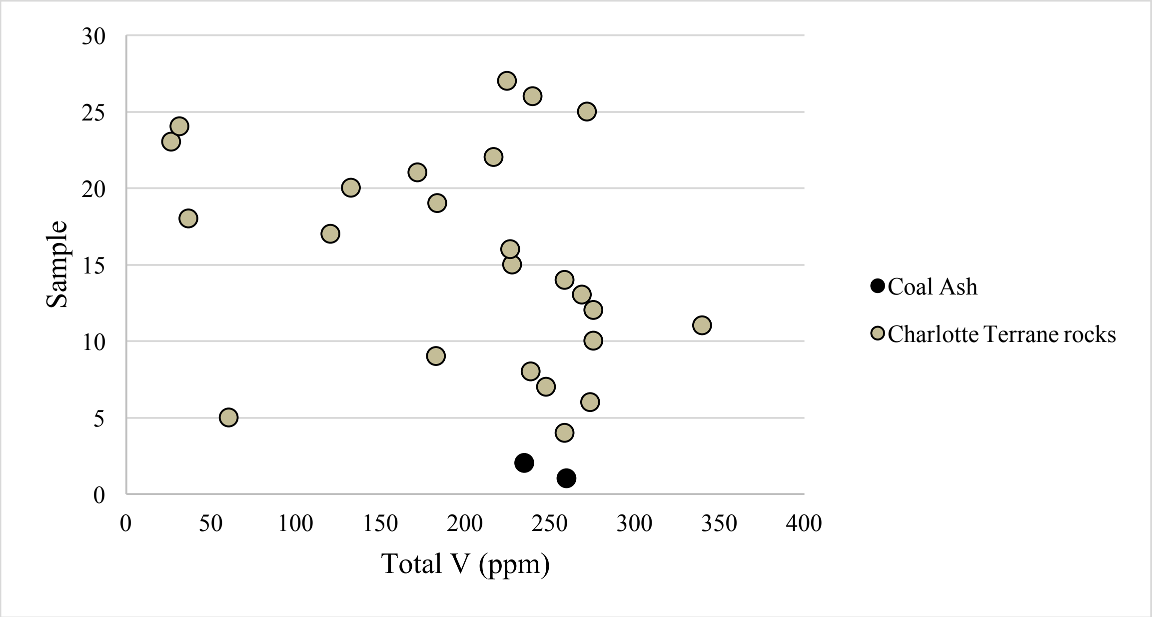


Figure 27: Total V (ppm) of coal ash vs total V (ppm) of Charlotte Terrane rocks. The coal ash values are from Nriagu (1998); Ondov et al. (1975)

5.3 Cr and V concentrations from sequential extractions

In terms of the hypothesis, the XRF data support higher levels of total Cr and V in mafic rocks compared to intermediate/felsic rocks. The second part of the hypothesis focuses on how much Cr and V and be easily leached into groundwater and how it relates to rock type. The expectation was to see more Cr and V being extracted with each sequential extraction step. This was expected because each chemical extraction step used stronger chemicals. It was also hypothesized that these elements would be more associated with Fe and Mn oxides, which needed a strong reagent, such as hydroxylamine hydrochloride, to extract them from the rock samples. The ICP-MS data suggests that overall, leachable Cr and V do increase with each sequential extraction step. Also, as mentioned in the results section, generally, there is a correlation between rock type and the amount of Cr and V available to be leached.

5.3.1 Extractable V

For V, $MgCl_2$ extraction was ineffective as hypothesized, indicating that V is not easily exchanged by salinity increases. All results were below the detection limit. Acetate-extractable V did produce some results above detection limit, but the majority of the samples were below the detection limit. Hydroxylamine-extractable V, overall, did not exhibit a correlation between rock type and the amount of V extracted. One sample had a high V content, creating slight bias in the correlation coefficient. When comparing the total V to the sum of extracted V for all 3 extractions, a small proportion of V is extractable. The highest amount of V extracted, from all 3 extractions, was ~9.3 ppm from a mafic rock (CH-7 29.7’). That sample had total V of 259 ppm suggesting that <5 % of total V in a mafic rock is leachable, specifically in an environment that has strong reducing conditions. Therefore, it can be concluded that V is correlated with oxides, due to the results produced from the hydroxylamine-hydrochloride extraction, but rock type does not seem to be a controlling factor in hydroxylamine-extractable V.

The finding that hydroxylamine-extractable V is similar among many of the mafic and felsic rocks in this study is unresolved. The XRF data show that total V (which is different than extractable V) is higher in mafic rocks, but when extracted, the rock type is irrelevant. The average hydroxylamine-extractable V is 3006 ppb (~3ppm) for felsic rocks and 3698 ppb (~3.7 ppm) for mafic rocks. When the hydroxylamine extracted V is compared to total V, only a small percentage of V has been extracted. For example, ~3.5% of the total V was extracted by hydroxylamine from felsic rocks and 1.5% for mafic rocks. This, again, could prove that V is more associated with oxides and hydroxylamine-hydrochloride is efficient in extracting oxides from felsic material, but isn't as efficient at extracting oxides from mafic materials. To understand the relationship between V and specific mineral types a microbeam method (microprobe or SEM) would be useful to identify what minerals contain V.

Weathering did not seem to be a factor in the distribution of total V when comparing mafic surface and bedrock samples. Since weathering can allow more oxides to be present on the mineral surfaces, higher hydroxylamine-extractable V would be expected for the surface samples compared to the bedrock samples. Again, the data seems to suggest that the depth of the sample (on the surface or below the surface) does not have an effect on the extractable V (Figure 28).

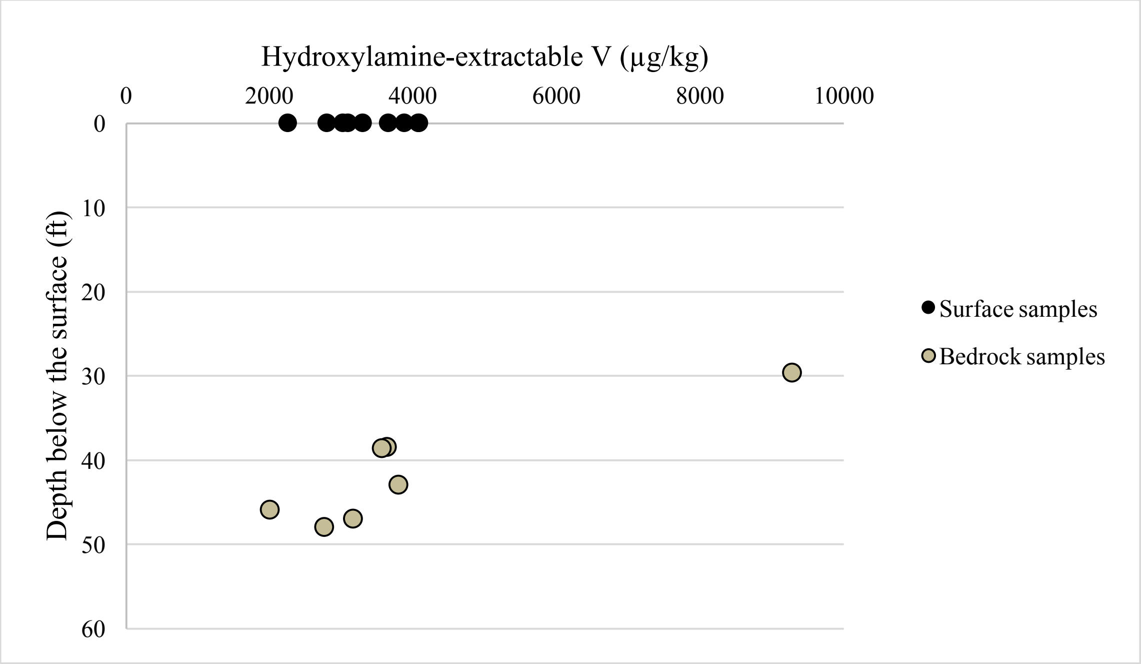


Figure 28: Hydroxylamine-extractable V vs. sample depth (depth below the surface) for the XRF confirmed mafic rocks in the Charlotte Terrane.

5.3.2 Extractable Cr

$MgCl_2$ extraction and acetate extraction were more efficient at extracting Cr than V. More Cr was extracted from the acetate solution than the $MgCl_2$ solution as expected. In terms of the hypothesis, more Cr overall was extracted from mafic rocks compared to intermediate/felsic rocks. The average value of Cr extracted by $MgCl_2$ was 17 ppb vs. 907 ppb for the acetate. It was predicted that more Cr would be extracted from mafic rocks rather than intermediate/felsic rocks using the hydroxylamine. The hydroxylamine-extractable Cr data are inconsistent with the hypothesis (Figure 17). There is a positive correlation between hydroxylamine-extractable Cr and SiO_2 content. Since this step targeted Fe and Mn oxides, it is surprising to see intermediate/felsic material yielding higher hydroxylamine-extractable Cr. When the average total Cr is compared to the average amount of Cr extracted during the hydroxylamine-extraction ~40.4% of the total Cr was extracted in the felsic/intermediate rocks and only ~3.7% of the total Cr was extracted from the mafic rocks. However, it is important to note that the XRF-based total Cr data are considered semiquantitative for the felsic rocks but more quantitatively reliable for the mafic rocks. Full dissolution, with analysis by ICP-MS, would provide more reliable quantitative total Cr data.

Mineralogy could be the controlling factor, specifically hydrous minerals. Mafic rocks tend to contain higher amounts of anhydrous minerals such as magnetite, ilmenite, and chromite. Felsic rocks tend to contain higher amounts of hydrous minerals such as quartz, plagioclase, and k-feldspar. Two other hydrous minerals are pyroxene and hornblende. Felsic and intermediate rocks can have small traces of mafic (hydrous) minerals, such as pyroxenes, which would be the Cr source (Raymond 1995). It is possible that the Cr is locked up in the anhydrous minerals in the mafic rock and the hydrous minerals in the felsic rocks. If this was the case, then the hydroxylamine would not be able to extract as much Cr in the mafic rocks compared to the felsic rocks. Whether the Cr is in hydrous or anhydrous would not affect the XRF results which is why the mafic rocks still contain higher Cr than the felsic rocks. A full dissolution of each rock sample would be useful in determining total Cr but to understand where the Cr is thin section analysis would be most appropriate.

Why is more extractable Cr (on average) from the intermediate/felsic samples rather than the mafic samples? On average, higher amounts of overall extractable Fe occur in intermediate/felsic rocks as well. This could prove that Cr is associated with Fe, but still doesn’t explain why it is higher in intermediate/felsic rocks, which lack Fe and Mn oxides. Looking closer at the felsic/intermediate rock samples, the highest hydroxylamine-extractable Cr value (46,665 ppb) was from a weathered surface sample collected in a stream bed. None of the other surface felsic/intermediate rock samples (only the XRF tested samples) seemed to display weathering as intense as the sample collected from the stream bed. It is possible the reason Cr is higher in the intermediate/felsic rocks is not due to the mineral structure, but the oxide coatings due to weathering.

One bedrock sample was collected from a fracture surface. Fracture coatings are coated with Fe and Mn oxides, increasing the potential for higher Cr content than suggested by the overall rock type. However, the fracture surface sample produced the third lowest hydroxylamine-extractable Cr value out of 9 intermediate/felsic samples. In this case, fracture surface weathering did not seem to produce Cr values as high as the weathered surface samples. Overall, on average, all the surface samples combined (not differentiating between rock type) have, on average, higher hydroxylamine-extractable Cr (18,054 ppb) than the bedrock samples (13,250 ppb) (Figure 30) influenced by a few surface samples yielding high extractable Cr. It might be inferred that weathering could cause higher hydroxylamine-extractable Cr concentration.

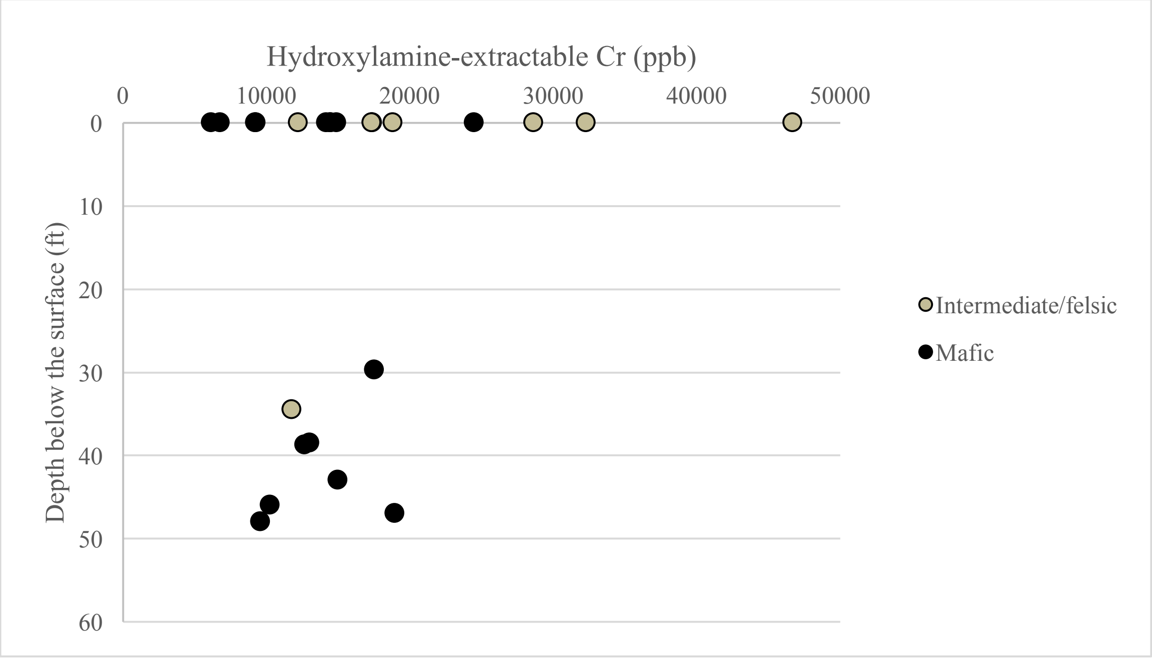


Figure 29: Hydroxylamine-extractable Cr (ppb) vs. sample depth (below land surface) for mafic and intermediate/felsic Charlotte Terrane rocks. The data projected represent the XRF confirmed intermediate/felsic and mafic rock types.

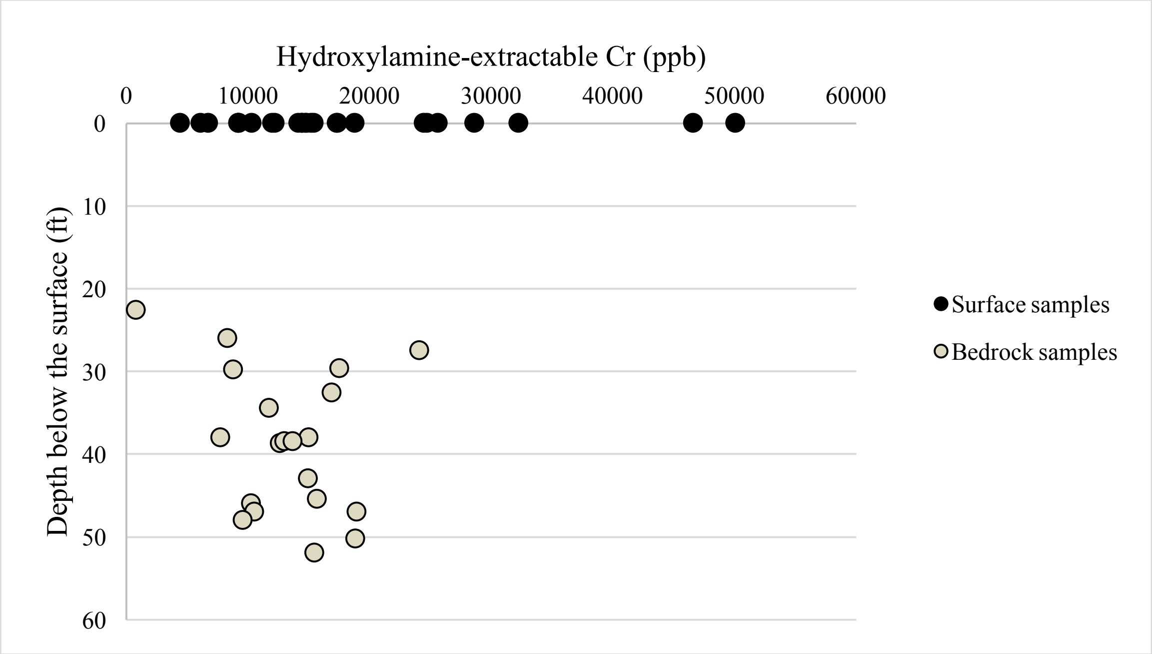


Figure 30: Hydroxylamine-extractable Cr (ppb) vs. sample depth (below land surface) for all surface samples and bedrock samples. These data include the XRF confirmed rock types and non-XRF confirmed rock types.

6 Conclusions

Rock collection from this study demonstrates that rock units and contacts mapped by Goldsmith et al. (1988) are approximate due to the mapped scale. Since the map scale was so broad, and many of the rock types collected did not match the map-scale rock unit described by Goldsmith et al. (1988), detailed mapping and coring would be recommended in this area. Being able to understand the geological contamination hazards in the area begins with the underlying rock type. The underlying rock units contain higher Cr and V content than coal and coal ash suggesting Charlotte Terrane rocks could potentially be an equal or perhaps greater source of Cr and V than coal ash.

This study has presented data suggesting that Cr and V contamination can be associated with specific rock type. The XRF data were consistent with the hypothesis that mafic rock types tend to have higher total Cr and V compared to intermediate/felsic rock types. Sequential extraction revealed that more Cr was extracted from felsic/intermediate rocks during the hydroxylamine extraction compared to mafic rocks. Overall, mafic rocks have a higher potential to contain Cr and V, and higher levels of Cr and V are able to be extracted from mafic rocks compared to the overall sum of the felsic/intermediate rocks. For reasons still unknown, higher Cr and V concentrations were extracted from intermediate/felsic rock types in the Charlotte Terrane rocks. No matter what the rock type is, it has been shown that the Charlotte Terrane rocks can be leached of Cr and V with possible, but unproven, implications for groundwater quality.

With more research, it could potentially be tested that rock type does play a major role in the extraction of Cr and V into the groundwater, but that the degree of weathering could be the major factor as well. The data from this study could potentially suggest that heavily weathered rocks are more likely release Cr from mineral surfaces compared to non-heavily weathered materials but there is not enough data to really conclude this as a primary conclusion for this study. More research needs to be conducted, but it is possible that it is easier for Cr to be extracted from Fe and Mn oxides than directly from a mineral structure.

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