# LANDSCAPE POSITION, FERROUS MINERAL OXIDATION, AND DISSOLVED OXYGEN: A CRITICAL ZONE PERSPECTIVE TO THE INNER PIEDMONT TERRANE

by

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#### ABSTRACT

## JUSTIN C. COLEY. Landscape Position, Ferrous Mineral Oxidation, and Dissolved Oxygen: A Critical Zone Perspective to the Inner Piedmont Terrane. (Under the direction of DR. DAVID VINSON)

The depth at which weathering starts has been studied by others in felsic and mafic protoliths. However, weathering initiation in foliated parent material, which is inherently more permeable, has not, and there is little understanding of what mineral is first to weather at depth in this setting. Nor has the difference in weathering profiles along a hillslope transect been studied to better understand the geochemical evolution of groundwater as it moves down gradient due to deep mineral weathering. Using pXRF and binocular microscopy, elemental and mineral abundances were analyzed in 2 drill cores collected from low and high topographic positions located in a gneiss lithology. Comparative mineral ratios and mass-transport values ( $\tau$ ) were used to identify weathering front depths of biotite, hornblende, and plagioclase. Pearson correlation coefficients for biotite (r = -0.32), hornblende (r = -0.19), and biotite + hornblende (r = -0.4) with respect to iron-oxides show a combination of biotite and hornblende weathering is likely the initiation of weathering at depth rather than weathering of either specific mineral. Greater depth to the water table coincided with formation of thicker saprolite, and the boundary between hardweathered rock and unweathered rock coincided with oxygen depletion. This study used nondestructive testing to identify the depths over which profile weathering occurs emphasizing ferrous mineral oxidation. The weathering of Fe-bearing minerals at depth releases solutes that directly impact dissolved oxygen, and trace metal solubility, while also enhancing permeability because of mineral grain swelling, both of which impact water quality with corresponding implications for human and environmental health.

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#### DEDICATION

This thesis is dedicated first and foremost to my wife Meghan for her steadfast love, support, and patience, and to my children Tucker and Lila who are my fundamental motivation. I could not have accomplished this without them. I also dedicate the work to my first chemistry teacher, my mother Susan. From an early age, she encouraged curiosity and excitement for learning about the way the natural world works.

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## LIST OF ABBREVIATIONS

As	Elemental arsenic
AWRS	Allison Woods Research Station, Iredell County, NC
BDD	Biotite Disappearance Depth
Ca	Elemental calcium
CH-2	Core-hole 2 and its corresponding drill core, from the mid-slope position
CH-4	Core-hole 4 and its corresponding drill core, from the lowest topographic position
Cr	Elemental chromium
DO	Dissolved oxygen
FBLS	Depth below the land surface in feet
Fe	Elemental iron
Fe <sup>2+</sup>	Ferrous iron
Fe <sup>3+</sup>	Ferric iron
FeO <sub>x</sub>	Iron oxides formed by chemical weathering of iron bearing minerals
HDD	Hornblende Disappearance Depth
HCO <sub>3</sub> -	Dissolved bicarbonate
HWR	Hard Weathered Rock
ICH	International Council for Harmonization of Technical Requirements for
	Pharmaceuticals for Human Use
IUPAC	International Union of Pure and Applied Chemistry
K	Elemental potassium
LOD	Limit of Detection
Mg	Elemental magnesium
Mn	Elemental manganese
MnO <sub>x</sub>	Manganese oxides formed by chemical weathering of manganese bearing
	minerals
MW-X	Monitoring wells associated with each corehole
Na	Elemental sodium
NCDEQ	North Carolina Department of Environmental Quality (f.k.a. N.C. Department of
	Environment and Natural Resources)

NIST-2710a	National Institute of Standards & Technology – Montana soil with highly elevated		
	trace element concentrations		
NIST-2711a	National Institute of Standards & Technology – Montana soil with moderately		
	elevated trace element concentrations		
PIM	Profile Initiating Mineral		
PWR	Partially Weathered Rock		
PWZ	Plagioclase Weathering Zone		
pXRF	Portable X-ray Fluorescence		
QLO-1a	USGS Quartz Latite Standard		
<i>r</i> Pearson's correlation coefficient			
Rb	Elemental rubidium		
REP	Piedmont and Mountains Resource Evaluation Program		
Si	Elemental silicon		
Sr	Elemental strontium		
τ	Open-system mass transport function, a ratio expressing the degree of elemental		
	enrichment or depletion in a geologic profile at a given depth		
Ti	Elemental titanium		
USGS	U.S. Geological Survey		
UWR	Unweathered Rock		
Zr	Elemental zirconium		

#### **1** INTRODUCTION

#### 1.1 Mineral Weathering

Rock weathering is driven by physical and chemical processes that increase porosity, permeability, mineral transformations, and the removal of smaller particles and soluble components. In general, chemical weathering processes are primarily controlled by water and oxygen, with other factors such as temperature and organic activity also playing important roles. Physical weathering processes apply stress to rock that results in disaggregation. Chemical weathering processes transform minerals through various reactions such as biotic respiration, dissolution, precipitation, hydrolysis, hydration, and reduction/oxidation (redox). While chemical weathering is thought to be dominant below the water table, physical weathering processes also occur due to mineral swelling and other processes, allowing for greater penetration of water and dissolved oxygen (DO) into otherwise impermeable rock (Gilkes and Suddhiprakarn, 1979; Anovitz et al., 2021). Therefore, physical weathering can enhance chemical weathering rates, and vice versa, in subsurface environments.

A site's position in the landscape can also affect weathering rates (Bailey et al., 2014; Gannon et al., 2014). On hillslopes, bedrock can lie closer to, or farther from, the land surface depending on uplift and erosion rates, relative to the rock's resistance to chemical weathering (Brantley et al., 2017). Likewise, the thickness of regolith (herein meaning all weathered material above unweathered bedrock), representing in-place weathered material, is variable depending on rock resistance to weathering, climate, and topography. The relationship of depth to bedrock and water table height likely exerts some control on whether oxic or anoxic conditions are prevalent at the interface of regolith and unweathered bedrock (Fig. 1) (Bourgault et al., 2017, 2022). As the water table is a source of open system inputs of oxygen, the depletion of DO along a local groundwater flow path will depend on removal from the water table and interaction with chemical reductants that consume DO. In some systems, especially organic-rich environments, microbial activity can be significant for consuming DO.



Figure 1 - An idealized hillslope profile showing water table height with respect to bedrock. At higher landscape positions, the water table is near the level of bedrock while at lower landscape positions (valleys) the water table lies above bedrock. As groundwater moves along the flow path from recharge zones to discharge zones it is gradually altered from oxic to anoxic.

The dominance of oxic versus anoxic conditions significantly impacts groundwater flowing through an aquifer by enabling or limiting heavy metal dissolution, speciation, and contaminant transport (Oh and Richter, 2005; Li et al., 2021). For example, chromium (Cr) is more prevalent in oxic groundwater. At the same time, arsenic (As) can occur in oxidized and reduced species with the reduced species being more toxic than the oxidized species (Vengosh et al., 2016; Coyte and Vengosh, 2020). Manganese (Mn) has received increasing scrutiny as a naturally occurring chronic toxin that predominates in anoxic groundwater (Homoncik et al., 2010; Gillispie et al., 2016; Ramachandran et al., 2021; Riedel et al., 2022). Further, oxidative weathering of silicate minerals has implications for landscape evolution, global chemical cycling, and the long-term stability of man-made structures (Anderson et al., 2019; Anovitz et al., 2021).



Figure 2 - The Goldich weathering series provides a framework to predict the order in which minerals will break down and weather away (generally in the same order that they crystallized). From (Churchman and Lowe, 2011)

Igneous mineral weathering is generally initiated in a well-established order (Goldich, 1938) (Fig. 2) at surface or near-surface conditions, i.e. the "critical zone." These patterns have been used to describe specific depth intervals (i.e., weathering fronts) over which weathering occurs. From the surface downward, Brantley et al. (2017) described the soil-initiating mineral as a low solubility mineral whose dissolution demarcates the soil – saprolite boundary through disaggregation and clay formation with alkali-rich minerals the most common example in

granitic rock (Brantley et al., 2017). The soil initiating mineral is generally the last major mineral to begin weathering in a profile. The next to last major mineral to begin weathering, or porosityinitiating mineral, is defined as an abundant, moderately soluble mineral whose weathering results in density reduction and porosity formation, and denotes the boundary between hardweathered rock and saprolite (Brantley et al., 2017). The porosity-initiating mineral and reaction in felsic (granite) rocks are most often dissolution of plagioclase (Bazilevskaya et al., 2013, 2015). The profile-initiating mineral (PIM) is the first (deepest) major mineral to initiate weathering in a geologic profile, representing the transition from weathered to substantially unweathered rock (Brantley et al., 2017). While ultramafic and mafic minerals are the first weathered in the Goldich series, a mineral must be present significantly to be the PIM in a given system. In granitic rocks, biotite has been considered by some to be the first mineral to initiate weathering in unweathered rock (Bazilevskaya et al., 2015; Brantley et al., 2017). It is thought that oxidation of biotite is the primary weathering process at work at the interface of hard weathered and unweathered bedrock, which may indicate the presence of oxygen at greater depths than previously expected (Fig. 3). Others have argued that crystallization pressure resulting from iron-oxide (FeO<sub>x</sub>) and clay crystal growth along mineral grain boundaries preempts biotite oxidation (Anovitz et al., 2021). Still, those studies relied on the examination of submicroscopic mineral crystals that is beyond the scope of this project.

For the purposes of this study, the term soil refers to the generally unreactive, porous sediment that no longer exhibits rock fabrics or mineral grain structures. Saprolite refers to highly porous and friable regolith in which rock fabrics and mineral grain structures can still be seen with the naked eye. Partially weathered rock (PWR) refers to competent regolith that is porous enough that advection is the main driver of weathering, while hard weathered rock

(HWR) refers to rock whose porosity is limited, and through which diffusion is the main weathering mechanism. Unweathered rock (UWR) is not yet altered by chemical weathering processes, and whose existing fractures are the result of tectonic forces (Fig. 3).

The PIM is specific to the mineralogy of the crystalline rock being studied. Where it is present, oxidative dissolution of pyrite has also been hypothesized to coincide with biotite oxidation during the initiation of weathering at depth (Brantley et al., 2017). Where pyrite is especially abundant (e.g. in some volcanic rocks), it is conceivable that pyrite is the PIM. In mafic rocks, the PIM could be a mafic mineral such as olivine, a pyroxene, or an amphibole (e.g. hornblende). There has been little work concerning what the PIM could be in rocks of intermediate composition, or with a foliated morphology, that exhibits high levels of lithologic heterogeneity and increased permeability. Biotite, pyrite, pyroxenes, and amphiboles all contain ferrous iron (Fe<sup>2+</sup>), which is a reduced form of Fe that functions as an electron donor, or reductant in the environment.

As biotite oxidizes,  $Fe^{2+}$  is transformed to insoluble ferric  $FeO_x$  (e.g.,  $Fe(OH)_3$  containing  $Fe^{3+}$ ), consuming DO and releasing potassium (K) ions to maintain charge balance (Gilkes and Suddhiprakarn, 1979). As a result of these alterations, biotite swells, which likely drives microfracturing, enhancing porosity, permeability, and groundwater flow, and allowing further weathering along newly exposed surfaces (Anovitz et al., 2021).



Figure 3 - Traditionally, weathering has been thought to be initiated at the bottom of the transition zone (red line). It is hypothesized here that PIM weathering occurs much deeper in fractured unweathered bedrock (blue line). (modified from Huffman and Abraham, 2010)

Hornblende oxidation also consumes DO, and releases calcium (Ca) ions to maintain charge balance. The final product of ferrous mineral oxidation is incongruent dissolution, resulting in FeO<sub>x</sub> and clay mineral (e.g. kaolinite) formation (Eq. 1 & 2).

### **Biotite Hydrolysis**

 $(\text{Eq. 1}) \text{ 4 KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 32 \text{ H}_2\text{O} + 3 \text{ O}_2(\text{aq}) + 4 \text{ H}^+ \rightarrow 12 \text{ Fe}(\text{OH})_3 + 2 \text{ Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4 \text{ K}^+ + 8 \text{ H}_4\text{SiO}_4$ 

#### Hornblende Hydrolysis

 $(\text{Eq. 2}) \text{ Ca}_2\text{Fe}_4\text{AlSi}_7\text{AlO}_{22}(\text{OH})_2 + 15 \text{ H}_2\text{O} + \text{O}_2(\text{aq}) + 4 \text{ H}^+ \rightarrow 4 \text{ Fe}(\text{OH})_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2 \text{ Ca}^{2+} + 5 \text{ H}_4\text{SiO}_4$ 

#### 1.2 Groundwater Redox Chemistry

Whereas acid-base neutralization reactions involve the exchange of protons, redox reactions are driven by electron exchanges. Electron-transport systems are fundamental to microbial metabolism, growth, reproduction, mineral and metal dissolution, and precipitation (Chapelle, 2001). Redox reactions require an electron acceptor and an electron donor, and the exchange can act as an energy source. At Earth's surface, oxygen is the primary electron acceptor. In the subsurface, oxygen levels decrease with depth as mineral weathering progresses, and microbes scavenge available oxygen during respiration. All groundwater systems contain microbes that use redox reactions to sustain their life cycles (Chapelle, 2001). In most groundwater systems organic carbon is the most common source of electrons for biota, and these microbial reactions catalyze many redox processes in the system (Chapelle, 2001; Jones et al., 2018; Li et al., 2021).

In the absence of oxygen, other electron acceptors, such as sulfate and nitrate, are utilized for respiration. Once DO becomes depleted, reducing conditions tend to dominate, and electron acceptors are used in an established order based on their energy potential and abundance under a given set of environmental conditions (Fig. 4) (Chapelle et al., 1995; Chapelle, 2001; Sapkota et al., 2022).



Figure 4 - The "redox ladder", a pattern of electron acceptor consumption based on the levels of acceptors present after the transition from oxic to anoxic conditions (modified from Sapkota et al., 2022)

Many contaminants and heavy metals (e.g., Fe and Mn) become more soluble in their reduced forms. Due to their redox sensitivity, both Fe and Mn play important biogeochemical roles (Scott et al., 2002; Herndon and Brantley, 2011; Herndon et al., 2015; Richardson, 2017; Jones et al., 2018; Coyte and Vengosh, 2020). When biotite and hornblende are oxidized, and DO is consumed, the conditions that enable the reductive dissolution of heavy metals are enhanced. However, the patterns of redox conditions and localized groundwater heterogeneity in association with complex lithologic heterogeneity are not well understood.

The primary objectives of this research were to identify the actual depth of weathering along a Piedmont hillslope transect, and determine what, if any, effect ferrous mineral oxidation at depth may have on DO levels and groundwater chemistry. However, the mechanisms by which groundwater becomes anoxic after recharge in the Piedmont groundwater system are relatively unpredictable at the scale of an individual well or hillslope. It has been argued that organic carbon, perhaps from the land surface and soils, is the primary reductant that drives anoxic groundwater in the Piedmont (Vinson et al., 2009). Others have argued that pyrite or biotite weathering provides Fe<sup>2+</sup> as a mineral reductant in the subsurface (Brantley et al., 2017). Improved understanding of the relationship of ferrous mineral weathering to oxic and anoxic groundwater conditions in the Piedmont region could improve our ability to predict naturally occurring trace elements of health significance, such as As, Cr, and Mn.

#### 1.3 Allison Woods Research Station – In General

This project is based on an examination of drill cores and water chemistry data collected at the Allison Woods Research Station (AWRS) in Iredell County, North Carolina (Fig. 5). The AWRS was established in approximately 2005 as part of a cooperative project between the U.S. Geological Survey (USGS) and the North Carolina Department of Environmental Quality (NCDEQ, formerly known as the N.C. Department of Environmental Natural Resources) known as the Piedmont and Mountains Resource Evaluation Program (REP). The REP ended in approximately 2012.



Figure 5 - Locations of AWRS, hydrogeologic units in Iredell County, and geologic belts in central and western NC (from Huffman and Abraham, 2010)

The climate at AWRS is humid, subtropical with average annual precipitation of 44.8 inches and a mean annual temperature of 59.5°F (Climate-Data.org, Undated). The area is rural with land cover dominated by forestland, but may have been the site of intense agricultural activity in the past. The site's topography is gently sloping with elevation ranging approximately 80 feet from hilltop to stream bottom (Huffman and Abraham, 2010).

The area has three soil units mapped with variation as a function of height above the stream channel (NRCS, U.S. Dept. of Agriculture, Undated). Clifford sandy loams and Clifford sandy clay loams lie atop summits and midslopes, respectively. Fairview sandy clay loams lie on midslopes, and Tomlin sandy clay loams cover valley bottoms. The Clifford and Fairview series are defined as fine, kaolinitic, mesic Typic Kanhapludults, common on hills and interfluves in Piedmont uplands, and derived from granitic, gneissic, or schistic saprolite. The Tomlin series is defined as fine, kaolinitic, mesic Rhodic Kanhapludult soils, common on hill slopes in Piedmont uplands, and derived from dioritic, gabbroic, diabasic, or gneissic saprolite (U.S. Department of Agriculture, Undated).

Four drill cores (CH-1 through CH-4) were collected at AWRS in 2005. The approximate location of the core collection is 35.907922° N and 80.825083° W. Cores were collected to depths ranging from 75 to 200 feet using split spoon sampling in regolith and saprolite and wire-line coring in the transition zone and unweathered bedrock. Drilling locations were chosen along topographic transects that were assumed to be parallel to groundwater flow paths (Fig. 6) (Huffman and Abraham, 2010).



Figure 6 - Transect orientations, core hole and monitoring well locations at AWRS (from Huffman and Abraham, 2010)

In addition to collecting drill cores, shallow, intermediate, and deep monitoring wells were installed adjacent to each core hole to capture water level and water quality data representative of the groundwater profile at each drilling location. Others have summarized the general redox conditions of Inner Piedmont aquifers based on nitrate, Mn, and Fe abundances where DO data was not available (Fig. 7) (Tashnia et al., 2023). It was expected that the AWRS site would be representative of those conditions.



## Inner Piedmont Groundwater DO Conditions

Figure 7 - Overall DO conditions in groundwaters of the Inner Piedmont terrane. In general, the Inner Piedmont is approximately 51% oxic/suboxic and 26% anoxic. It is hypothesized that the AWRS site is representative of these conditions (modified from Tashnia et al., 2023)

#### 1.4 Allison Woods Research Station – Geology

The AWRS lies in the Inner Piedmont terrane which is a composite of the subordinate Tugaloo and Cat Square terranes (Fig. 8 and 9) (Merschat and Hatcher, 2007). Specifically, the AWRS lies at the eastern edge of the Cat Square terrane, just west of the Central Piedmont Suture (N.C. Geological Survey, Undated). The Inner Piedmont and Cat Square terranes are dominated by compressional and transpressional structures, and component rocks are metamorphosed to sillimanite grade (Merschat et al., 2010). The Cat Square terrane is composed of Siluro-Devonian metapsammite and pelitic schists which have been hypothesized to have been metamorphosed from sedimentary and volcanic rocks (i.e. greywacke and turbidites) that made up an ancient ocean basin and volcanic island chain. Metamorphism is thought to have been driven by Devonian intrusion of granitoids and the Neoacadian orogeny that formed the southern Appalachian crystalline core (Merschat and Hatcher, 2007; Merschat et al., 2010, 2023).

At AWRS bedrock is metamorphosed to amphibolite grade, consisting of biotite gneiss and amphibolite with subordinate mica schist (Huffman and Abraham, 2010). This site was chosen for study because of the predominance of biotite and amphibolite gneiss, providing a site to study the hypothesis of a ferrous mineral being the PIM. USGS and NCDEQ selected the AWRS to represent a mafic gneiss hydrogeologic unit (Daniel, III and Dahlen, 2002) typical of the Inner Piedmont litho-tectonic terrane.



Figure 8 - Geologic map of the Inner Piedmont and other structured terranes in the southeastern United States Piedmont (from Huffman and Abraham, 2010)



Figure 9 - Detailed map of the Inner Piedmont showing subordinate Cat Square terrane and the approximate location of AWRS. Modified from Merschat et al. (2023)

The map-scale bedrock unit at the scale of the Charlotte 1° x 2° quadrangle (CZbga) is described as interlayered biotite gneiss, hornblende gneiss, amphibolite, metagabbro, and subordinate mica schist which can locally contain granitoid rock and form migmatites. An adjacent bedrock unit (CZbg) near AWRS is described as gray to dark-gray, thin- to thick-layered biotite-quartz-feldspar gneiss, in part garnetiferous, locally inequigranular and porphyroblastic, and interlayered with calc-silicate rock, sillimanite-mica schist, mica schist, and amphibolite (Fig. 10) (Goldsmith et al., 1988b). Mapped units, and other unmapped units, can occur at sub-map scale within the Piedmont (Goldsmith et al., 1988a), and are evidenced by lithologic changes along cores.



Figure 10 - Mapped bedrock units in the vicinity of AWRS (modified from Goldsmith et al. 1988b)

In this area, bedrock strikes generally east to west and dips approximately 20° to the north. The biotite gneiss is fine- to medium-grained and consists of quartz, plagioclase, biotite, hornblende, and lesser amounts of garnet, epidote, and FeO<sub>x</sub>. The amphibolite schist is fine- to

medium-grained and contains variable amounts of hornblende and biotite (Huffman and Abraham, 2010). Based on descriptions in the AWRS core reports, biotite gneiss and amphibolite gneiss are estimated to account for 49% and 35% of bedrock, respectively, with the remaining 16% being composed of varying amounts of granite, kyanite schist, augen gneiss, and leucocratic gneiss (Huffman and Abraham, 2010).

Depth to competent bedrock is approximately 70 feet in the upper slope cores (CH-1 & CH-2), and approximately 30-40 feet in the lower cores (CH-3 & CH-4), which indicate regolith and transition zone thickness are greater in upslope positions (Huffman and Abraham, 2010), consistent with region-wide assumptions (Daniel, III and Dahlen, 2002). AWRS regolith is composed of soil, sediment, and weathered bedrock that contains reddish-brown clayey silt with minor amounts of sand and mica, and becomes sandy silt with depth. The saprolite contains mostly brown, yellowish-brown to olive-brown micaceous silt with low-angle foliations, and grades into partially weathered rock. The transition zone is generally composed of schists, with deeper bedrock represented by biotite gneiss and amphibolite gneiss.

In the transition zone, kyanite-biotite schist contains many low-angle fractures, and is distinguished from unweathered bedrock by the number of fractures. Bedrock fractures are generally horizontal with few vertical fractures, and show water movement as evidenced by the presence of Fe- and Mn-oxide (MnO<sub>x</sub>) staining that decreases with depth. Water-bearing fractures in the biotite gneiss generally dip less than 30°, but can be as much as 60° (Huffman and Abraham, 2010). These fractures, in addition to existing foliation, represent the primary routes by which ferrous minerals are accessed by DO and water at depth in otherwise impermeable rock. Water-bearing fractures are denoted in the core reports where mineral dissolution and

precipitation occurred, and by the presence of FeO<sub>x</sub> with dip angle of fractures having been recorded (Huffman and Abraham, 2010).

Because of generally low mineral solubilities, mineral assemblages can be used to reveal how much water has flowed across a reaction front. Large quantities of water are usually required to dissolve small amounts of a mineral, meaning that small differences in minerals can amplify differences in cumulative water flow (Brantley et al., 2017). An examination of drill cores with the intent of identifying the depth at which ferrous mineral weathering is initiated, and the depth at which they are completely replaced by FeO<sub>x</sub>, should be indicative of the depth range over which ferrous mineral weathering occurs in crystalline Piedmont rocks (Bazilevskaya et al., 2015; Brantley et al., 2017). However, there is not a good understanding of what this continuum looks like in the lithologically heterogeneous crystalline rocks of the Piedmont. Most other studies have focused on homogenous bedrock types (i.e. granite and diabase) (Bazilevskaya et al., 2013, 2015). Is the change in lithologically complex profiles abrupt or gradual, or is there significant variability with changes in depth? Do depth profiles differ among different topographic positions?

The AWRS site is appropriate for this study for several reasons. The AWRS lies in the Piedmont of the eastern United States which, as a result of long periods of geologic stability, exposure, and low erosion rates, has been argued to be in a geomorphological steady state (Pavich et al., 1989). Others have more recently disputed the geomorphological steady state (St. Clair et al., 2015), but the area is generally accepted to exhibit low tectonic activity that would otherwise lead to constant exposure of fresher, less weathered earth materials with corresponding effects on weathering rates and weathering front depths. The site is typical of the Piedmont in general, and specifically of the Inner Piedmont terrane, a region of metamorphosed granitoid and gneissic rocks with significant amounts of ferrous and other indicator minerals (Goldsmith et al., 1988a).

The AWRS drill cores were located and drilled to capture groundwater evolution as it moves downgradient (Fig. 6), which provides a useful proxy for chemical changes across the hillslope transect. Because the REP was focused on groundwater quality, periodic water chemistry sampling data, including physicochemical and solute concentration measurements, are available for the period from November 2006 to March 2009 (N.C. Department of Environmental Quality, Undated).

The objectives of this study were to determine whether, and which, ferrous mineral is a PIM at AWRS based on detailed analysis of saprolite and bedrock cores; and to relate ferrous mineral weathering depths to groundwater chemistry and/or landscape position in a lithologically complex setting in the Inner Piedmont terrane. Meeting these objectives could lead to better prediction of groundwater conditions that directly affect anthropogenic and naturally occurring contaminant mobility in a region where groundwater is commonly used as a source of drinking water (Lindsey et al., 2014).

#### 1.5 Hypotheses

This research project was based on the following hypotheses:

 Hillslope position plays a role in the height of the water table above the reactive unweathered rock. At lower hillslope positions, the water table is believed to lie higher in less reactive, weathered rock and soil meaning anoxic weathering processes likely dominate at the unweathered rock interface. At higher hillslope positions, the water table is believed to lie at or near the depth of unweathered rock where oxic weathering processes are more likely to occur, and possibly dominate.

- Biotite, or some other ferrous mineral such as hornblende, is the first mineral to initiate weathering, and ferrous minerals and FeO<sub>x</sub> are reliable indicators of the weathering front. The weathering front can be distinguished with respect to the water table by visual examination and X-ray fluorescence analysis.
- Ferrous mineral weathering depth ranges influence DO levels, exerting control on oxic versus anoxic conditions, with related effects on redox-sensitive elements' solubility. Below the depth of weathering initiation, it is believed that conditions are anoxic while above the Biotite and/or Hornblende Disappearance Depths (BDD and HDD, the depth at which biotite and hornblende are completely replaced by FeO<sub>x</sub>), oxic conditions are dominant with a transition zone that corresponds to the ferrous mineral weathering depth range. It is believed that these oxic, anoxic, and transition zones correspond to redox-sensitive element (e.g. Fe, Mn, As, etc.) concentration thresholds in solution.

#### 2 METHODOLOGY

#### 2.1 Study Site

This study utilized drill cores collected from AWRS. As a component of the REP, several groundwater well clusters were constructed along a hillslope transect in a manner similar to other REP sites (Chapman et al., 2005; Huffman and Abraham, 2010). Each well cluster consisted of one corehole adjacent to three monitoring wells drilled to shallow, intermediate, and deep depths. The REP constructed 4 well clusters in total at AWRS to capture water quality and water level data along presumed groundwater flow paths from recharge to discharge areas (Fig. 6) which provides a useful proxy for chemical changes across the hillslope transect. Of the four clusters constructed, this study focused on the drill cores collected from the mid-slope and lowest topographic positions, CH-2 and CH-4, respectively.

The REP cores used in this study were collected in April (CH-2) and May (CH-4) of 2005 using split spoon sampling in regolith and saprolite and wire-line coring in the transition zone and unweathered bedrock. Cores were received from NCDEQ in October 2023. After cores were logged by USGS and NCDEQ, they were stored in plastic flip top core boxes on wire racks at a NCDEQ facility with no climate control. Ideally, the analyses described herein would have been completed at the time the drill cores were collected. Without that having been the case, there is some uncertainty as to the true baseline characteristics of these cores prior to being exposed to surface temperature, humidity, and oxygen conditions.

Both cores were examined to a depth of 100 feet below the land surface (FBLS). Approximately 56 and 97 feet, of the top 100 feet, of core were recovered for CH-2 and CH-4, respectively. Poor recovery was most prevalent in soil layers in both cores. In general, CH-2 was more fractured with 178 fractures than CH-4 with 92 fractures. A visible change from soil to weathered rock occurs at approximately 37.5 and 29 FBLS in CH-2 and CH-4, respectively.

The transition zone in CH-2 begins at 55 feet and extends to 70 FBLS with bedrock below that depth. CH-2 is characterized as a biotite garnet schist transitioning to amphibolite gneiss in the transition zone. From the top of bedrock downward, CH-2 alternates between amphibolite gneiss and biotite gneiss with interspersed granitic bands and augen gneiss becoming predominant near 90 FBLS. Water bearing fractures were noted throughout the transition zone and bedrock in CH-2 with evidence of dissolution at 84 FBLS (Huffman and Abraham, 2010).

The transition zone in CH-4 begins at 23 feet and extends to 40 FBLS with bedrock below that depth. CH-4 is characterized as a kyanite biotite schist in the transition zone. From the top of bedrock downward, CH-4 alternates between kyanite biotite garnet gneiss, kyanite-garnet schist, kyanite schist, and kyanite garnet biotite schist to a depth of approximately 62 FBLS. From this depth downward, CH-4 begins to alternate between biotite gneiss and amphibolite gneiss. All sections of CH-4 bedrock were interspersed with coarse grained quartz-feldspar zones. No water bearing fractures were noted below a depth of 74 feet in CH-4 (Huffman and Abraham, 2010).

Adjacent to each coring site, a nest of research groundwater wells was installed. Each well cluster was installed in a manner such that the intermediate well depth would correspond to the transition zone just above the top of competent bedrock. The CH-2 cluster was located in a conceptual recharge area, an area where precipitation and surface water infiltrate and percolate down to the water table. CH-2 itself was drilled to a depth of 200 feet with an open borehole interval from 60 - 200 FBLS. The shallow, intermediate, and deep monitoring wells at CH-2

were drilled to depths of 38, 70, and 400 feet, respectively with screened intervals of 23 - 38, 60 - 70, and 87 - 400 FBLS, respectively. The CH-4 cluster was located in a conceptual discharge area, an area where groundwater is discharged to the surface. CH-4 itself was drilled to a depth of 100 feet with an open borehole interval of 33 -100 FBLS. The shallow, intermediate, and deep monitoring wells at CH-4 were drilled to depths of 23, 40, and 300 feet, respectively, with screened intervals of 8 - 23, 30 - 40, and 45 - 300 FBLS (Table 1).

Table 1 – Core-hole and well construction characteristics, R = regolith, I = transition zone, B = bedrock (modified from Huffman and Abraham, 2010)

Station Name	Construction Date	Land-Surface Altitude (ft. above NAVD 88)	Screened interval or open borehole interval (FBLS)	Screen Type	Monitoring Zone
MW-2S	6/14/2005	870.93	23 - 38	0.01 slotted PVC	R
MW-2I	10/18/2005	871.39	60 - 70	0.01 slotted PVC	Ι
MW-2D	10/4/2005	871.47	87 - 400	Open hole	В
CH-2	4/7/2005	870.58	60 - 200	Open hole	I - B
MW-4S	6/8/2005	836.02	8 - 23	0.01 slotted PVC	R
MW-4I	3/15/2006	837.41	30 - 40	0.01 slotted PVC	Ι
MW-4D	3/9/2006	836.79	45 - 300	Open hole	В
CH-4	5/24/2005	836.26	33 - 100	Open hole	I - B

#### 2.2 Mineralogy

#### 2.2.1 Hand Lens Measurements

To gain an initial, high-level understanding of the mineralogy in each core, and to provide initial identification of the depth and extent of weathering, the REP cores were screened semi-quantitatively in the lab from bottom to top (from unweathered to weathered depths) for the relative presence or absence of biotite, hornblende, pyrite, and FeO<sub>x</sub>. The screening was used to assess the depth range where more detailed examination would be useful to identify weathering features. A Belomo Triplet 10x hand lens with a field of view approximately 0.79 inches wide was used.

In this work, the abundance of dark or metallic luster minerals (vs. light minerals) was estimated, and the dark or metallic minerals were subsequently identified. Where possible, visual measurements with the hand lens were made at no greater than three-foot intervals along the core. Existing broken spots and fracture surfaces were used for a non-destructive approach, to examine mineral faces and relief, and to avoid uncertainty with respect to inner core composition that would have otherwise been the case if the core exterior was measured. Where possible, the entire core cross-section was examined using this method (core cross-sectional area =  $4.6 \text{ in}^2$ ). In some cases, areas less than the entire cross-section were examined due to breakage and core friability. Where this was the case, the measurement recorded was based on the largest surface available for the corresponding depth. Exceptions to the general interval length were due to either poor recovery resulting in missing core sections, or core lengths greater than three feet with no fracture surface. Such was the case in CH-2 from 60.0 - 64.2 FBLS and in CH-4 from 70.0 - 66.4 FBLS. Because of poor recovery, fine particle size, and core friability, hand lens measurements were not possible from the land surface to depths of 46.3 feet in CH-2 and 28.0 feet in CH-4. Semiquantitative scores of the indicator minerals were recorded for each depth examined according to the index below:

Indicator Mineral Index		
1 - Not present		
2 - Less than 10%		
3 - 10% - 25%		
4 - 25% - 50%		
5 - More than 50%		

Index scores were based on the discernable minerals at the surface. Scores do not add up to 100% because other minerals such as quartz and feldspar were not included in the analysis. (See Appendix A)
## 2.2.2 Binocular Microscope Examination of Core Mineralogy

Detailed semiquantitative examinations of existing fracture surfaces that exposed the entire circumference of each core were made with a Meiji Techno EMZ-8TR binocular microscope with a variable field of view (0.84 - 0.16 inches wide) (Fig. 11).



Figure 11 - Meiji Techno EMZ-8TR with typical core sample

As described above, emphasis was placed on fracture surfaces that give a more complete picture of the core's internal structure and composition. Percentage composition of the same minerals of interest as measured with the hand lens were estimated by comparison to figure 12 (Eppes and Johnson, 2022).



Figure 12 - Percentage estimator used during hand lens and binocular microscope analyses (from Eppes and Johnson, 2022).

In a manner similar to the hand lens measurements, there were gaps in microscope measurements either due to poor recovery or core friability. In CH-2 such gaps exist from 0.0 - 5.8, 9.6 - 10.0, 14.3 - 35.0, and 42.0 - 42.5 FBLS. The gap in CH-4 due to poor recovery and friability exists from 0 - 28.5 FBLS, and includes core sections too long to fit under the microscope. Those lengths exist from 61.5 - 64.2, 66.4 - 72.1, 80.7 - 83.5, 86.7 - 93.2, and 98.3 - 100 FBLS. Estimated mineral percentages do not add to 100% because no attempt was made to estimate major minerals such as quartz and plagioclase.

Estimated mineral percentages were plotted as a function of depth to characterize mineralogical composition. In addition to estimated mineral percentages, ratios were computed for FeO<sub>x</sub> : biotite, FeO<sub>x</sub> : hornblende, and FeO<sub>x</sub> : (biotite + hornblende). X-ray fluorescence only provides information on total Fe concentrations, and does not discern between Fe<sup>2+</sup> and ferric iron (Fe<sup>3+</sup>). However, these FeO<sub>x</sub> ratios do provide information about the Fe speciation present at a given depth with Fe<sup>2+</sup> contained in unweathered biotite and hornblende and Fe<sup>3+</sup> contained in their weathering products, FeO<sub>x</sub>. At depths where biotite and or hornblende abundances were found to be zero, the denominator in the ratio was set at 0.5%, which was considered to be half of the visual detection limit, to avoid calculating undefined values or setting ratio values at the corresponding depth to some notional value (i.e. zero). (See Appendix B for tabular mineralogy results)

Pearson correlation coefficients (r) were calculated for each mineral of interest and depth and the FeO<sub>x</sub> ratios discussed above and depth, using the CORREL function in Microsoft Excel to show what, if any, relationships might exist. r values were also calculated for biotite, hornblende, and the FeO<sub>x</sub> ratios discussed above. Where r is +1, a positive relationship exists meaning when one variable increases the other increases at the same rate. When r is -1, a negative relationship exists meaning as one variable increases the other decreases at the same rate. An *r* of zero signifies no correlation. An *r* with magnitude of 0.8 or higher is generally accepted to represent a strong correlation, and 0.5 represents a moderate correlation. Below 0.5, *r* represents a weak or no correlation. However, because of the large sample sizes, we calculated critical values for each core using a two-tailed test at a statistical significance of 0.05. While *r* values may be below 0.5 for a given dataset, if they are greater than the critical value, there is an indication of statistical significance, and an implication that the results observed were not random. With a greater number of data pairs comes lower critical values, and statistical significance at lower *r* values. In total, there were 337 and 119 mineral abundance data pairs in CH-2 and CH-4, respectively. At a statistical significance of 0.05, this results in critical values of  $\pm$  0.1069 and  $\pm$  0.1801 for CH-2 and CH-4, respectively (Dunaetz, 2017).

2.3 Whole-rock Geochemistry by Hand-Held X-Ray Fluorescence Spectrometry

After visual inspection and mineralogical characterizations were completed, the cores underwent whole-rock geochemical analysis for weathering-related elements from bottom to top at no greater than one-foot intervals along the core with an Olympus DELTA Handheld DP-6000 X-ray fluorescence (pXRF) spectrometer. One of the main goals of this study was to geochemically test the core material in a non-destructive manner. The pXRF device provides composition data for a wide range of elements, over very short time periods, without the need to break, crack, crush, or destroy the core material (i.e. as would thin section microscopy or conventional XRF pressed samples). However, the pXRF device used cannot provide information for many light elements, including sodium (Na), magnesium (Mg), or K, in its current configuration. This study focused on the concentrations of Fe, Mn, Ca, Rb, Sr, Si, and Zr. Fe is of interest because of its inclusion in the indicator minerals and their weathering products, FeO<sub>x</sub>. Mn plays an important role in redox chemistry and water quality. Ca is an integral part of both hornblende and early forming plagioclase. K was also of interest because of its inclusion in biotite and orthoclase, but was not detectable with the pXRF device used. Because it is in the same group and one period below K, Rb was considered an acceptable proxy for K. For the same reason Sr was considered an acceptable proxy for Ca, and to use as support of measured Ca values. Si was measured to provide a means of classifying core sections as either felsic, mafic, or intermediate depending on SiO<sub>2</sub> concentrations. Finally, Zr was measured for use as an immobile element in the  $\tau$  calculations discussed below.

### 2.3.1 pXRF Analysis

Scan time using this pXRF device was approximately 4 minutes per scan. During this time, it was critical that the pXRF device and target be in close proximity and not move. It was also critical that the distance and angle the pXRF device and target surface were with respect to each other (the "counting geometry") be as consistent as possible for each scan. To limit movement the scanner was mounted in a vertical, downward facing manner using a large lab stand and clamp. Core sections were placed directly below the scanner with the scanner placed as close as possible to the fracture surface to avoid pXRF device proximity errors (Fig. 13). Target surfaces were cleaned of dust and loose surface material with blasts of air from a lens cleaning bellows before analysis. Where mud from drilling had dried on the fracture surface, the surface was thoroughly rinsed with deionized water and allowed to air dry before analysis.



Figure 13 - pXRF device mounted with core sample

Where core sections were too long to use the lab stand, they were laid on their side on a countertop with the pXRF on its side, adjacent to and touching the fracture surface (Fig. 14).



Figure 14 - pXRF device lying on its side for core sections too long for lab stand

Where core sections had intervals greater than one foot between fracture surfaces the core's exterior was scanned at points no greater than a foot apart between fractures. In all cases, care was taken to place the pXRF device's view pane as close to the target sample as possible, in a consistent counting geometry, and to not have the pXRF device pointed at large individual crystals to avoid giving any element or group of elements greater weight at a depth than truly existed.

Each day before analysis of the core began, the pXRF device was used to scan four certified standards. The standards used were an SiO<sub>2</sub> blank provided by the pXRF manufacturer, a USGS quartz latite sample (QLO-1a), and two Montana soil samples, one with highly elevated trace element levels (NIST-2710a) and one with moderately elevated trace element levels (NIST-2711a). These unadjusted elemental concentrations were then compared to accepted values shown on Certificates of Analysis that accompanied each standard. No Certificate of Analysis was available for the SiO<sub>2</sub> blank, but there were never any values returned by the pXRF device for any element of interest, other than Si, above the machine's manufacturer's Limit of Detection (LOD), with two exceptions. On the first and final days of analysis the XRF device returned values of 406 and 2,332 ppm for Fe when scanning the SiO<sub>2</sub> blank, respectively. This is most likely attributable to  $FeO_x$  dust on the surface of the SiO<sub>2</sub> standard. It is not believed to have had a material effect on results. The unadjusted and accepted values were then analyzed via linear regression. Unadjusted concentrations were then calibrated using the equation of the best fit line for each element's standard runs of that day, and recorded with respect to the corresponding depth below land surface. (See Appendix C for tabular results)

### 2.3.2 Limits of Detection

To verify and ensure pXRF data quality, a LOD was calculated for each element of this study's focus. Each LOD was calculated using the calibration curve method adopted by the International Council for Harmonization (ICH) and the International Union of Pure and Applied Chemistry (IUPAC) (Kadachi and Al-Eshaikh, 2012; Swartz and Krull, 2012; Gazulla et al., 2021). According to that method:

$$LOD = 3.3 \left(\frac{\sigma}{S}\right)$$

In which  $\sigma$  is the standard deviation of the response (the unadjusted concentrations for each element from each standard in this case), and *S* is the slope of the calibration curve, calculated by linear regression, as discussed above. Because no Certificate of Analysis was available for the SiO<sub>2</sub> blank, it was only used as a "zero standard" for the major elements (Fe, Mn, Ca, and Si), because we could be reasonably assured that it contained negligible levels of major elements. The SiO<sub>2</sub> blank was not included in LOD calculations for the trace elements (Rb, Sr, and Zr) because we could not be assured of negligible levels of trace elements. The LODs for each element are shown in table 2. Columns A and B of the table show the total number and percentage of all measured values below the LOD. Columns C and D show the number and percentage of measured values below the LOD when excluding measured zero values.

Limits of Detection									
		А	В	С	D				
Element	LOD (ppm)	<u># &lt; LOD</u>	<u>% &lt; LOD</u>	$\underline{\# < \text{LOD} > 0}$	$\underline{\% < \text{LOD} > 0}$				
Iron	6,605	25	4%	25	4%				
Managanese	642	445	72%	108	18%				
Calcium	8,178	225	37%	172	28%				
Rubidium	16	52	8%	41	7%				
Strontium	74	154	25%	150	24%				
Silicon	74,764	0	0%	0	0%				
Zirconium	8	1	0%	0	0%				

 Table 2 - Limits of detection calculated for each element of interest, including the number and percentage of measurements below the respective LOD. Columns C and D exclude measured zero values.

While the number and percentage of measurements below the LOD may seem dramatic for Mn, Ca, and Sr, the curves shown in figure 15 indicate that the pXRF analyzer was generally oscillating around mean values for all elements rather than trending systematically upward or downward for any element of interest during the period of the study.



Figure 15 - Unadjusted concentrations as measured by XRF analysis of mid-range standards for each element throughout the course of the project. Si has been excluded here because it was the only element with no measured values below the LOD.

The lack of an upward or downward trend suggests the reliability of these measurements for the purpose of generalizations about mineral weathering fronts. With that in mind, no values were excluded from the final dataset, whether below the LOD or not.

2.4 Determination of Elemental Enrichment and Depletion

In a manner similar to the mineralogy findings, elemental concentrations of the focus elements were plotted as a function of depth. Because of the gneissic nature of these cores there were high levels of heterogeneity and fast transitions between dominantly felsic and mafic sections. % Si was converted to % SiO<sub>2</sub>, and plotted as a function of depth to highlight transitions in the cores from overall felsic to mafic occurrences with SiO<sub>2</sub> concentrations greater than 63% being considered felsic, 52% to 63% considered intermediate, and below 52% considered mafic (Yager and Bove, 2007).

Elemental concentrations generally showed few trends. To highlight elemental mobility, and degree of weathering, a variation of the open-system mass-transport function ( $\tau$ ) was calculated for each element, at each depth measurement, as follows:

$$\tau_{j,w} = \frac{m_{j,flux}}{m_{j,p}} = \left(\frac{\frac{c_{j,w}}{c_{i,w}}}{\frac{c_{j,p}}{c_{i,p}}}\right) - 1$$

In this case  $\tau_{j,w}$  is the ratio of  $m_{j,flux}$  to the mass of element j, in the core material. Here,  $c_{j,w}$  represents the concentration of the mobile element in weathered material,  $c_{i,w}$  represents the concentration of the immobile element in weathered material,  $c_{j,p}$  represents the concentration of the mobile element in unweathered material, and  $c_{i,p}$  represents the concentration of the immobile element in unweathered material. Where  $\tau_{j,w}$  is +1 for a given element it represents 100% enrichment meaning 50% of the element in the weathered material is sourced from the protolith and 50% externally, but values greater than 1 are possible. If  $\tau_{j,w}$  is -1, complete

depletion has occurred with 100% removal of the element from the protolith as a result of weathering (Oh and Richter, 2005; Fisher et al., 2017).

Selection of the protolith is an important factor when using this method as it has a direct effect on elemental starting points. For the purpose of this study, the unweathered protolith was deemed to start where the original USGS core report (Huffman and Abraham, 2010) stopped mentioning weathered rock, and extended to the deepest depth studied. In CH-2 this depth was from 69.5 - 100 FBLS, and in CH-4 unweathered rock was from 64.7 - 100 FBLS. Over these depth ranges, elemental concentrations were averaged to arrive at a nominal unweathered value. This was done both for convenience, and as a means of integrating the otherwise high levels of heterogeneity intrinsic to these gneissic rocks.

Selection of what element to consider as immobile is also an important consideration (Oh and Richter, 2005). Originally, the intent was to measure both Zr and titanium (Ti) for use as immobile elements, and to compare  $\tau$  results. However, the pXRF device used never showed reliable results measuring Ti concentrations, and the original plan was abandoned in favor of solely examining  $\tau$  values calculated with Zr as the immobile element. The low Zr LOD calculated (7.68 ppm) and single measurement below that LOD (shown above) would seem to indicate that Zr measurements were reliable and appropriate for use in this study.

au values were plotted as a function of depth to highlight trends in enrichment or depletion. To show what, if any, relationships might exist between the two variables, *r* values were also calculated for au and depth using the same CORREL function in Microsoft Excel as discussed above. *r* values were also calculated for au-to-au values for each element of interest in each core (e.g.  $au_{\text{Fe}}$  in CH-2 to  $au_{\text{Mn}}$  in CH-2, etc.) to identify any correlated relationships between elements. In the case of both au-to-depth and au-to-au correlations, critical values were calculated in the same manner, and at the same level of statistical significance, used for the mineral and depth correlations discussed above. There were 365 and 250  $\tau$  data pairs which result in critical values of ± 0.1027 and ± 0.1241 for CH-2 and CH-4, respectively (Dunaetz, 2017).

## 2.5 Groundwater Data

Water levels and water quality data were not field collected for this study, but were rather obtained from external sources. Parameters including DO, pH, specific conductance, temperature, and ionic concentrations (Ca, Na, HCO<sub>3</sub>, etc.) were collected intermittently using multiparameter water-quality probes from the period November 28, 2006 to March 17, 2009 by USGS and NCDEQ. Groundwater levels were measured continuously with a submersible pressure transducer with an internal data logger (Huffman and Abraham, 2010). Water quality data was downloaded from an online NCDEQ storage site (N.C. Department of Environmental Quality, Undated), and water level data was downloaded from USGS' National Water Information System database (U.S. Geological Survey, Undated).

# 3 RESULTS

## 3.1 Mineralogy

Both cores showed a pattern of decreasing amounts of weathering as depth increased (Fig. 16). Fresh, unweathered rock was dominant at greater depths with degree of weathering and the presence of secondary minerals such as FeO<sub>x</sub> and MnO<sub>x</sub> increasing at shallower depths. However, both cores had zones of significant weathering and secondary mineral presence layered within the otherwise unweathered rock. These zones generally coincided with water-bearing fractures that allowed for higher DO levels and greater water-rock contact (Table 3). In both cores, there was a very high level of lithologic variation with banded gneiss being the predominant rock type, but both cores displayed a felsic weathering pattern like that described by Brantley et al. (2017) rather than a mafic weathering pattern.



Figure 16 - The upper 40 feet of CH-2 and a representative section of unweathered rock typical of the deepest sections of CH-2

CH-2 Lithology				CH-4 Lithology			
Depth		H <sub>2</sub> O Bearing	Depth		H <sub>2</sub> O Bearing		
(FBLS)	Rock Name	Fractures (FBLS)	(FBLS)	Rock Name	Fractures (FBLS)		
5			5				
10			10				
15			15	Regolith (residuum)			
20			20				
25			23				
30	Regolith (residuum)		28	Transition Zana			
35			30	If ansmon Zone			
40			35	Kyanite Biotite Schist	32.5 & 33.5 - 35		
45			40	Kyanite Schist	35 - 37		
50			43	Kyanite Biotite Garnet Gneiss	42.5 & 43		
55			45	Quartz Faldsnar Zana			
60	Sanralitia Riatita Carnat Sahist	56 - 60	47	Quartz-reidspar Zone			
65	Sapronuc Bionce Garnet Schist	60.5	48	Kyanite-Garnet-Schist	48		
68.5	Schist	65 - 69	49	Quartz-Feldspar Zone			
71	Amphibolite Gneiss	70.5	50	Kyanite Schist			
74	Biotite Garnet Gneiss	73 - 74	55	Kyanite Biotite Garnet Gneiss			
77.5	Amphibolite Gneiss	75.5 <b>&amp;</b> 77.5	58	Kyanite Garnet Biotite Schist			
78	Migmatitic Zone		60	Quartz-Feldspar Zone			
80	Biotite Gneiss	80	62	Quarte i chuspai Zone			
	Alternating Biotite and			Alternating Biotite and			
83	Amphibolite Gneiss		65	Amphibolite Gneiss	64.5		
84	Migmatitic Zone	82 - 85	67	Biotite Gneiss	66		
	Alternating Biotite and						
85	Amphibolite Gneiss		70	Leucocratic Gneiss			
85.5	Migmatitic Zone	85.5	73		72.5 - 74		
87	Biotite and Amphibolite Gneiss	87-88	75	Alternating Biotite and			
90	-	89.2	80	Amphibolite Gneiss			
95	Augen Gneiss	90, 90.8, 92.5, 94.7,	85	85 90 Amphibolite Gneiss			
100		95.8 - 97, & 98.2	90				
			<b>9</b> 5	Alternating Biotite and			
			100	Amphibolite Gneiss			

Table 3 - Summary of lithologies at each core location (modified from Huffman and Abraham (2010))

Beginning at 100 FBLS, CH-2 was predominantly amphibolite gneiss with interspersed zones of augen gneiss and biotite gneiss (Table 3). At approximately 66 FBLS, the deepest occurrence of highly weathered rock was noted in CH-2 (Huffman and Abraham, 2010) with weathered biotite schist and biotite gneiss dominating above this depth. Accordingly, most intact hornblende was observed below 66 FBLS in CH-2 with biotite and FeO<sub>x</sub> being the predominant

mafic minerals at shallower depths (Fig. 17). CH-2 had a fracture density of 1.9 cracks per foot and 352 fracture surfaces that were used for mineral and XRF analysis.



Figure 17 - CH-2 typical mineralogy visible by binocular microscope, clockwise from top left: A) unweathered hornblende and quartz (69.3 FBLS), B) weathered hornblende and garnet (circled) (68.5 FBLS), C) MnO<sub>x</sub> (black staining at arrows) on highly weathered biotite (38.2 FBLS), and D) well developed FeO<sub>x</sub> on highly weathered biotite (64.0 FBLS), field of view in all pictures is approximately 0.75 inches

Beginning at 100 FBLS, CH-4 alternated between biotite gneiss and amphibolite gneiss until a zone of leucocratic gneiss was found from 70 – 73 FBLS (Table 3). Above this biotite gneiss alternated with kyanite schist and kyanite gneiss with interspersed quartzofeldspathic zones. Hornblende was generally only present in CH-4 below 75 FBLS. Above this depth, biotite and FeO<sub>x</sub> were the dominant mafic minerals (Fig. 18). CH-4 had a fracture density of 1.3 cracks per foot and 184 fracture surfaces used for mineral and pXRF analysis.



Figure 18 - CH-4 typical mineralogy visible by binocular microscope, clockwise from top left: A) unweathered biotite (95.1 FBLS), B) weathered biotite with FeO<sub>x</sub> (73.3 FBLS), C) well-developed FeO<sub>x</sub> and MnO<sub>x</sub> (black staining at arrows) on highly weathered biotite (31.6 FBLS), and D) unweathered kyanite (circled) and quartz (54.8 FBLS), field of view in all pictures is approximately 0.75 inches

In general, CH-2 was more mafic than CH-4. 80.6% of the pXRF scans in CH-2 indicate a mafic composition whereas 68.0% of scans in CH-4 were mafic. Both cores were found to be mafic throughout the soil layers, down to approximately 35 FBLS in CH-2 and 30 FBLS in CH-4. This is most likely due to Fe coatings on soil particles that had oxidized after being brought to the surface.

While both cores alternate between mafic and felsic compositions, CH-2 shows distinctly felsic zones from 45.9 - 54.17, 65.0 - 70.0, and 76.3 - 88.4 FBLS. CH-4 shows a large felsic zone extending from 37.1 - 62.9 FBLS. High levels of heterogeneity were expected when this project was conceived, but figure 19 puts heterogeneity in each core on display.



Figure 19 - Felsic & Mafic portions of each core with mafic zones falling in the gray shaded region and felsic zones in the unshaded region. Here, 63% & 52 % SiO<sub>2</sub> are taken as the felsic and mafic boundaries, respectively (Yager and Bove, 2007).

While both CH-2 and CH-4 biotite abundances varied from 0 - 90%, biotite showed differing patterns between the cores (Fig. 20). In CH-2, biotite generally increased with depth reaching a maximum abundance of 90% at 78.0 – 79.6 FBLS, and showing large alternations below that depth. In CH-4, biotite showed large alternation throughout the core profile, with its maximum abundance of 90% occurring at 36.1 FBLS. Biotite was positively correlated with depth in CH-2 (r = 0.58), but not in CH-4 (r = -0.01) (Table 4). An initial goal of the project was to attempt to identify a BDD to serve as an indicator of the biotite weathering front. However, no specific depth of continuous biotite disappearance was noted. Instead, there was a zone of discontinuous biotite occurrence in which biotite was weathered close to water-bearing fractures and unweathered away from the fractures. Above the discontinuous zone, biotite was absent or highly weathered, and below the zone biotite was generally unweathered.

In both cores, hornblende abundances varied from 0 - 75%, generally increasing with depth (Fig. 20). Hornblende was weakly correlated with depth in CH-2. There was a positive correlation between hornblende and depth in CH-4 (r = 0.36) greater than the critical value ( $\pm$  0.1801) (Table 4). We suspect the low hornblende correlation coefficients are the result of the limited number of hornblende occurrences observed, the distribution of hornblende throughout each core, and the banded nature of the bedrock which means that depth was not the only factor controlling the occurrence of hornblende. In CH-2, large spikes of hornblende were noted at 57.0, 69.0, 82.8, and 85.0 FBLS. In general, CH-2 displayed more, and wider, bands of hornblende occurrences at 59.5, 64.7, 72.5, 95.1 FBLS. The HDDs were 56.8 and 57.4 FBLS in CH-2 and CH-4, respectively. No hornblende was observed at depths shallower than the HDD in either core.



Figure 20 - Abundances of primary minerals (biotite & hornblende) throughout each core profile as measured by binocular microscope.

FeO<sub>x</sub> showed a moderate negative correlation with depth in both cores with a CH-2 *r* value of -0.51 (Table 4). In CH-2, FeO<sub>x</sub> showed a maximum abundance of 80% at 37.5 FBLS (Fig. 21). This depth is less than 2 feet above the average depth to the water table in CH-2 (39.3 FBLS), and falls within the range of fluctuation for depth to the water table in CH-2 as discussed below. Secondary FeO<sub>x</sub> spikes in CH-2 of 60% and 75% were noted at 59.2 and 66.5 FBLS, respectively. FeO<sub>x</sub> abundances reached zero at 59.5 and 69.5 FBLS, and were never greater than 30% at depths below 69.5 FBLS. Tertiary FeO<sub>x</sub> abundance spikes of 20% were noted at 75.6, 77.7, and 82.8 FBLS while spikes to 30% were noted at 85.8 and 87.3 FBLS. Compared to the original core report (Huffman and Abraham, 2010), all depths where secondary and tertiary FeO<sub>x</sub> spikes were found in CH-2 correspond with water-bearing fractures observed during drilling.

FeO<sub>x</sub> in CH-4 showed a higher degree of variability, but overall, the same negative correlation with depth as that observed in CH-2 with r = -0.48 (Table 4). FeO<sub>x</sub> abundance in CH-4 peaked at 80% at 28.7 FBLS, but dropped to zero at 30.5 FBLS (Fig. 21). A comparison of FeO<sub>x</sub> abundances and depth to the water table was not possible for CH-4 because the water table never fell below 9.0 FBLS, which is approximately 19.5 feet above the shallowest measurement in CH-4, due to core friability and thick coatings of drilling mud. FeO<sub>x</sub> spiked to 50% and 60% again at 33.2 and 36.4 FBLS, respectively. Again, these depths correspond to water-bearing fractures noted in the original core report (Huffman and Abraham, 2010). After falling to 1% at 45.5 FBLS FeO<sub>x</sub> abundances were never greater than 25% below that depth. FeO<sub>x</sub> spikes to 25% were observed at 50.0, 51.5, and 73.3 FBLS. Spikes to 20% were noted at 64.2 and 94.8 FBLS. All secondary and tertiary FeO<sub>x</sub> abundance spikes in CH-4 were found to coincide with water-bearing fractures pointed out in the original core report (Huffman and Abraham, 2010) with the exception of the 50.0 and 51.5 FBLS spikes that probably correspond to a water bearing

fracture noted at 48.0 FBLS with the discrepancy being due to differing length measurement methods.

Correlation coefficients were calculated to identify any relationships between FeO<sub>x</sub> and primary mineral abundances (biotite, hornblende, and biotite + hornblende). While there were no correlations between FeO<sub>x</sub> and any of the primary minerals in either core greater in magnitude than 0.49, all correlations were negative (as expected) and greater than the critical values calculated for each core. In CH-2, FeO<sub>x</sub> was moderately negatively correlated with biotite + hornblende (r = -0.49).

Table 4 - Depth and mineral correlations calculated based on binocular microscope mineral examinations. All correlations calculated exceed the critical value (CH-2 =  $\pm$  0.1069, CH-4 =  $\pm$  0.1801) with the exception of depth correlations for hornblende in CH-2 and biotite in CH-4. Correlations above the critical value indicate statistically significant relationships.

<u>CH-2</u> Depth Correlations (n = 337,	, p < 0.05)	CH-2 Mineral Correlations (n = 337, p < 0.05)		
Biotite	0.58	FeOx : Biotite	-0.40	
Hornblende	0.10	FeOx : Hornblende	-0.19	
FeOx	-0.51	FeOx : (Biotite + Hornblende)	-0.49	
FeOx / Biotite	-0.29			
FeOx / Hornblende	-0.52			
FeOx / (Biotite + Hornblende)	-0.29			
<u>CH-4 Depth Correlations (n = 119</u> ,	, p < 0.05)	<u>CH-4 Mineral Correlations (n = 119, p &lt; 0.05)</u>		
Biotite	-0.01	FeOx : Biotite	-0.23	
Hornblende	0.36	FeOx : Hornblende	-0.18	
FeOx	-0.48	FeOx : (Biotite + Hornblende)	-0.30	
FeOx / Biotite	-0.27			
FeOx / Hornblende	0.40			
	-0.42			



Figure 21 - Secondary mineral (FeOx) abundances throughout each core profile as measured by binocular microscope.

Ratios were also calculated to highlight FeO<sub>x</sub> and Fe-bearing mineral relationships based on the abundances discussed above and according to the following ratios:

 $Biotite - oxide \ ratio = \frac{FeO_x \ Abundance}{Biotite \ Abundance} \qquad Hornblende - oxide \ ratio = \frac{FeO_x \ Abundance}{Hornblende \ Abundance}$  $Total \ ratio = \frac{FeO_x \ Abundance}{(Biotite \ Abundance + Hornblende \ Abundance)}$ 

In CH-2, the biotite-oxide ratio shows a distinctive maximum of 80 at 37.5 FBLS, and a secondary peak to 70 at 35.0 FBLS (Fig. 22). Below 69.1 FBLS, the biotite-oxide ratio quickly settles to near zero and never again rises above 1.5 in CH-2 with one exception (6 at 84.0 FBLS). In CH-4, the biotite-oxide ratio's maximum of 23.3 occurs at 29.2 FBLS, with secondary peaks of 16.7, 10, and 5.0 at 28.7, 37.1, and 43.3 FBLS, respectively. Below 45.4 FBLS, the biotiteoxide ratio never rises above 1.25 in CH-4. In both cores, the total ratio generally corresponds to the biotite-oxide ratio, which is most likely due to the greater amounts of biotite observations than hornblende in these cores. The biotite and total ratios were weakly negatively correlated with depth in each core, but r values were greater than the critical values for each core (Table 4).

In CH-2, the hornblende-oxide ratio has a distinctive maximum of 160 at 37.5 FBLS (Fig. 22). There were numerous spikes in the hornblende-oxide ratio throughout CH-2. However, beginning at 68.6 FBLS and below, there were more zero or near zero values and local maximums were lower than at shallow depths. In CH-4, the hornblende-oxide ratio showed a maximum of 160 at 28.7 FBLS. Below 66.4 FBLS in CH-4 the hornblende-oxide ratio begins to show more zero or near zero values with subdued local maximums when compared to shallower depths. The hornblende-oxide ratio was moderately negatively correlated with depth in both cores (Table 4).



Figure 22 - FeO<sub>x</sub> ratios for biotite and hornblende. While not shown here, the ratio of FeO<sub>x</sub> to total Fe-bearing minerals generally corresponds to the biotite-oxide ratio curve in both cores.

#### 3.2 Whole-rock Geochemistry

#### 3.2.1 Elemental Abundance

No Ca values above the LOD (8,178 Ca ppm) were measured shallower than 42.5 FBLS in CH-2. Beginning at that depth, CH-2 Ca concentrations showed a high degree of variability, but with a generally upward trend. There is a distinctive peak of 186,003 Ca ppm at 87.3 FBLS with what appears to be a general downward trend after that (Fig. 23).

Sr values in CH-2 showed a similar pattern at shallow depths with the first measurement above the LOD (74 Sr ppm) of 80.2 Sr ppm at 6.0 FBLS. Otherwise, Sr concentrations stayed below the LOD until 37.0 FBLS where they spike to 887.7 Sr ppm. From 40.0 - 47.4 FBLS Sr concentrations stayed elevated and ranged from 93 - 1,155 Sr ppm before beginning a downward trend. In a manner similar to the Ca concentrations observed there was a distinctive spike to 3,623 Sr ppm at 87.1 FBLS with the downward trend continuing thereafter (Fig. 23).



Figure 23 - Ca (L) and Sr (R) concentrations in CH-2 as a function of depth.

Fe concentrations showed few if any trends in CH-2. With one exception, they generally oscillated from 3,524 to 125,393 Fe ppm throughout the core profile. There was a distinctive spike to 210,495 Fe ppm at 56.9 FBLS (Fig. 24).

Mn concentrations in CH-2 ranged from 0 to 4,322 ppm throughout the core profile, with two exceptions. Strong spikes were to 16,674 and 13,176 ppm at 9.6 and 37.3 FBLS, respectively. After the spike at 37.3 FBLS, maximum Mn concentrations show a downward trend with increasing depth. The Mn spike observed at 9.6 FBLS is difficult to explain, but the spike noted at 37.3 FBLS coincided with the upper limit of the depth to the water table range observed in CH-2 (Fig. 24).



Figure 24 - Fe (L) and Mn (R) concentrations in CH-2 as a function of depth.

Rb concentrations in CH-2 ranged from 0 - 642 Rb ppm throughout the core without any discernable pattern. There were abrupt spikes to 367 and 643 Rb ppm at 65.5 and 66.0 FBLS. Strong secondary peaks to 340, 310, and 342 Rb ppm were noted at 43.9, 84.8, and 85.6 FBLS, respectively. No other Rb concentration measured in CH-2 was greater than 289 Rb ppm (Fig. 25).

Zr concentrations in CH-2 ranged from 9 - 1,590 Zr ppm throughout the core profile. The maximum value was observed at 79.1 FBLS with no concentrations greater than 687 Zr ppm occurring anywhere else in CH-2. Zr concentrations showed a general downward trend until reaching the depth of the maximum concentration observed before again showing a downward trend (Fig. 25).



Figure 25 - Rb (L) and Zr (R) concentrations in CH-2 as a function of depth.

No Ca values above the LOD (8,178 Ca ppm) were measured in CH-4 shallower than 21.0 FBLS. Beginning at that depth, CH-4 Ca concentrations varied from 0 to 208,323 Ca ppm, with a generally increasing trend as depth increased. The maximum Ca concentration of 208,323 Ca ppm in CH-4 occurred at 72.1 FBLS, with a strong secondary peak to 150,296 Ca ppm at 68.0 FBLS (Fig. 26).

Sr values in CH-4 showed a similar pattern at shallow depths with the first measurement above the LOD (74 Sr ppm) of 216 Sr ppm occurring at 7.0 FBLS. Beginning at 29.0 FBLS, Sr concentrations began to oscillate, with a general upward trend in maximum values thereafter. Similar to the Ca concentrations observed in CH-4, there were distinctive spikes to 1,717 and 2,319 Sr ppm at 68.0 and 72.1 FBLS (Fig. 26).



Figure 26 - Ca (L) and Sr (R) concentrations in CH-4 as a function of depth.

Fe concentrations showed no trends in CH-4. Fe concentrations ranged from 1,476 – 115,321 Fe ppm throughout the core profile. The maximum observed Fe concentration in CH-4 of 115,321 Fe ppm occurred at 35.7 FBLS. There were distinctive secondary peaks of 109,796, 112,315, and 113,430 Fe ppm at 6.0, 58.0, and 97.1 FBLS, respectively (Fig. 27).

Mn concentrations in CH-4 ranged from 0 - 4,973 Mn ppm throughout the core profile. The maximum Mn concentration of 4,973 Mn ppm in CH-4 was observed at 33.2 FBLS. There were also fast spikes to 4,053, 4,644, 4,213, 3,616, and 2,703 Mn ppm at 21.0, 29.0, 31.6, 58.0 and 95.0 FBLS, respectively. No continuous trends in Mn concentrations were noted in CH-4. While Mn showed a very distinctive peak near the depth to water table in CH-2, such was not the case in CH-4. In CH-4 Mn levels were elevated near the depth to water table, but were much lower than Mn concentrations at lower depths. Also, unlike CH-2, Mn and Fe concentrations show local maximums at or near the same depths (Fig. 27).



Figure 27 - Fe (L) and Mn (R) concentrations in CH-4 as a function of depth.

Rb concentrations in CH-4 ranged from 0 - 384 Rb ppm throughout the core without any discernable pattern. The maximum Rb concentration of 384 Rb ppm observed in CH-4 occurred at 81.8 FBLS. No other Rb concentration measured in CH-4 was greater than 257 Rb ppm (Fig. 28).

Zr concentrations in CH-4 ranged from 8 – 921 Zr ppm throughout the core profile. The maximum value of 921 Zr ppm was observed at 26.0 FBLS. A strong secondary peak of 689 Zr ppm occurred at 5.0 FBLS with no concentrations greater than 526 Zr ppm occurring anywhere else in CH-4. Zr concentrations showed a general downward trend throughout the core below the depth of the observed maximum concentration (Fig. 28).



Figure 28 - Rb (L) and Zr (R) concentrations in CH-4 as a function of depth.
#### 3.2.2 Elemental Enrichment and Depletion

In CH-2,  $\tau_{Ca,w}$  was negative, indicating depletion, from the land surface down to a depth of 45.4 FBLS (Fig. 29).  $\tau_{Ca,w}$  stopped showing any -1 values, indicating complete depletion, at 42.0 FBLS. At depths greater than 45.7 FBLS,  $\tau_{Ca,w}$  showed a high level of variation, oscillating between -0.963 and 31.9, but with a general increasing trend until 75.6 FBLS. From 67.4 to 75.6 there were fast oscillations in  $\tau_{Ca,w}$  from -0.65 to 31.9. This zone coincides with shear zones, as evidenced by stretched quartz and feldspar grains, high garnet abundance (up to 20%), and interspersed amphibolite gneiss observed when the core was logged (Huffman and Abraham, 2010). The maximum  $\tau_{Ca,w}$  value was found at 69.0 FBLS, and  $\tau_{Ca,w}$  was positively correlated with depth in CH-2 (Table 5).  $\tau_{Ca,w}$  in CH-2 showed strong positive correlations with  $\tau_{Sr,w}$ ,  $\tau_{Fe,w}$ , and  $\tau_{Mn,w}$  (Table 6).

In CH-4,  $\tau_{Ca,w}$  was negative from the land surface down to 20.0 FBLS at which point it began to show quick oscillations between negative and positive values (Fig. 29). Beginning at 46.1 FBLS, and deeper, there were no further observations of complete Ca depletion. Maximum Ca enrichment in CH-4 was found at 84.1 FBLS with a  $\tau_{Ca,w}$  value of 10.9 which coincides with a migmatite zone (Huffman and Abraham, 2010). In CH-4,  $\tau_{Ca,w}$  showed the strongest correlation (positive) with depth of all elements (Table 5) and a strong positive correlation with  $\tau_{Fe,w}$  only (Table 6). Interestingly,  $\tau_{Ca,w}$  in CH-4 showed less dramatic variation and substantially less maximum enrichment than  $\tau_{Ca,w}$  in CH-2. This was the general case for all elements for which  $\tau$ values were calculated.



Figure 29 -  $\tau$  values for Ca as a function of depth in each core profile.

In CH-2,  $\tau_{Sr,w}$  was negative from the land surface down to a depth of 36.9 FBLS (Fig. 30). At 85.6 FBLS and below,  $\tau_{Sr,w}$  stopped showing any -1 values. However,  $\tau_{Sr,w}$  began to indicate enrichment at 42.5 FBLS. At depths greater than 37.0 FBLS,  $\tau_{Sr,w}$  showed a high level of variation, oscillating between -1 and 18.7.  $\tau_{Sr,w}$  was positively correlated with depth (Table 5), and the maximum  $\tau_{Sr,w}$  value of 18.7 was found at 58.7 FBLS.  $\tau_{Sr,w}$  in CH-2 showed positive correlations with  $\tau_{Ca,w}$  and  $\tau_{Fe,w}$  (Table 6).

In CH-4,  $\tau_{Sr,w}$  was negative from the land surface down to 30.0 FBLS at which point it began to show sharp oscillations between negative and positive values (Fig. 30). Beginning at 51.5 FBLS, and deeper, there were no further observations of complete Sr depletion.  $\tau_{Sr,w}$  was positively correlated with depth (Table 5), and the maximum Sr enrichment in CH-4 was found at 72.5 FBLS with a  $\tau_{Sr,w}$  value of 9.08. In CH-4,  $\tau_{Sr,w}$  correlations with other  $\tau$  values were weak, but positive correlations with  $\tau_{Ca,w}$  and  $\tau_{Rb,w}$  were greater than the critical value (± 0.1241) (Table 6).



Figure 30 -  $\tau$  values for Sr as a function of depth in each core profile.

Fe was never completely depleted in CH-2. The highest degree of Fe depletion in CH-2 ( $\tau_{Fe,w} = -0.92$ ) was found at 41.4 FBLS (Fig. 31). Between the land surface and 30.0 FBLS  $\tau_{Fe,w}$  oscillated between -0.55 and 1.99. A distinct  $\tau_{Fe,w}$  peak to 8.91 at 35.0 FBLS was notable. From 35.2 – 67.4 FBLS  $\tau_{Fe,w}$  showed a generally increasing trend in maximum enrichment values.  $\tau_{Fe,w}$  was positively correlated with depth (Table 5), and the maximum  $\tau_{Fe,w}$  value of 25.3 was found at 84.9 FBLS.  $\tau_{Fe,w}$  in CH-2 showed a strong positive correlation with  $\tau_{Ca,w}$ , and positive correlations with  $\tau_{Sr,w}$ ,  $\tau_{Rb,w}$ , and  $\tau_{Mn,w}$  (Table 6).

Similarly,  $\tau_{Fe,w}$  was never completely depleted in CH-4 as was the case with CH-2 (Fig. 31). The maximum Fe depletion of  $\tau_{Fe,w} = -0.97$  was found at 70.0 FBLS which coincides with a zone of leucocratic gneiss containing low levels of Fe. Between the land surface and 17.0 FBLS,  $\tau_{Fe,w}$  oscillated between -0.79 and 0.65 followed by fast spikes to 1.76, 5.34, and 6.34 at 18.0, 21.0, and 23.0 FBLS, respectively.  $\tau_{Fe,w}$  was positively correlated with depth (Table 5), and the maximum Fe enrichment in CH-4 was found at 81.8 FBLS with a  $\tau_{Fe,w}$  value of 15.8. In CH-4,  $\tau_{Fe,w}$  showed positive correlations with  $\tau_{Ca,w}$ ,  $\tau_{Rb,w}$ , and  $\tau_{Mn,w}$  (Table 6).



Figure 31 -  $\tau$  values for Fe as a function of depth in each core profile.

In CH-2,  $\tau_{Mn,w}$  was negative from the land surface down to a depth of 5.81 FBLS (Fig.

32).  $\tau_{Mn,w}$  showed high levels of variation throughout CH-2, oscillating between -1 and 144. The maximum  $\tau_{Mn,w}$  value of 144 was found at 67.4 FBLS. There were distinct local  $\tau_{Mn,w}$  maximums of 33.8, 65.9, and 36.8 at 9.6, 37.3, and 85.6 FBLS with the shallowest local maximum lying within one foot of the maximum observed depth to water table (Table 7). Despite this,  $\tau_{Mn,w}$  was not correlated with depth in CH-2 or CH-4 (Table 5). However,  $\tau_{Mn,w}$  in CH-2 did show strong positive correlations with  $\tau_{Ca,w}$  and  $\tau_{Fe,w}$  (Table 6).

In CH-4,  $\tau_{Mn,w}$  began to show enrichment as shallow as 3.0 FBLS. Like CH-2,  $\tau_{Mn,w}$  in CH-4 varied significantly throughout the core, ranging between -1 and 70.6, but localized zones of enrichment were noted at 28.8 – 37.0 and 81.2 – 90.0 FBLS (Fig. 32). Maximum Mn enrichment in CH-4 was found at 21.0 FBLS with a  $\tau_{Mn,w}$  value of 70.6. In CH-4,  $\tau_{Mn,w}$  showed a positive correlation with  $\tau_{Fe,w}$  only (Table 6).



Figure 32 -  $\tau$  values for Mn as a function of depth in each core profile.

In CH-2,  $\tau_{Rb,w}$  was negative from the land surface down to a depth of 5.0 FBLS, and became positive at 5.81 FBLS (Fig. 33).  $\tau_{Rb,w}$  showed a high level of variation, oscillating between -1 and 45.4 throughout the core. The maximum  $\tau_{Rb,w}$  value of 45.4 was found at 66.0 FBLS. There were distinct local  $\tau_{Rb,w}$  maximums of 5.1, 16.1, and 41.2 at 35.0, 45.7, and 84.9 FBLS, and  $\tau_{Rb,w}$  was weakly positively correlated with depth (Table 5).  $\tau_{Rb,w}$  in CH-2 showed a positive correlation with  $\tau_{Fe,w}$  only (Table 6).

In CH-4,  $\tau_{Rb,w}$  was negative from the land surface down to 12.0 FBLS at which point it became positive at 13.0 FBLS (Fig. 33). Throughout CH-4  $\tau_{Rb,w}$  varied between -1 and 42.7 with the maximum Rb enrichment found at 81.8 FBLS with a  $\tau_{Rb,w}$  value of 42.7. In CH-4,  $\tau_{Rb,w}$  was not correlated with depth (Table 5), and  $\tau_{Rb,w}$  was positively correlated with  $\tau_{Fe,w}$  only, similar to CH-2 (Table 6).



Figure 33 -  $\tau$  values for Rb as a function of depth in each core profile.

<u>Correlation Coefficients (τ : depth)</u>							
	<u>C</u>	<u>H-2</u>	CH-4				
Ca	0.24		0.48				
Mn	0.07	n = 365	0.03	n = 250			
Fe	0.24	p < 0.05	0.34	n < 0.05			
Rb	0.14		0.11	p < 0.05			
Sr	0.18		0.28				

Table 5 -  $\tau$ : depth correlations. All correlations exceed critical values (CH-2 = ± 0.1027 and CH-4 = ± 0.1241) except Mn in both cores, and Rb in CH-4.

Table 6 -  $\tau$ :  $\tau$  correlations calculated based on XRF analyses. Values shaded orange indicate moderate to strong correlations. All CH-2 correlations exceed the critical value (CH-2 =  $\pm$  0.1027). All CH-4 correlations exceed the critical value ( $\pm$  0.1241) except Ca : Rb, Mn : Sr, and Fe : Sr.

<u>CH-2 Correlation Coefficients (<math>\tau</math> : <math>\tau</math>)</u>									
	Sr	Rb	Fe	Mn					
Ca	0.65	0.16	0.80	0.61					
Mn	0.34	0.22	0.65						
Fe	0.52	0.55							
Rb	0.27								
CH-4 Correlation Coefficients ( $\tau$ : $\tau$ )									
	Sr	Rb	Fe	Mn					
Ca	0.39	0.06	0.71	0.37					
Mn	-0.05	0.20	0.60						
Fe	0.09	0.56							
Rb	0.13								

# 3.3 Water Levels and Water Chemistry

USGS and NCDEQ continuously monitored groundwater levels at each coring site. The dataset we had access to spans the time periods June 1, 2007 - July 29, 2008 for CH-2 and May 12, 2006 - September 30, 2009 for CH-4. During the CH-2 measurement period, the depth to water ranged from 37.4 - 40.5 FBLS, and averaged 39.3 FBLS (Table 7). During the CH-4 measurement period, the depth to water ranged from 7.2 - 9.0 FBLS, and averaged 8.2 FBLS.

It should be noted that 60% and 54.5% of depth to water measurements in CH-2 and CH-4 were made during the growing season when the water table typically fluctuates the most due to increased evapotranspiration. Both CH-2 and CH-4 are sited in a forested area where it can be reasonably expected that plant transpiration drove such fluctuations during most of the measurement period. This undoubtedly influenced the temperature and amount of oxygen and other dissolved reactants in direct contact with bedrock and regolith, affecting bedrock weathering in general and FeO<sub>x</sub> formation specifically in addition to dissolved constituents. It is beyond the scope of this investigation to quantify what, if any, effect this had on results.

<u>CH-2</u>	
Average Depth Below Land Surface (ft.)	39.29
Maximum Depth Below Land Surface (ft.)	40.51
Minimum Depth Below Land Surface (ft.)	37.42
Range (ft.)	3.09
<u>CH-4</u>	
Average Depth Below Land Surface (ft.)	8.24
Maximum Depth Below Land Surface (ft.)	8.97
Minimum Depth Below Land Surface (ft.)	7.22
Range (ft.)	1.75

Table 7 - Summarized water level data for each core hole

Measurements for a wide range of water chemistry variables were collected by NCDEQ and USGS, samples of which are included in tables 8 and 9. Of the data collected for this study, DO, pH, water temperature, and concentrations of dissolved Ca, Na, HCO<sub>3</sub><sup>-</sup>, K, and Mn were considered most relevant. All dissolved Fe concentrations were below the LOD for all water samples logged (N.C. Department of Environmental Quality, Undated).

In both cores a decreasing trend in DO was notable with oxic groundwater at the shallowest depths grading to suboxic and anoxic as depth increased. In CH-2, the highest

measured DO level occurred in March of 2009 (10.5 mg/L) at 33 FBLS, and the lowest DO level occurred in November of 2006 (0.7 mg/L) at 194 FBLS. Average DO levels in CH-2 were 8.6, 2.5, 1.0, and 1.5 mg/L at 33, 62, 140, and 194 FBLS, respectively (Table 8). In CH-4 the highest (10.6 mg/L) and lowest (0.0 mg/L) measured DO levels both occurred at 39 FBLS in July of 2007 and November of 2006, respectively. Average DO levels in CH-4 were 6.9, 7.2, 2.6, and 0.2 mg/L at 22, 39, 88, and 121 FBLS, respectively (Table 9).

Conversely, pH showed an increasing trend, from acidic to slightly basic, as depth increased in both cores. In CH-2 the lowest pH measured was 5.0 at 33 FBLS in March of 2009, and the highest pH was 7.6 at 194 FBLS in November of 2006. Average pH in CH-2 was 5.2, 7.0, 7.0, and 7.3 at 33, 62, 140, and 194 FBLS (Table 8). In CH-4 the lowest pH measured was 4.8 at 22 FBLS in November of 2006, and the highest pH was 8.4 at 121 FBLS in November of 2006. Average pH in CH-4 was 5.1, 6.2, 8.0, and 8.2 at 22, 39, 88, and 121 FBLS (Table 9).

Sampling	Sampling	DO	pH, Field	Water	[Ca]	[Na]	[HCO <sub>3</sub> ]	[K]	[Mn]
Date	Depth (ft.)	(mg/L)	(std units)	Temp (°C)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
11/28/2006	33	6.0	5.3	14.8	0.47	0.69	4.0	1.2	22
3/5/2007	33	6.9	5.1	14.5	0.48	0.66	3.0	1.1	16
7/10/2007	33	9.4	5.2	14.8	0.52	0.60	4.8	1.2	11
11/5/2007	33	9.1	5.1	14.5	0.50	0.67	3.3	1.2	<10
5/27/2008	33	9.4	5.2	15.2	0.55	0.72	n/a	1.2	<10
3/17/2009	33	10.5	5.0	14.4	0.50	0.64	3.3	1.2	<10
Average	33	8.6	5.2	14.7	0.5	0.7	3.7	1.2	13.2
11/28/2006	62	1.7	6.6	15.6	20	5.8	72	5.4	150
3/5/2007	62	n/a	7.2	16.5	23	5.5	79	5.5	160
7/10/2007	62	1.9	7.0	16.2	17	4.1	60	5.4	140
11/6/2007	62	n/a	6.9	14.6	n/a	n/a	55	n/a	n/a
5/27/2008	62	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
3/17/2009	62	3.8	7.2	14.5	19	4.6	58	5.9	350
Average	62	2.5	7.0	15.5	19.8	5.0	64.8	5.6	200.0
3/16/2009	140	1.0	7.0	15.4	16	4.4	54	4.8	<10
11/28/2006	194	0.7	7.6	16.7	18	5.0	68	5.0	10
3/5/2007	194	1.1	7.4	16.6	17	4.6	62	4.7	10
7/9/2007	194	2.2	7.2	15.8	16	4.3	58	4.7	10
11/5/2007	194	n/a	7.4	16.5	17	4.7	56	4.9	<10
5/27/2008	194	1.8	7.1	16.1	17	4.6	52	4.9	<10
Average	194	1.5	7.3	16.3	17.0	4.6	59.2	4.8	10.0

Table 8 - CH-2 Selected water quality data

Water temperature also increased with depth in both core holes. In CH-2, the lowest temperature (14.4 °C) was measured at 33 FBLS in March of 2009, and the highest temperature (16.7 °C) was measured at 194 FBLS in November of 2006. Average water temperatures in CH-2 were 14.7, 15.5, 15.4, and 16.3 °C at 33, 62, 140, and 194 FBLS (Table 8). In CH-4, the lowest temperature (13.9 °C) was measured at 22 FBLS in May of 2008, and the highest temperature (16.5 °C) was measured at 121 FBLS in March of 2007. Average water temperatures in CH-4 were 14.6, 14.4, 15.4, and 16.0 °C at 22, 39, 88, and 121 FBLS (Table 9).

Sampling	Sampling	DO	pH, Field	Temp	[Ca]	[Na]	[HCO <sub>3</sub> ]	[K]	[Mn]
Date	Depth (ft.)	(mg/L)	(std units)	(°C)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
11/29/2006	22	2.6	4.8	15.5	7.3	3.6	6.0	1.5	<10
3/6/2007	22	5.5	5.3	14.2	0.76	1.1	2.0	0.71	<10
7/10/2007	22	8.4	5.2	14.6	0.77	1.1	5.9	0.72	<10
11/6/2007	22	8.6	5.4	15.4	0.87	1.3	5.3	0.85	<10
5/28/2008	22	8.0	5.0	13.9	0.75	1.2	4.3	0.71	<10
3/17/2009	22	8.0	4.9	14.0	0.72	1.2	5.8	0.68	<10
Average	22	6.9	5.1	14.6	1.9	1.6	4.9	0.9	<10
11/29/2006	39	0.0	6.1	14.4	8.3	10	31	4.2	200
3/6/2007	39	8.6	6.0	14.3	6.0	3.1	14	1.4	<10
7/10/2007	39	10.6	6.4	14.4	7.0	3.4	31	1.5	<10
11/6/2007	39	7.5	6.5	14.4	9.0	4.0	33	1.7	<10
5/28/2008	39	6.9	6.3	14.6	8.0	3.8	31	1.5	<10
3/17/2009	39	9.7	6.1	14.5	7.5	3.5	30	1.5	<10
Average	39	7.2	6.2	14.4	7.6	4.6	28.3	2.0	200.0
7/10/2007	88	2.6	8.0	15.4	20.0	5.2	64	3.5	16
11/29/2006	121	0.1	8.4	16.4	15	14	62	5.3	<10
3/6/2007	121	0.4	8.3	16.5	19	5.5	31	3.4	19
7/10/2007	121	0.3	8.3	15.9	19	5.4	61	3.4	22
11/6/2007	121	0.1	8.3	15.7	21	5.7	61	3.8	24
5/28/2008	121	0.1	8.2	15.7	19	5.2	57	3.5	25
3/17/2009	121	0.2	7.9	15.8	19	5.2	59	3.7	26
Average	121	0.2	8.2	16.0	18.7	6.8	55.2	3.9	23.2

Table 9 - CH-4 Selected water quality data

All dissolved ionic concentrations generally showed increasing trends in both core holes with maximum values observed at intermediate or maximum depths. Maximum Ca concentrations of 23 and 21 mg/L were found at 62 and 121 FBLS in CH-2 and CH-4, respectively. Minimum Ca concentrations of 0.47 and 0.72 mg/L were found at 33 and 22 FBLS, respectively. The same pattern held for HCO<sub>3</sub><sup>-</sup> in both cores with maximum concentrations of 79 and 64 mg/L at 62 and 88 FBLS in CH-2 and CH-4, respectively. Minimum HCO<sub>3</sub><sup>-</sup> concentrations of 3.0 and 2.0 mg/L were found at 33 and 22 FBLS. Maximum dissolved Na concentrations of 5.8 and 14 mg/L were found at 62 and 121 FBLS, and minimum dissolved Na

concentrations of 0.60 and 1.1 mg/L were found at 33 and 22 FBLS in CH-2 and CH-4, respectively (Table 8 and 9). Similarly, maximum K concentrations of 5.9 and 5.3 mg/L were found at 62 and 121 FBLS in CH-2 and CH-4. Minimum K concentrations of 1.1 and 0.68 mg/L were found at 33 and 22 FBLS in each, respectively. Mn concentrations showed high variability in both coreholes, with many values below the LOD (<10 mg/L). Mn was generally highest in CH-2 at 62 FBLS with a maximum concentration of 350 mg/L in March of 2009, but typically lowest from 140 – 194 FBLS. In CH-4, the highest Mn concentration (200 mg/L) was found at 39 FBLS in November of 2006, and the lowest concentrations were found at 22 FBLS. However, the high Mn concentration at 39 FBLS appears anomalous as all other values at that depth were recorded as below the LOD. More consistent Mn concentrations were found at 121 FBLS in CH-4 with an average of 23.2 mg/L.

### 4 DISCUSSION

# 4.1 How Mineralogical Changes Relate to Weathering Patterns

A primary goal of this study was to identify the PIM, the most soluble mineral that weathers first at depth whose reaction front delimits the boundary between HWR and UWR (Brantley et al., 2017). Biotite and pyrite oxidation in granites and pyroxene (e.g. augite) dissolution in diabase (mafic intrusive rock) are common examples of PIMs and their first reactions at depth (Bazilevskaya et al., 2013, 2015). Brantley et al. (2017) argued that oxidation is the more common PIM reaction in felsic rock compared to mafic rock because felsic rock consumes CO<sub>2</sub> faster than O<sub>2</sub>, leaving more O<sub>2</sub> available for reaction at depth. It is for the opposite reason that mafic rock (diabase) shows acid dissolution as its most common PIM reaction, because of higher O<sub>2</sub> consumption at shallower depths. In other words, the mafic rock contains electron donors, such as  $Fe^{2+}$ , in greater abundance than felsic rock. Brantley et al. (2017) also described porosity-initiating and soil-initiating minerals and reactions as complements to PIM. The porosity-initiating mineral is defined as an abundant, moderately soluble mineral that weathers above the PIM depth, resulting in density reduction and porosity formation, and denotes the boundary between hard-weathered rock and saprolite (Brantley et al., 2017). The porosity-initiating mineral and reaction in felsic (granite) rocks most often dissolve plagioclase (Bazilevskaya et al., 2013, 2015). Brantley et al. (2017) described the soil-initiating mineral as a low solubility mineral whose dissolution demarcates the soil – saprolite boundary through disaggregation and clay formation with alkali-rich minerals serving the role in granitic rock and plagioclase in diabase (Brantley et al., 2017). A key consideration is that for a mineral to be the PIM, it must be abundant enough for its weathering to have a material effect, and it

must be high enough in the Goldich weathering series (Fig. 34) (Goldich, 1938) to be reactive enough for substantial or complete removal.

As expected, both cores generally displayed a pattern of fresh unweathered rock at depth grading into highly weathered rock as depth decreased. This change with depth from primary minerals such as biotite and hornblende (an amphibole) to secondary minerals such as FeO<sub>x</sub> agrees with the Goldich weathering series (Fig. 34), and is supported by the negative FeO<sub>x</sub>-to-depth and ratio-to-depth correlations (Table 4).



Figure 34 - The Goldich weathering series provides a framework to predict the order in which minerals will break down and weather away (generally in the same order that they crystallized). From (Churchman and Lowe, 2011)

This weathering pattern is also consistent with decreased oxygen and water-rock contact as depth increases. As discussed above, notable spikes in  $FeO_x$  at depths containing otherwise

unweathered rock coincided with known water-bearing fractures which enabled water-rock contact and intrusion of DO that would not have otherwise been possible at such depths. While others have noted acid dissolution as the PIM reaction in mafic rock (Bazilevskaya et al., 2015; Brantley et al., 2017), their arguments were based on a gabbroic or diabase end member. CH-2 and CH-4, while described as mafic in the original core report (Huffman and Abraham, 2010), contain extensive felsic and intermediate zones (Fig. 18) and increased permeability due to foliation. This composition, permeability, and fracture zones at depth, most likely mean that oxidative dissolution is the PIM reaction in these cores. Considering that oxidative dissolution is the likely PIM reaction in this system, the PIM most likely contains a reducing agent such as  $Fe^{2+}$ , which is converted to  $Fe^{3+}$  during the weathering process (i.e. biotite and/or hornblende).

# 4.1.1 Mineral Correlations

Correlations for depth-to-mineral and mineral-to-mineral agree to the expected paradigm of the Goldich weathering series and lead to interesting inferences. In both cores, all FeO<sub>x</sub>-toprimary mineral correlations were negative, and greater than critical values, indicating statistical significance at the p<0.05 level. As primary mineral abundance decreased, FeO<sub>x</sub> abundance increased. However, the FeO<sub>x</sub> : (Biotite + Hornblende) correlation was strongest in both cores, rather than FeO<sub>x</sub>'s correlation to solely biotite or hornblende (Table 4). The strength of the FeO<sub>x</sub> : (Biotite + Hornblende) correlation, coupled with overlapping occurrence across lithologically variable bands, and their similar weathering behavior, suggests that some combination of biotite and hornblende should be considered as the PIM in this system. Both contain enough Fe to reduce O<sub>2</sub>, and are abundant in this system.

While  $FeO_x$  was negatively correlated with depth, it is notable that some  $FeO_x$  was still observed on fracture surfaces in both cores below 95 FBLS (Fig. 21). There is a possibility that

100 FBLS may not be deep enough to find the complete disappearance depth of  $FeO_x$ . Despite this notion, the negative correlations between  $FeO_x$  and depth (Table 4) in both cores supports the interpretations' reliability.

4.1.2 Mineral Ratios and Primary Mineral Weathering Depths

In CH-2, The biotite-oxide ratio and hornblende-oxide ratio peaked at the same depth (37.5 FBLS, Fig. 22), which is near the top of the water table depth range (37.4 FBLS, Table 7), representing the level the water table reaches after winter/spring recharge. This coincided with a secondary  $\tau_{Mn,w}$  peak at 37.3 FBLS (Fig. 32), and the top of the range over which  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  began to show positive (non-depleted or enriched) values (36.9 – 45.4 FBLS, Fig. 29 and 30). The HDD in CH-2 was found at 56.8 FBLS (Fig. 20), above which no further observations of hornblende were found. Interestingly, in the same way they peaked at the same depth, the biotite and hornblende-oxide ratios also showed a "quieting" trend over a narrow depth range in CH-2 (65.0 – 69.1 FBLS, Fig. 22). Over this depth range, both ratios showed rapid and abrupt spikes, followed by zero or near-zero values and local maxima much lower than at shallower depths. These local maxima were found to coincide with water-bearing fractures that were noted in the field (Huffman and Abraham, 2010). The settling of ratio values near zero suggests this depth range likely contains the bottom of the biotite and hornblende weathering fronts in CH-2.

In CH-4, the biotite and hornblende-oxide ratios also peaked near the same depth (29.2 and 28.7 FBLS, respectively, Fig. 22). This was shallower in the core profile compared to ratio peaks in CH-2, but much deeper when compared to the water table depth range (7.2 – 9.0 FBLS, Table 7). The ratio peaks coincided with the bottom of the range over which  $\tau_{Ca,w}$  and  $\tau_{sr,w}$  began to show positive values (21.0 – 30.0 FBLS) (Fig. 29 and 30). The HDD in CH-4 was found at

59.5 FBLS (Fig. 20). The biotite and hornblende-oxide ratios were not as tightly linked in CH-4 compared to CH-2. In CH-4, the biotite-oxide ratio dropped and stayed below 1 at 61.5 FBLS and all depths below (Fig. 22), suggesting this is the deepest depth of the biotite weathering front. The hornblende-oxide ratio in CH-4 never showed as quiet a pattern. At 75.0 FBLS the hornblende-oxide ratio spiked to 30 followed by a quick fall to zero or near zero values. Still, it again showed high values at lower depths (i.e., 40 and 20 at 94.0 and 94.8 FBLS, respectively, Fig. 22). It is for this reason it is difficult to identify the deepest depth of the hornblende weathering front in CH-4.

An initial goal of this project was to identify a BDD. Neither core ever displayed complete removal of biotite. Brantley et al. (2017) discussed a situation in which an easily erodible rock contains only moderately soluble minerals. In this case, mineral grains pass through the weathering front without completely dissolving before reaching the land surface, resulting in an "incompletely developed profile" and "weathering-limited" regime. However, at AWRS, the chemical weathering rate is likely faster than the erosion rate. While no attempt was made to analyze biotite abundance in soil layers (due to generally poor recovery), there is likely a depth in soil layers at which biotite becomes rare enough to be difficult to identify because of low abundance and weathering damage. 4.2 Changes in Elemental Concentrations and Their Relationship to Mineral Weathering Fronts

Several concepts should be reiterated concerning pXRF analysis. While care was taken throughout the XRF scanning process to avoid overweighting any specific mineral or rock type, due to the size of the XRF target size, scanning geometry, and core morphology, the possibility exists that only mafic or felsic mineral crystals were captured in any given scan. However, this is a minor consideration because of the degree of lithologic heterogeneity inherent in these cores. The alternation between felsic and mafic zones was abrupt in these cores, and zones ranged from meter to millimeters wide.

The choice of protolith is an important consideration for the  $\tau$  calculations used by this study. It sets the baseline by which weathered values are compared to produce  $\tau$  values. Because of the high lithologic variation fundamental to these gneissic rocks, it would have been difficult to find a representative section of the core. With that being the case, the protolith used here was determined by comparison to the original core report (Huffman and Abraham, 2010). The top of the protolith was taken to be the shallowest depth immediately below the last mention of weathered rock. Elemental concentrations from this depth to the lowest analyzed were averaged to arrive at nominal unweathered values.

# 4.2.1 Elemental correlations

 $\tau$  values were noisy along depth in both cores because of lithologic heterogeneity, and displayed ranges as great as -1 to 144 (i.e.,  $\tau_{Mn,w}$  in CH-2). At first glance, the  $\tau$  ranges found seemed unreasonable, but  $\tau$ -to-depth and  $\tau$ -to- $\tau$  correlations support the results.  $\tau_{Ca,w}$  in CH-4 showed the strongest correlation with depth, but all  $\tau$ -to-depth correlations were greater than critical values except for Mn and Rb (Table 5). While other  $\tau$ -to-depth correlations were noisy and weak, they were all positive. The positive nature of the  $\tau$ -to-depth correlations is in keeping with others' findings (Oh and Richter, 2005; Brantley et al., 2017) showing elemental depletion near the surface followed by enrichment with an increase in depth.  $\tau_{Ca,w}$  showed the strongest correlation with depth in both cores, which is most likely due to how early Ca-rich plagioclase weathers compared to other minerals in the Goldich weathering series (Fig. 34).

Interestingly, the  $\tau$ -to- $\tau$  correlations were much stronger than the depth correlations. In both cores, Fe : Ca, Fe : Mn, and Fe : Rb showed moderate to strong positive correlations (Table 6). The level of noise in the  $\tau$ -to-depth correlations is likely the result of lithologic heterogeneity, but the strength of the  $\tau$ -to- $\tau$  correlations implies a stronger link that may be more useful than just  $\tau$ -to-depth for future work. The fact that the two cores are so different lithologically, yet show similar  $\tau$ -to- $\tau$  correlations further supports the link.



Figure 35 - The interpreted weathering front profile of CH-2, scales on left and right denote feet below the land surface, Green = soil layers, Brown = Saprolite, Red = Partially Weathered Rock, Gray = Hard Weathered Rock, Blue = Unweathered Rock, middle column shows the approximate depths of important transitions, far right column shows the fronts over which redox states are changing and reactions are happening. Triangles numbered 1 thru 3 indicate the depths at which water quality samples were collected (1 = 33 FBLS, 2 = 62 FBLS, and 3 = 140 FBLS), The depth to water table shown is based on the average of levels observed during the data collection period.



Figure 36 - The interpreted weathering front profile of CH-4, scales on left and right denote feet below the land surface, Green = soil layers, Brown = Saprolite, Red = Partially Weathered Rock, Gray = Hard Weathered Rock, Blue = Unweathered Rock, middle column shows the approximate depths of important transitions, far right column shows the fronts over which redox states are changing and reactions are happening. Triangles numbered 1 thru 3 indicate the depths at which water quality samples were collected (1 = 22 FBLS, 2 = 39 FBLS, and 3 = 88 FBLS), The depth to water table shown is based on the average of levels observed during the data collection period.

### 4.2.2 $\tau$ Values as Indicators of Weathering Fronts

K is a fundamental component of biotite, muscovite, and orthoclase, all of which commonly occur in soil layers in the Inner Piedmont. Alkali-rich minerals, such as orthoclase, have been suggested as soil-initiating minerals by others (Brantley et al., 2017). In this study, Rb was used as a proxy for K. In both cores,  $\tau_{Rb,w}$  shows positive values at relatively shallow depths (Fig. 33). In CH-2,  $\tau_{Rb,w}$  flips from negative to positive at 5.81 FBLS, and in CH-4 at 13.0 FBLS. Both of these depths are comparable to those over which alkali-rich minerals were found to disappear (3 meters, or approximately 10 feet) by others (Bazilevskaya et al., 2013, 2015; Brantley et al., 2017). These changes from depletion to enrichment imply a transition from highly weathered to less weathered, or unweathered, mineral components. While the elemental concentrations and  $\tau_{\rm Rb,w}$  values do not give us information about what specific minerals Rb, and thereby K, are contained in, it does support the argument of a distinct change in the degree of weathering of those minerals. It is also of note that, according to the Goldich weathering series, muscovite and orthoclase are generally more stable than most other minerals. Given the shallow depths of the  $\tau_{Rb,w}$  flip to positive, and the general stable nature of K-containing minerals, this transition has been inferred to be the soil – saprolite boundary in both cores (Fig. 35 and 36).

Brantley et al. (2017) suggested a boundary between saprolite and weathered rock at which porosity formation is initiated as a specific mineral weathers. In felsic lithologies, plagioclase is believed to be the porosity-initiating mineral (Brantley et al., 2017). While plagioclase can have a wide range of compositions, its earliest forming, and earliest weathering, forms are dominated by Ca cations. As discussed above, in CH-2,  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  begin to show positive values at 45.4 and 36.9 FBLS, respectively, and rapid and abrupt oscillations between negative and positive values below these depths. In CH-4,  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  begin to show positive values at 21.0 and 30.0 FBLS, respectively, and the same rapid and abrupt oscillations between negative and positive values below as those seen in CH-2. These oscillations between depletion and enrichment imply a transition from the absence or presence of highly weathered plagioclase to less weathered plagioclase. Because of the implication that there has been a change from no (or highly weathered) plagioclase to present, but weathered, plagioclase the shallower limits of these ranges, in both cores, have been interpreted to represent the saprolite – PWR boundary (Fig. 35 and 36).

Brantley et al. (2017) do not differentiate between different forms of weathered rock. However, this study distinguishes between PWR, where porosity exists and advection is dominant, and HWR, where porosity is minimal and weathering occurs predominantly by diffusion. Plagioclase is important for the boundary between PWR and HWR. In CH-2,  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  stopped showing -1 values at, and below, 36.9 and 85.6 FBLS, respectively. In CH-4,  $\tau_{Ca,w}$ and  $\tau_{Sr,w}$  stopped showing any -1 values at, and below, 46.1 and 51.5 FBLS, respectively with the bottom of this range considered the deepest extent of the plagioclase weathering zone (PWZ) in CH-4 (Fig. 36). The PWZ is difficult to interpret in CH-2 because of the wide depth range (36.9 – 85.6 FBLS) over which  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  values imply the transitions from unweathered to partially weathered and partially weathered to highly weathered, or absent, plagioclase. This is most likely due to the high degree of heterogeneity in gneissic rock compared to granitic rock. Both  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  begin showing values greater than 2, implying significant enrichment at and below 45.7 and 42.5 FBLS, respectively in CH-2. Because of the high degree of lithologic variability, the deeper Other weathering indicators combine with the PWZ to imply the formation of porosity and new minerals in PWR. As noted, the biotite-oxide ratio peaks at 37.5 and 29.2 FBLS, and the hornblende-oxide ratio peaks at 37.5 and 28.7 FBLS in CH-2 and CH-4, respectively. These depths lie in the range over which  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  values imply the transition from absent, or highly weathered, to present but weathered plagioclase. Biotite and plagioclase are similarly situated on the Goldich weathering series (Fig. 34), and it makes sense that biotite and plagioclase begin to show changes at nearly the same depths. This is in combination with the general state of near complete depletion of Ca at depths shallower than 42.0 and 21.0 FBLS in CH-2 and CH-4, respectively. Additionally,  $\tau_{Mn,w}$  shows a strong secondary peak in CH-2 at 37.3 FBLS and a primary peak in CH-4 at 21.0 FBLS. The bottom of the range over which  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  values flip to positive (45.4 FBLS in CH-2 and 30.0 FBLS in CH-4), in combination with the depths at which  $\tau_{Mn,w}$  and the biotite and hornblende-oxide ratios peak, have been interpreted to represent the PWR – HWR boundary in both cores (Fig. 35 and 36).

The data support different interpretations each core's HWR – UWR boundary. In CH-2 the HDD was found at 56.8 FBLS which does not coincide with any other notable metric used in this study. The biotite and hornblende-oxide ratios show zones of local maxima from approximately 65.0 - 69.1 FBLS followed by either zero or near zero values or subdued local maxima that correspond to water-bearing fractures. These rapid and abrupt spikes followed by quiescence, imply the boundary of the biotite and hornblende weathering zone. This coincides

with the maximum observed  $\tau_{Mn,w}$  value of 144 at 67.4 FBLS. For this reason, 69.1 FBLS has been interpreted to be the HWR – UWR boundary in CH-2 (Fig. 35).

In CH-4, the HDD was found at 59.5 FBLS which is two feet above the depth at which the biotite-oxide ratio drops below 1 permanently (61.5 FBLS).  $\tau_{Ca,w}$  and  $\tau_{Sr,w}$  stopped showing -1 values over a much narrower range (46.1 – 51.5 FBLS) than that found in CH-2, better indicating the bottom of the plagioclase weathering front. The deepest indicator of weathering in CH-4 was the hornblende-oxide ratio which showed a local maximum at 73.3 FBLS followed by a general "quieting" trend denoting the likelihood of the deepest point of the hornblende weathering front. For that reason, 73.3 FBLS has been interpreted to be the HWR – UWR boundary in CH-4 (Fig. 36). In comparison to 69.1 FBLS in CH-2 and 73.3 FBLS in CH-4, Bazilevskaya et al. (2015) found PIM reactions that started at approximately 20 meters deep (65 FBLS) (Bazilevskaya et al., 2015).

# 4.2.3 Weathering Fronts Across the Hillslope Transect

These observations and interpretations highlight several notable differences and similarities between CH-2 and CH-4, the most obvious of which is the depth from the land surface to the water table in each core. The average depth to water is 31.1 feet greater in CH-2 than CH-4, and the water table lay in PWR layers in CH-2 compared to lying in the soil layers in CH-4. This is notable for the differences in type and thickness of highly weathered material water moves downward through in each core. The soil layers in CH-4 were more than twice as thick as the soil layers in CH-2 (12 feet compared to 5.8 feet). The thickness of the saprolite, HWR, and PWZs also showed marked differences between the two cores. Saprolite thickness was 23.1 feet greater in CH-2 than CH-4. However, HWR and the PWZ were 21.6 and 21.7 feet

thicker in CH-4 than CH-2, respectively. When viewed as a whole (Fig. 37), the saprolite thickness differences appear similar to the "pinched" or "bowtie" topography described by others using geophysical methods to investigate hillslope weathering (St. Clair et al., 2015). In these "pinched" settings, weathering fronts appear thicker in upslope positions compared to downslope positions.



Figure 37 - The "pinched" topography similar to that described by St. Clair et al. (2015) is seen in saprolite layers (brown). The saprolite to UWR thickness is comparable, but the depth of weathering is deeper in the valley (CH-4). It should be remembered that the land surface at CH-2 is approximately 34.3 feet higher in elevation than the land surface at CH-4. Green = soil layers, Brown = Saprolite, Red = Partially Weathered Rock, Gray = Hard Weathered Rock, Blue = Unweathered Rock

Conversely, the cores showed similar PWR (8.5 and 9.0 feet) thicknesses. At 56.8 and 59.5 FBLS, the HDD was found at similar depths and lay in HWR in each core. Despite the thickness difference noted above, the PWZ falls across both the PWR and HWR in both cores, and most interestingly, the total thickness of weathered rock (considered from the top of saprolite to the bottom of HWR here) was comparable in both cores (63.3 and 60.3 feet). Of note was the difference of the depth of  $\tau_{Mn,w}$  maxima in each core.  $\tau_{Mn,w}$  peaked at 67.4 and 21.0 FBLS in CH-2 and CH-4, respectively. However, a strong secondary  $\tau_{Mn,w}$  peak in CH-2 was found at 37.3 FBLS, just above the average depth to the water table. It is unknown whether a scanning error is the reason for the deep  $\tau_{Mn,w}$  spike in CH-2, but  $\tau_{Mn,w}$  peaks near the water table agree with others' observations (Sparrow and Uren, 2014; Gillispie et al., 2016; Jones et al., 2018; Bourgault et al., 2022). The general Mn weathering pattern implied by  $\tau_{Mn,w}$  seems reasonable, but the source minerals containing Mn at this site are unknown without further study.

As noted above, the depth of weathering initiation in the AWRS system was comparable to that of a biotite-containing granite system studied by Bazilevskaya et al. (2015), who found plagioclase dissolution to occur over a 9 - 10 meter depth range (30 - 33 feet) which almost exactly matches the range of the PWZ found in CH-4 (30.5 feet), but is larger than the range for plagioclase weathering in CH-2 (8.8 feet). Others have noted that weathering fronts in mafic rocks tend to lie within centimeters of each other, but can lie over tens of meters in felsic rock (Brantley and Lebedeva, 2021). The AWRS cores follow Brantley and Lebedeva's (2021) felsic pattern despite being more mafic than, for example, granite. This is most likely due to the high permeability levels resulting from foliation and fracturing in gneiss. Additionally, the AWRS cores display a large grain size comparable to a granite that enhances porosity as weathering proceeds. There is also the belief that weathering fronts in felsic rocks are enhanced by advection

through porosity propped open by quartz grains and intergrowths of mica and quartz after weathering (Brantley et al., 2017). The AWRS cores contain a not unsubstantial amount of quartz and micas that can serve this role of porosity preservation, allowing for the observed weathering pattern that more closely mimics felsic rock.

### 4.3 Mineral Weathering and Groundwater Evolution

Minerals weather and dissolve as long as the reacting minerals have not completely dissolved and the surrounding water has not equilibrated (Brantley and Lebedeva, 2021). The volume of water flow through a given rock matrix required to dissolve and remove a mineral is high, approximately 10<sup>3</sup> times the volume of the mineral being dissolved, which means that small differences in mineral volumes weathered across depths can record and magnify cumulative water flow (Brantley et al., 2017). A control of groundwater equilibration is the porosity and permeability of the surrounding bedrock that can enhance groundwater flow, allowing for removal of weathered solutes and maintaining favorable thermodynamic conditions. This means that where porosity and permeability are large enough, mineral weathering in the subsurface can be autocatalyzing. This is especially the case where biotite is oxidized. Biotite oxidation generally involves swelling of the mineral grains that further contribute to fracturing and permeability formation (Fletcher et al., 2006). This fracturing allows for greater exposure of fresh mineral surface and advective transport of weathering solutes with widening of weathering fronts and deeper penetration of weathering fronts into UWR (Brantley and Lebedeva, 2021).

As noted, the PIM reaction can be either incongruent dissolution (hydrolysis) or oxidation. In the AWRS system, it is believed that biotite and hornblende are the first minerals to be weathered at depth. Both biotite and hornblende contain  $Fe^{2+}$ , which weathers to  $FeO_x$  and consumes DO in the process. Recall equations (1) and (2):

#### **Biotite Hydrolysis:**

# $(Eq. 1) 4 KFe_{3}AlSi_{3}O_{10}(OH)_{2} + 32 H_{2}O + 3 O_{2}(aq) + 4 H^{+} \rightarrow 12 Fe(OH)_{3} + 2 Al_{2}Si_{2}O_{5}(OH)_{4} + 4 K^{+} + 8 H_{4}SiO_{4} + 4 K$

#### Hornblende Hydrolysis:

 $(Eq. 2) Ca_2Fe_4AlSi_7AlO_{22}(OH)_2 + 15 H_2O + O_2(aq) + 4 H^+ \rightarrow 4 Fe(OH)_3 + Al_2Si_2O_5(OH)_4 + 2 Ca^{2+} + 5 H_4SiO_4 + 2 Ca^{2+} + 5 H_4Si$ 

These reactions combine incongruent dissolution (proton exchange) and oxidation (electron exchange). In both cases, oxidation leads to the removal of an electron from ferrous Fe in the primary mineral resulting in the formation of ferric Fe in the product mineral (i.e.  $Fe^{2+}$  in biotite/hornblende  $\rightarrow$   $Fe^{3+}$  in FeO<sub>x</sub>). Both consume acidity and DO, leading to transitions in pH and oxic – anoxic conditions in groundwater.

CH-2 groundwater was highly oxic (8.6 mg/L) and acidic (pH = 5.2) near the water table (33 FBLS) (Table 8), and just above the saprolite – PWR boundary (Fig. 35). This was followed by DO depletion (and anoxic conditions) and a large increase to neutral pH at 62 FBLS, lying in HWR. Similarly large increases in dissolved Ca, Na, HCO3<sup>-</sup>, K, and Mn were noted across the same depth interval. Ca indicates hornblende and plagioclase weathering, Na of plagioclase weathering, and K of biotite weathering. Below 62 FBLS, there was little further evolution of ionic concentrations in groundwater in CH-2, and DO at 140 FBLS is nearly completely anoxic (1.0 mg/L). This implies that most weathering is taking place in PWR and HWR in CH-2, and supports the weathering front interpretations discussed above for CH-2. The peak in dissolved Mn at 62 FBLS is significant, and shows a sharp drop below that depth. As noted earlier, it is not known what Mn-bearing minerals exist in this system without further study, but the dissolved Mn peak aligns closely with the  $\tau_{Mn,w}$  maximum value found in CH-2 at 67.4 FBLS.

CH-4 groundwater showed a similar pattern, with a few exceptions. The shallowest depth for which water chemistry data was available was approximately 14 feet deeper than the average depth to the water below the land surface. With that being the case, DO was oxic (6.9 mg/L) and pH was acidic (5.1) at 22 FBLS (near the saprolite – PWR boundary, same as CH-2). There were again large increases in Ca, Na, HCO3<sup>-</sup>, K and Mn from 22 – 39 FBLS (Table 9). However, DO slightly increased, instead of decreasing, and the pH increase (5.1 to 6.2) was much more subdued than that found in CH-2 (5.2 to 7.0). The AWRS cores come from a low-order headwater catchment with local groundwater flow patterns. This, coupled with the small range (22 - 39 FBLS), suggests the DO increase and subdued pH increase are likely the result of oxygenated interflow infiltrating nearby and percolating through layers with low reactivity (i.e. soil and saprolite). At 88 FBLS in CH-4, DO was depleted and approaching anoxic (2.6 mg/L), but pH had settled at, and would stay near 8.0. There were large increases in dissolved Ca, Na,  $HCO_3^-$ , and K, but a large decrease in Mn from 39 - 88 FBLS in CH-4. The large decrease is due to a single high Mn concentration measured on one day, where Mn concentrations were otherwise below the LOD. Dissolved Mn was consistently highest at 121 FBLS in CH-4, which is in disagreement with others' findings of peak Mn concentrations occurring near the water table (Gillispie et al., 2016). DO was not found to be completely anoxic in CH-4 until a depth of 121 FBLS (Table 9). This complicates and somewhat detracts from the weathering front interpretations made for CH-4. Here, it seems that DO consumption is happening deeper in UWR rather than in HWR as would be expected. The large distance between measurements of DO in CH-4 hinders a better understanding of where exactly these DO transitions are occurring making interpretation difficult. However, the consistency of other solute concentrations from 88 FBLS downward implies that most weathering occurs in HWR in CH-4.

Despite the DO levels found in UWR in CH-4, there is a marked difference in DO levels in both cores across the HWR – UWR boundary, supporting this as the boundary of profile initiation. There is a large difference in the distance from the water table to UWR in the cores. This distance is approximately 29.8 feet in CH-2 compared to 65.1 feet in CH-4, which may be a factor in the difference in depths of anoxic waters. PWR thicknesses are similar between the two cores, implying they are likely not a factor in depth to anoxic water.

Biotite and hornblende weather to FeO<sub>x</sub> (specifically to Fe(OH)<sub>3</sub>, among other FeO<sub>x</sub>). As a result of FeO<sub>x</sub> formation, pH is raised and DO is consumed. Both variables affect the solubility of metals such as Mn, As, and Cr which play a role in human and environmental health. Specifically, Mn and As are tightly linked to the disappearance of DO, and others have noted that dissolved Mn and As commonly co-occur with dissolved Fe (Siegel et al., 2022; Arienzo et al., 2022), an intermediate product of the reactions shown above. Groundwater is an essential source of drinking water for many people (McMahon and Chapelle, 2008; Gillispie et al., 2016; Ying et al., 2017; Coyte and Vengosh, 2020), and its quality is subject to many controlling factors.

In many cases when hydrogeologists characterize an aquifer as a potential source of drinking water, they are most concerned with groundwater yield and discuss the "depth to competent rock" (i.e., Huffman and Abraham, 2010), which most closely relates here to the PWR – HWR transition discussed above. However, when we think about the chemical evolution of groundwater, the leading edge of DO transitions seems lie in HWR near the HWR – UWR boundary generally. With that being the case, the depth to UWR, rather than the depth to competent rock, may be more important for water quality with respect to metals such as Mn and As, among others.

### 4.4 Future Recommendations

Several gaps exist in the results of this study that would benefit from further investigation. Specifically, this study was based on an analysis of the composition of two of the four drill cores collected from this watershed (CH-2 & CH-4), representing the mid-slope and low-slope positions. Examining at least CH-1 (high slope/ridgeline) would provide more detail on mineral weathering and the evolution of groundwater along the entire hillslope transect. Analysis of CH-3 would provide similar information for an adjacent transect and flowpath for comparison to the results discussed here. Additionally, analysis of greater depths in the cores would be useful. FeO<sub>x</sub> were found in CH-2 and CH-4 at 98.1 and 98.3 FBLS, respectively. This suggests that 100 FBLS may not be deep enough to find the true disappearance depth of FeO<sub>x</sub> in these cores, and additional analysis may support different conclusions.

Higher data resolution would likely better illustrate the high levels of lithologic heterogeneity discussed here. Specifically, XRF data for lighter elements such as Na, K, and Mg would have been useful in interpreting weathering depths of albite, orthoclase, and phyllosilicates such as biotite and muscovite, with higher levels of certainty than those proposed here. XRF data for Ti would have been useful for utilization as a secondary immobile element in the  $\tau$  calculations made here. Any similarity or difference in  $\tau$  values calculated with Ti as the immobile element would have been useful in determining the reliability of the methods used during this investigation. Concerning the calibrated elemental concentrations obtained through XRF analysis, and used to calculate  $\tau$  values, a more significant number of known standards would have helped to narrow the range of acceptable concentration values and likely lower LODs. Higher resolution in the water level and water quality data would also have been helpful. A review of Tables 8 and 9 shows the large depth ranges between water samples collected for
solute concentration analysis. Had samples been collected at depths closer together, greater detail may have highlighted changes in solute concentrations that were occurring faster than those portrayed by the data available here.

Thin sections sourced from throughout the core profile could have been useful. Specifically, thin sections would provide greater detail for the abundance of sulfide minerals, quartz, feldspars, and possibly plagioclase transformation to clay minerals. However, due to the rapid and abrupt alternation in composition and extreme lithologic heterogeneity present in these cores, the number of thin sections required to capture an adequate level of detail would be time and cost-prohibitive. Thin sections would also be difficult to manufacture from shallower depths of these cores where highly weathered rock is present, and is too fragile to cut and polish. Even if possible, at these depths, the binocular microscope was adequate for the identification of weathering products such as FeO<sub>x</sub> and MnO<sub>x</sub>. Additionally, thin sections require destruction of the source material, and non-destructive testing was a goal of this project.

Finally, geophysical data collected along the AWRS hillslope transect may support this study's interpretations. Specifically, seismic and electrical resistivity data like that collected by St. Clair et al. (2015) would provide detail regarding depth to bedrock and interlayer wave velocities that may support or negate the weathering boundaries noted here. The seismic data would provide a valuable contrast to what we have accumulated through mineralogy and geochemistry, and would give another non-destructive means of testing. It may also allow for the creation of a 3D subsurface model similar to others' (Flinchum et al., 2018) showing weathering fronts over a greater area than that represented by the cores used here.

## **5** CONCLUSIONS

The goal of this study was to expand understanding of the relationships between landscape position and DO that link ferrous mineral oxidation and profile formation to groundwater quality in the critical zone of the Inner Piedmont terrane. Using comparative mineral ratios, abundances, and pXRF, interpretations were made of the depths at which profile boundaries occurred, including those separating soil, saprolite, PWR, HWR, and UWR in midslope and valley bottom landscape positions. These interpretations were accomplished with minimal destruction to the drill cores that would have otherwise been unavoidable.

The study's findings and interpretations offer generalized concepts that may be useful across different lithologies. Specifically, mineral ratios imply that rather than an individual PIM, a combination of biotite and hornblende is most likely the PIM in AWRS profiles. At both landscape positions the total ratio (FeO<sub>x</sub> / (biotite + hornblende)) was better correlated with FeO<sub>x</sub> abundance than either individual ratio.

pXRF proved a useful tool for identifying profile boundaries. Specifically,  $\tau$  values for Rb were found to be helpful in identifying the soil – saprolite boundary, and a combination of  $\tau$  values for Ca and Sr were useful for identification of the saprolite – PWR boundary. However,  $\tau$  values for Ca and Sr were not as useful for identifying the lower boundary of plagioclase weathering, most likely due to lithologic variability in gneissic rocks, and lack of detail regarding the specific minerals, other than plagioclase, in AWRS rocks that contain Ca and Sr.

Other similarities and differences were noted across the mid-slope and valley positions. While not indicative of a boundary, biotite and hornblende-oxide ratio maxima were always found to lie in PWR, while the HDD lay in HWR. The HWR – UWR boundary was found to coincide with biotite and hornblende-oxide ratio quiescence, and DO depletion, indicating oxidation of biotite and hornblende in HWR. Most weathering was found to occur in PWR and HWR at both landscape positions, but the depths over which weathering occurred differs. While weathering extended deeper into the subsurface at the valley position, the depth range of HWR was almost double that found on the hillslope.

An understanding of weathering front depths in low-order catchments is important both because of the local groundwater flow patterns that characterize them, and because of the ubiquity of groundwater well usage for drinking water that taps similar local groundwater flowpaths in the Inner Piedmont terrane. While the specific mineralogical and elemental observations discussed here may not apply to other lithologies, the methods and interpretations have utility in a wide range of settings. A central premise of this study was to understand where along the flowpath is DO consumption highest (i.e. the PIM weathering depth). Others have shown that different geologic formations exhibit different DO depletion characteristics (Tashnia et al., 2023) which implies lithology is exerting control on DO with corresponding effects on the solubility of metals such as As, Mn, etc. A link between the initiation of ferrous mineral oxidation and DO content at the HWR – UWR boundary has been shown here that has ramifications for metal solubility and contaminant transport that could affect groundwater, and the depth of DO depletion could be important for predicting water quality. This study provides an example of using rock cores to predict the depth of DO depletion that could potentially be used in different lithologies. As climate change progresses, populations grow, and the reliance on groundwater increases, a better understanding on the subsurface interaction of water and rock is essential.

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CH-2 – Hand Lens Index Scores						
Depth (ft.)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>		
99.00	4	1	1	1		
98.13	3	1	1	2		
98.13	5	1	1	2		
98.10	5	1	1	1		
98.10	5	1	1	1		
96.82	5	1	1	2		
96.82	5	1	1	2		
96.78	5	1	1	2		
96.78	5	1	1	2		
96.58	4	1	1	2		
96.58	4	1	1	1		
96.54	5	1	1	1		
96.54	5	1	1	1		
95.92	5	1	1	1		
95.92	5	1	1	1		
95.17	3	1	1	2		
95.17	3	1	1	2		
94.63	5	1	1	2		
94.63	5	1	1	1		
92.48	5	1	1	1		
92.48	5	1	1	1		
91.60	5	1	1	1		
91.60	5	1	1	1		
90.85	5	1	1	1		
90.85	5	1	1	1		
90.00	5	1	1	3		
90.00	5	1	1	3		
89.31	4	1	1	3		
89.31	4	1	1	3		
88.38	5	1	1	1		
88.38	5	1	1	1		
87.58	3	1	1	1		
87.58	4	1	1	1		
87.50	3	1	1	2		
87.50	5	1	1	2		
87.42	5	1	1	2		
87.42	5	1	1	2		
87.31	3	1	1	5		

## APPENDIX A: Tabular Hand Lens Index Results

CH-2 – Hand Lens Index Scores							
Depth (ft.)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>			
87.31	3	1	1	5			
87.29	1	1	1	1			
87.29	3	1	1	3			
87.09	3	3	1	3			
87.09	3	1	1	4			
85.84	5	1	1	3			
85.84	5	1	1	2			
85.56	4	1	1	3			
85.56	4	1	1	3			
85.46	4	1	1	3			
85.00	3	4	1	2			
84.98	3	4	1	2			
84.98	1	4	1	3			
84.96	1	4	1	3			
84.96	4	4	1	2			
84.88	5	2	1	1			
84.88	5	1	1	2			
84.75	5	1	1	2			
84.75	5	1	1	2			
84.04	2	1	1	2			
84.04	2	1	1 1				
83.96	3	3	1	1			
83.96	3	3	1	1			
83.88	2	5	1	1			
83.88	4	4	1	1			
83.75	4	4	1	1			
83.75	4	4	1	1			
83.17	3	4	1	1			
83.17	4	1	1	1			
82.83	4	1	1	3			
82.83	4	4	1	2			
82.42	4	4	1	3			
82.42	4	4	1	2			
82.27	3	1	1	2			
82.27	3	1	1	2			
82.23	4	3	1	3			
82.23	4	3	1	3			
81.00	5	1	1	1			
81.00	5	1	1	1			
80.00	5	1	1	1			

CH-2 – Hand Lens Index Scores						
Depth (ft.)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>		
80.00	5	1	1	3		
79.06	5	1	1	1		
79.06	5	1	1	1		
78.00	5	1	1	1		
78.00	5	1	1	1		
77.67	3	1	1	2		
77.67	3	1	1	2		
75.58	4	3	1	2		
75.58	5	3	1	2		
75.00	5	3	1	2		
75.00	4	3	1	1		
74.58	4	1	1	1		
74.58	5	1	1	1		
73.33	4	2	1	3		
73.33	4	2	1	3		
72.58	3	1	1	1		
72.58	3	1	1	1		
70.69	4	1	1	1		
70.69	4	1	1	1		
70.52	2	4	1	1		
70.52	2	4	1	1		
70.00	4	4	1	1		
70.00	4	1	1	1		
69.46	3	5	1	2		
69.46	3	5	1	2		
69.35	3	5	1	2		
69.35	3	4	1	2		
69.27	3	4	1	2		
69.27	3	4	1	3		
69.08	2	5	1	3		
69.08	2	5	1	3		
68.96	2	5	1	2		
68.96	2	5	1	2		
68.60	4	1	1	4		
68.60	4	1	1	4		
68.00	4	1	1	3		
68.00	4	1	1	3		
67.50	3	3	1	3		
67.50	4	3	1	4		
67.42	2	4	1	4		

CH-2 – Hand Lens Index Scores							
Depth (ft.)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>			
67.42	2	4	1	4			
67.13	4	1	1	3			
67.13	4	1	1	3			
66.92	4	1	1	2			
66.92	1	2	1	4			
66.75	4	1	1	4			
66.75	3	1	1	5			
66.54	1	1	1	5			
66.54	2	2	1	5			
66.29	2	3	1	5			
66.29	2	3	1	5			
66.21	2	3	1	5			
66.21	3	1	1	4			
65.96	3	1	1	5			
65.96	3	1	1	5			
65.50	3	1	1	5			
65.50	3	4	1	3			
65.00	4	4	1	2			
65.00	4	1	1	2			
64.54	3	3	1	4			
64.54	2	1	1	5			
64.44	2	1	1	5			
64.44	2	2	1	5			
64.23	2	2	1	5			
64.23	3	3	1	4			
60.00	2	1	1	5			
60.00	2	4	1	3			
59.65	3	1	1	3			
59.65	3	1	1	3			
59.54	3	1	1	3			
59.54	3	4	1	3			
59.48	3	1	1	4			
59.48	1	3	1	2			
59.23	3	1	1	5			
59.23	3	1	1	5			
59.08	3	1	1	5			
59.08	3	1	1	5			
58.71	2	2	1	3			
58.71	2	2	1	3			
58.58	2	4	1	3			

CH-2 – Hand Lens Index Scores						
Depth (ft.)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>		
58.58	2	4	1	3		
58.35	2	2	1	5		
58.35	1	3	1	5		
58.15	3	1	1	4		
58.15	3	1	1	4		
58.02	2	3	1	4		
58.02	3	3	1	4		
57.58	2	4	1	4		
57.38	2	4	1	4		
57.38	2	4	1	4		
57.23	2	4	1	4		
57.23	2	4	1	4		
57.15	2	4	1	4		
57.15	2	4	1	4		
56.96	2	4	1	4		
56.96	2	4	1	4		
56.92	2	4	1	4		
56.92	2	4	1	4		
56.90	2	4	1	4		
56.90	2	4	1	4		
56.87	2	4	1	4		
56.87	2	4	1	4		
56.85	2	4	1	4		
56.85	2	4	1	4		
56.83	2	4	1	4		
56.83	2	4	1	4		
56.58	3	1	1	5		
56.58	3	2	1	4		
56.33	4	1	1	4		
55.00	3	3	1	4		
54.75	3	1	1	4		
54.75	3	1	1	4		
54.38	3	1	1	4		
54.17	2	3	1	4		
54.08	2	3	1	4		
54.08	2	4	1	4		
53.88	1	3	1	4		
53.88	2	3	1	5		
53.71	3	2	1	5		
53.71	3	2	1	5		

CH-2 – Hand Lens Index Scores						
Depth (ft.)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>		
53.25	3	2	1	5		
52.58	3	1	1	5		
52.21	2	1	1	5		
52.21	3	1	1	4		
52.17	3	1	1	4		
52.17	3	1	1	4		
52.00	2	1	1	3		
52.00	3	1	1	4		
51.65	3	1	1	3		
51.48	3	1	1	3		
51.21	3	1	1	3		
51.21	3	1	1	4		
50.92	3	1	1	2		
50.92	3	1	1	2		
50.75	3	1	1	4		
50.75	4	1	1	4		
50.50	3	1	1	4		
49.67	3	1	1	3		
49.67	2	1	1	4		
49.58	3	1	1	3		
49.58	3	1	1	3		
49.50	3	1	1	3		
49.50	3	1	1	4		
49.21	3	1	1	4		
49.21	3	1	1	4		
48.90	3	1	1	4		
48.90	3	1	1	4		
48.00	3	1	1	4		
47.75	3	1	1	4		
47.75	3	1	1	4		
47.56	3	1	1	4		
47.56	1	1	1	2		
47.40	1	1	1	2		
47.40	1	1	1	2		
47.08	2	1	1	4		
47.08	2	1	1	4		
46.56	2	2	1	5		

CH-4 Hand Lens Index Scores							
Depth (ft.)	Biotite	Sulfides	FeO <sub>x</sub>				
100.00	5	1	2				
98.26	4	1	2				
97.13	5	1	2				
96.38	4	1	2				
95.12	4	1	2				
94.76	5	1	3				
93.98	4	1	3				
93.21	2	1	2				
91.71	3	1	1				
90.00	2	1	1				
87.71	2	1	1				
86.71	2	1	1				
84.96	2	1	1				
84.08	4	1	2				
83.45	3	1	1				
81.79	5	1	2				
80.68	4	1	3				
80.00	4	1	3				
77.19	3	1	2				
76.46	3	1	2				
75.83	3	1	1				
75.03	2	1	1				
73.53	2	1	1				
73.42	4	1	1				
73.28	3	1	3				
72.53	3	1	2				
72.10	1	1	1				
70.00	2	1	1				
66.40	5	1	3				
65.73	4	1	3				
64.69	4	1	3				
64.38	4	1	2				
64.15	4	1	3				
62.93	2	1	2				
61.53	2	1	1				
60.71	4	1	2				
60.00	4	1	2				
59.48	3	1	1				
57.38	4	1	3				
56.44	4	1	2				

CH-4 Hand Lens Index Scores							
Depth (ft.)	Biotite	Sulfides	FeO <sub>x</sub>				
55.25	4	1	4				
54.81	4	1	4				
52.88	4	1	4				
52.46	4	1	2				
51.52	4	1	4				
50.79	4	1	3				
50.00	2	1	2				
49.43	1	1	1				
47.79	4	1	4				
47.78	4	1	2				
46.69	3	1	3				
45.48	2	1	1				
45.44	2	1	1				
45.17	1	1	2				
44.91	1	1	2				
43.31	2	1	2				
42.93	3	1	1				
41.69	2	1	1				
40.00	5	1	2				
37.07	4	1	4				
37.02	2	1	3				
36.75	5	1	4				
36.38	4	1	4				
36.08	4	1	1				
35.65	4	1	3				
35.63	4	1	3				
35.38	3	1	3				
35.00	1	1	1				
34.73	3	1	3				
34.33	3	1	1				
34.19	3	1	4				
33.88	3	1	4				
33.21	2	1	4				
33.17	3	1	4				
31.60	2	1	1				
30.50	2	1	1				
30.17	2	1	2				
30.08	2	1	2				
30.00	2	1	3				
29.83	3	1	2				

CH-4 Hand Lens Index Scores							
Depth (ft.)	Biotite	Sulfides	FeO <sub>x</sub>				
29.65	2	1	2				
29.21	2	1	5				
29.17	1	1	4				
29.15	4	1	3				
29.10	3	1	3				
29.04	2	1	4				
28.99	4	1	4				
28.85	3	1	4				
28.77	3	1	4				
28.71	4	1	4				
28.67	4	1	4				
28.52	4	1	4				

	CH-2 Binocular Microscope Mineralogy						
Depth	Biotite	Hornblende	Sulfides	FeOx	Biotite-	Hornblende-	Total
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio
99.00	70%	0%	0%	0%	0.000	0.000	0.000
98.13	25%	0%	0%	10%	0.400	20.000	0.400
98.13	30%	0%	0%	3%	0.100	6.000	0.100
98.10	50%	0%	0%	0%	0.000	0.000	0.000
98.10	50%	0%	0%	0%	0.000	0.000	0.000
96.82	50%	0%	0%	10%	0.200	20.000	0.200
96.82	40%	0%	0%	10%	0.250	20.000	0.250
96.78	30%	0%	0%	3%	0.100	6.000	0.100
96.78	60%	0%	0%	5%	0.083	10.000	0.083
96.58	20%	0%	0%	0%	0.000	0.000	0.000
96.58	30%	0%	0%	0%	0.000	0.000	0.000
96.54	30%	0%	0%	0%	0.000	0.000	0.000
96.54	15%	0%	0%	0%	0.000	0.000	0.000
95.92	10%	0%	0%	0%	0.000	0.000	0.000
95.92	20%	0%	0%	0%	0.000	0.000	0.000
95.17	25%	3%	0%	5%	0.200	1.667	0.179
95.17	50%	0%	0%	15%	0.300	30.000	0.300
94.63	70%	0%	0%	2%	0.029	4.000	0.029
94.63	70%	0%	0%	2%	0.029	4.000	0.029
92.48	70%	0%	0%	2%	0.029	4.000	0.029
92.48	75%	0%	0%	0%	0.000	0.000	0.000
91.60	60%	0%	0%	0%	0.000	0.000	0.000
91.60	60%	0%	0%	0%	0.000	0.000	0.000
90.85	80%	0%	0%	0%	0.000	0.000	0.000
90.85	70%	0%	0%	0%	0.000	0.000	0.000
90.00	80%	0%	0%	0%	0.000	0.000	0.000
90.00	40%	0%	0%	0%	0.000	0.000	0.000
89.31	25%	0%	0%	3%	0.120	6.000	0.120
89.31	30%	0%	2%	3%	0.100	6.000	0.100
88.38	20%	0%	0%	0%	0.000	0.000	0.000
88.38	80%	0%	0%	0%	0.000	0.000	0.000
87.58	30%	0%	0%	0%	0.000	0.000	0.000
87.58	40%	0%	0%	0%	0.000	0.000	0.000
87.50	40%	0%	0%	0%	0.000	0.000	0.000
87.50	40%	0%	0%	0%	0.000	0.000	0.000
87.42	40%	0%	0%	0%	0.000	0.000	0.000
87.42	50%	0%	0%	2%	0.040	4.000	0.040

APPENDIX B: Tabular Binocular Microscope Mineralogy Results

	CH-2 Binocular Microscope Mineralogy						
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio
87.31	40%	0%	0%	30%	0.750	60.000	0.750
87.31	40%	0%	0%	30%	0.750	60.000	0.750
87.29	0%	0%	0%	0%	0.000	0.000	0.000
87.29	20%	0%	0%	3%	0.150	6.000	0.150
87.09	20%	0%	0%	30%	1.500	60.000	1.500
87.09	20%	0%	0%	30%	1.500	60.000	1.500
85.84	20%	0%	0%	30%	1.500	60.000	1.500
85.84	40%	0%	0%	0%	0.000	0.000	0.000
85.56	75%	0%	0%	5%	0.067	10.000	0.067
85.56	30%	0%	0%	3%	0.100	6.000	0.100
85.46	40%	0%	0%	10%	0.250	20.000	0.250
85.46	40%	0%	0%	10%	0.250	20.000	0.250
85.00	40%	0%	0%	10%	0.250	20.000	0.250
85.00	40%	7%	0%	20%	0.500	2.857	0.426
84.98	25%	0%	0%	5%	0.200	10.000	0.200
84.98	15%	70%	0%	10%	0.667	0.143	0.118
84.96	15%	70%	0%	10%	0.667	0.143	0.118
84.96	10%	40%	0%	10%	1.000	0.250	0.200
84.88	80%	0%	0%	0%	0.000	0.000	0.000
84.88	80%	0%	0%	0%	0.000	0.000	0.000
84.75	60%	0%	0%	5%	0.083	10.000	0.083
84.75	60%	0%	0%	5%	0.083	10.000	0.083
84.04	0%	0%	0%	3%	6.000	6.000	6.000
84.04	10%	0%	0%	0%	0.000	0.000	0.000
83.96	50%	15%	0%	0%	0.000	0.000	0.000
83.96	20%	15%	0%	0%	0.000	0.000	0.000
83.88	20%	25%	0%	0%	0.000	0.000	0.000
83.88	25%	15%	0%	0%	0.000	0.000	0.000
83.75	25%	15%	0%	0%	0.000	0.000	0.000
83.75	25%	25%	0%	0%	0.000	0.000	0.000
83.17	40%	0%	0%	0%	0.000	0.000	0.000
83.17	50%	0%	0%	0%	0.000	0.000	0.000
82.83	50%	0%	0%	20%	0.400	40.000	0.400
82.83	10%	75%	0%	0%	0.000	0.000	0.000
82.42	30%	30%	0%	20%	0.667	0.667	0.333
82.42	30%	30%	0%	20%	0.667	0.667	0.333
82.27	50%	0%	0%	0%	0.000	0.000	0.000
82.27	50%	0%	0%	2%	0.040	4.000	0.040
82.23	25%	0%	0%	15%	0.600	30.000	0.600

	CH-2 Binocular Microscope Mineralogy						
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio
82.23	25%	0%	0%	15%	0.600	30.000	0.600
81.00	50%	0%	0%	0%	0.000	0.000	0.000
81.00	50%	0%	0%	0%	0.000	0.000	0.000
80.00	70%	0%	0%	0%	0.000	0.000	0.000
80.00	70%	0%	0%	0%	0.000	0.000	0.000
79.06	90%	0%	0%	0%	0.000	0.000	0.000
79.06	90%	0%	0%	0%	0.000	0.000	0.000
78.00	90%	0%	0%	0%	0.000	0.000	0.000
78.00	75%	0%	0%	0%	0.000	0.000	0.000
77.67	40%	0%	0%	20%	0.500	40.000	0.500
77.67	40%	0%	0%	20%	0.500	40.000	0.500
75.58	40%	0%	0%	20%	0.500	40.000	0.500
75.58	40%	15%	0%	5%	0.125	0.333	0.091
75.00	40%	15%	0%	5%	0.125	0.333	0.091
75.00	75%	0%	0%	0%	0.000	0.000	0.000
74.58	75%	0%	1%	0%	0.000	0.000	0.000
74.58	75%	0%	1%	0%	0.000	0.000	0.000
73.33	75%	0%	1%	0%	0.000	0.000	0.000
73.33	40%	0%	0%	15%	0.375	30.000	0.375
72.58	30%	0%	0%	5%	0.167	10.000	0.167
72.58	30%	0%	0%	5%	0.167	10.000	0.167
70.69	30%	0%	0%	5%	0.167	10.000	0.167
70.69	60%	0%	0%	0%	0.000	0.000	0.000
70.52	5%	30%	0%	0%	0.000	0.000	0.000
70.52	5%	30%	0%	0%	0.000	0.000	0.000
70.00	25%	20%	0%	0%	0.000	0.000	0.000
70.00	80%	0%	0%	0%	0.000	0.000	0.000
69.46	60%	15%	0%	3%	0.050	0.200	0.040
69.46	20%	25%	0%	0%	0.000	0.000	0.000
69.35	20%	25%	0%	0%	0.000	0.000	0.000
69.35	7%	30%	0%	0%	0.000	0.000	0.000
69.27	7%	30%	0%	0%	0.000	0.000	0.000
69.27	10%	40%	0%	10%	1.000	0.250	0.200
69.08	20%	40%	0%	2%	0.100	0.050	0.033
69.08	7%	45%	0%	20%	2.857	0.444	0.385
68.96	0%	50%	0%	5%	10.000	0.100	0.100
68.96	2%	50%	0%	5%	2.500	0.100	0.096
68.60	40%	0%	0%	40%	1.000	80.000	1.000
68.60	40%	0%	0%	40%	1.000	80.000	1.000

CH-2 Binocular Microscope Mineralogy								
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total	
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio	
68.00	20%	0%	0%	7%	0.350	14.000	0.350	
68.00	20%	0%	0%	7%	0.350	14.000	0.350	
67.50	60%	5%	0%	20%	0.333	4.000	0.308	
67.50	30%	15%	0%	30%	1.000	2.000	0.667	
67.42	10%	30%	0%	40%	4.000	1.333	1.000	
67.42	10%	30%	0%	40%	4.000	1.333	1.000	
67.13	25%	0%	0%	20%	0.800	40.000	0.800	
67.13	25%	0%	0%	20%	0.800	40.000	0.800	
66.92	30%	0%	0%	10%	0.333	20.000	0.333	
66.92	5%	0%	0%	50%	10.000	100.000	10.000	
66.75	15%	0%	0%	40%	2.667	80.000	2.667	
66.75	15%	0%	0%	60%	4.000	120.000	4.000	
66.54	3%	0%	0%	35%	11.667	70.000	11.667	
66.54	10%	2%	0%	75%	7.500	37.500	6.250	
66.29	15%	0%	0%	60%	4.000	120.000	4.000	
66.29	5%	0%	0%	40%	8.000	80.000	8.000	
66.21	10%	0%	0%	30%	3.000	60.000	3.000	
66.21	25%	0%	0%	30%	1.200	60.000	1.200	
65.96	25%	0%	0%	30%	1.200	60.000	1.200	
65.96	25%	0%	0%	30%	1.200	60.000	1.200	
65.50	15%	0%	0%	25%	1.667	50.000	1.667	
65.50	35%	0%	0%	15%	0.429	30.000	0.429	
65.00	40%	20%	0%	0%	0.000	0.000	0.000	
65.00	40%	20%	0%	0%	0.000	0.000	0.000	
64.00	20%	15%	0%	25%	1.250	1.667	0.714	
64.00	15%	0%	0%	40%	2.667	80.000	2.667	
62.60	10%	0%	0%	30%	3.000	60.000	3.000	
62.60	10%	0%	0%	30%	3.000	60.000	3.000	
61.60	30%	0%	0%	40%	1.333	80.000	1.333	
61.60	20%	0%	0%	45%	2.250	90.000	2.250	
60.60	10%	0%	0%	40%	4.000	80.000	4.000	
60.60	25%	0%	0%	30%	1.200	60.000	1.200	
59.65	5%	7%	0%	7%	1.400	1.000	0.583	
59.65	20%	0%	0%	10%	0.500	20.000	0.500	
59.54	15%	0%	0%	20%	1.333	40.000	1.333	
59.54	30%	0%	0%	20%	0.667	40.000	0.667	
59.48	15%	0%	0%	25%	1.667	50.000	1.667	
59.48	5%	0%	0%	0%	0.000	0.000	0.000	
59.23	10%	0%	0%	40%	4.000	80.000	4.000	

CH-2 Binocular Microscope Mineralogy								
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total	
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio	
59.23	15%	0%	0%	60%	4.000	120.000	4.000	
59.08	15%	0%	0%	60%	4.000	120.000	4.000	
59.08	30%	0%	0%	40%	1.333	80.000	1.333	
58.71	5%	15%	0%	15%	3.000	1.000	0.750	
58.71	10%	20%	0%	30%	3.000	1.500	1.000	
58.58	20%	0%	0%	20%	1.000	40.000	1.000	
58.58	20%	0%	0%	20%	1.000	40.000	1.000	
58.35	15%	0%	0%	30%	2.000	60.000	2.000	
58.35	30%	0%	0%	25%	0.833	50.000	0.833	
58.15	40%	0%	0%	15%	0.375	30.000	0.375	
58.15	25%	0%	0%	25%	1.000	50.000	1.000	
58.02	10%	0%	0%	7%	0.700	14.000	0.700	
58.02	35%	0%	0%	25%	0.714	50.000	0.714	
57.58	25%	0%	0%	30%	1.200	60.000	1.200	
57.58	15%	40%	0%	7%	0.467	0.175	0.127	
57.38	15%	40%	0%	7%	0.467	0.175	0.127	
57.38	15%	40%	0%	7%	0.467	0.175	0.127	
57.23	15%	40%	0%	7%	0.467	0.175	0.127	
57.23	15%	40%	0%	7%	0.467	0.175	0.127	
57.15	5%	60%	0%	15%	3.000	0.250	0.231	
57.15	5%	60%	0%	15%	3.000	0.250	0.231	
56.96	5%	60%	0%	15%	3.000	0.250	0.231	
56.96	5%	60%	0%	15%	3.000	0.250	0.231	
56.92	5%	60%	0%	15%	3.000	0.250	0.231	
56.92	5%	60%	0%	15%	3.000	0.250	0.231	
56.90	5%	60%	0%	15%	3.000	0.250	0.231	
56.90	5%	60%	0%	15%	3.000	0.250	0.231	
56.87	5%	60%	0%	15%	3.000	0.250	0.231	
56.87	5%	60%	0%	15%	3.000	0.250	0.231	
56.85	5%	60%	0%	15%	3.000	0.250	0.231	
56.85	5%	60%	0%	15%	3.000	0.250	0.231	
56.83	5%	60%	0%	15%	3.000	0.250	0.231	
56.83	50%	0%	0%	15%	0.300	30.000	0.300	
56.58	30%	0%	0%	30%	1.000	60.000	1.000	
56.58	30%	0%	0%	30%	1.000	60.000	1.000	
55.75	30%	0%	0%	30%	1.000	60.000	1.000	
55.75	20%	0%	0%	15%	0.750	30.000	0.750	
55.00	20%	0%	0%	15%	0.750	30.000	0.750	
55.00	25%	0%	0%	20%	0.800	40.000	0.800	

CH-2 Binocular Microscope Mineralogy								
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total	
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio	
54.75	30%	0%	0%	25%	0.833	50.000	0.833	
54.75	20%	0%	0%	20%	1.000	40.000	1.000	
54.38	20%	0%	0%	20%	1.000	40.000	1.000	
54.38	15%	0%	0%	30%	2.000	60.000	2.000	
54.17	15%	0%	0%	30%	2.000	60.000	2.000	
54.17	20%	0%	0%	15%	0.750	30.000	0.750	
54.08	30%	0%	0%	25%	0.833	50.000	0.833	
54.08	40%	0%	0%	30%	0.750	60.000	0.750	
53.88	20%	0%	0%	7%	0.350	14.000	0.350	
53.88	20%	0%	0%	7%	0.350	14.000	0.350	
53.71	15%	0%	0%	40%	2.667	80.000	2.667	
53.71	15%	0%	0%	40%	2.667	80.000	2.667	
53.25	15%	0%	0%	35%	2.333	70.000	2.333	
53.25	20%	0%	0%	50%	2.500	100.000	2.500	
52.58	15%	0%	0%	30%	2.000	60.000	2.000	
52.58	15%	0%	0%	40%	2.667	80.000	2.667	
52.21	25%	0%	0%	35%	1.400	70.000	1.400	
52.21	25%	0%	0%	35%	1.400	70.000	1.400	
52.17	25%	0%	0%	45%	1.800	90.000	1.800	
52.17	25%	0%	0%	45%	1.800	90.000	1.800	
52.00	20%	0%	0%	15%	0.750	30.000	0.750	
52.00	25%	0%	0%	30%	1.200	60.000	1.200	
51.65	30%	0%	0%	20%	0.667	40.000	0.667	
51.65	30%	0%	0%	20%	0.667	40.000	0.667	
51.48	30%	0%	0%	20%	0.667	40.000	0.667	
51.48	20%	0%	0%	30%	1.500	60.000	1.500	
51.21	30%	0%	0%	20%	0.667	40.000	0.667	
51.21	35%	0%	0%	30%	0.857	60.000	0.857	
50.92	15%	0%	0%	5%	0.333	10.000	0.333	
50.92	15%	0%	0%	5%	0.333	10.000	0.333	
50.75	25%	0%	0%	15%	0.600	30.000	0.600	
50.75	30%	0%	0%	25%	0.833	50.000	0.833	
50.50	10%	0%	0%	55%	5.500	110.000	5.500	
50.50	10%	0%	0%	15%	1.500	30.000	1.500	
50.25	10%	0%	0%	20%	2.000	40.000	2.000	
50.25	20%	0%	0%	10%	0.500	20.000	0.500	
50.00	20%	0%	0%	10%	0.500	20.000	0.500	
50.00	10%	0%	0%	15%	1.500	30.000	1.500	
49.67	10%	0%	0%	15%	1.500	30.000	1.500	

CH-2 Binocular Microscope Mineralogy								
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total	
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio	
49.67	10%	0%	0%	25%	2.500	50.000	2.500	
49.58	40%	0%	0%	40%	1.000	80.000	1.000	
49.58	40%	0%	0%	40%	1.000	80.000	1.000	
49.50	40%	0%	0%	40%	1.000	80.000	1.000	
49.50	20%	0%	0%	20%	1.000	40.000	1.000	
49.21	25%	0%	0%	20%	0.800	40.000	0.800	
49.21	25%	0%	0%	20%	0.800	40.000	0.800	
48.90	20%	0%	0%	20%	1.000	40.000	1.000	
48.90	20%	0%	0%	15%	0.750	30.000	0.750	
48.67	20%	0%	0%	15%	0.750	30.000	0.750	
48.67	20%	0%	0%	15%	0.750	30.000	0.750	
48.38	30%	0%	0%	25%	0.833	50.000	0.833	
48.38	30%	0%	0%	25%	0.833	50.000	0.833	
48.21	20%	0%	0%	30%	1.500	60.000	1.500	
48.21	20%	0%	0%	10%	0.500	20.000	0.500	
48.00	20%	0%	0%	25%	1.250	50.000	1.250	
48.00	20%	0%	0%	10%	0.500	20.000	0.500	
47.75	20%	0%	0%	10%	0.500	20.000	0.500	
47.75	30%	0%	0%	20%	0.667	40.000	0.667	
47.56	20%	0%	0%	15%	0.750	30.000	0.750	
47.56	20%	0%	0%	15%	0.750	30.000	0.750	
47.40	7%	0%	0%	15%	2.143	30.000	2.143	
47.40	7%	0%	0%	15%	2.143	30.000	2.143	
47.08	15%	0%	0%	40%	2.667	80.000	2.667	
47.08	5%	0%	0%	40%	8.000	80.000	8.000	
46.56	5%	0%	0%	45%	9.000	90.000	9.000	
46.56	7%	0%	0%	30%	4.286	60.000	4.286	
46.33	15%	0%	0%	25%	1.667	50.000	1.667	
46.33	7%	0%	0%	30%	4.286	60.000	4.286	
45.92	3%	0%	0%	3%	1.000	6.000	1.000	
45.92	3%	0%	0%	3%	1.000	6.000	1.000	
45.67	30%	0%	0%	15%	0.500	30.000	0.500	
45.67	30%	0%	0%	15%	0.500	30.000	0.500	
45.38	15%	0%	0%	15%	1.000	30.000	1.000	
45.38	15%	0%	0%	15%	1.000	30.000	1.000	
45.00	15%	0%	0%	15%	1.000	30.000	1.000	
45.00	20%	0%	0%	25%	1.250	50.000	1.250	
44.79	20%	0%	0%	25%	1.250	50.000	1.250	
44.79	20%	0%	0%	25%	1.250	50.000	1.250	

CH-2 Binocular Microscope Mineralogy								
Depth	Biotite	Hornblende	Sulfides	FeO <sub>x</sub>	Biotite-	Hornblende-	Total	
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio	
44.67	20%	0%	0%	10%	0.500	20.000	0.500	
44.67	20%	0%	0%	7%	0.350	14.000	0.350	
44.46	25%	0%	0%	15%	0.600	30.000	0.600	
44.46	25%	0%	0%	15%	0.600	30.000	0.600	
44.25	25%	0%	0%	15%	0.600	30.000	0.600	
44.25	25%	0%	0%	20%	0.800	40.000	0.800	
43.90	5%	0%	0% 0% 20% 4.000		40.000	4.000		
43.90	15%	0%	0%	40%	2.667	80.000	2.667	
43.73	15%	0%	0%	40%	2.667	80.000	2.667	
43.73	15%	0%	0%	40%	2.667	80.000	2.667	
43.00	3%	0%	0%	15%	5.000	30.000	5.000	
43.00	3%	0%	0%	15%	5.000	30.000	5.000	
42.50	15%	0%	0%	40%	2.667	80.000	2.667	
42.04	5%	0%	0%	20%	4.000	40.000	4.000	
41.85	5%	0%	0%	20%	4.000	40.000	4.000	
41.85	3%	0%	0%	15%	5.000	30.000	5.000	
41.65	15%	0%	0%	20%	1.333	40.000	1.333	
41.65	20%	0%	0%	30%	1.500	60.000	1.500	
41.40	20%	0%	0%	30%	1.500	60.000	1.500	
41.40	7%	0%	0%	15%	2.143	30.000	2.143	
40.75	2%	0%	0%	40%	20.000	80.000	20.000	
40.75	5%	0%	0%	25%	5.000	50.000	5.000	
40.00	10%	0%	0%	50%	5.000	100.000	5.000	
40.00	10%	0%	0%	50%	5.000	100.000	5.000	
39.83	7%	0%	0%	35%	5.000	70.000	5.000	
39.83	25%	0%	0%	45%	1.800	90.000	1.800	
39.58	5%	0%	0%	40%	8.000	80.000	8.000	
39.58	3%	0%	0%	40%	13.333	80.000	13.333	
39.25	20%	0%	0%	40%	2.000	80.000	2.000	
39.25	20%	0%	0%	20%	1.000	40.000	1.000	
38.98	25%	0%	0%	30%	1.200	60.000	1.200	
38.98	10%	0%	0%	45%	4.500	90.000	4.500	
38.58	20%	0%	0%	40%	2.000	80.000	2.000	
38.58	5%	0%	0%	25%	5.000	50.000	5.000	
38.15	10%	0%	0%	40%	4.000	80.000	4.000	
38.15	10%	0%	0%	40%	4.000	80.000	4.000	
37.83	2%	0%	0%	35%	17.500	70.000	17.500	
37.83	1%	0%	0%	10%	10.000	20.000	10.000	
37.63	1%	0%	0%	10%	10.000	20.000	10.000	

CH-2 Binocular Microscope Mineralogy									
Depth	Biotite Hornblende Sulfides FeO <sub>x</sub> Biotite- Hornblende-								
(ft.)	%	%	%	%	oxide ratio	oxide ratio	Ratio		
37.63	1%	0%	0%	10%	10.000	20.000	10.000		
37.50	1%	0%	0%	10%	10.000 20.000		10.000		
37.50	1%	0%	0%	80%	80.000	160.000	80.000		
37.33	1%	0%	0%	80%	80.000	160.000	80.000		
37.33	1%	0%	0%	80%	80.000	160.000	80.000		
37.10	1%	0%	0%	35%	35.000	70.000	35.000		
37.10	1%	0%	0%	35%	35.000	70.000	35.000		
36.98	0%	0%	0%	7%	14.000	14.000	14.000		
36.98	0%	0%	0%	7%	14.000	14.000	14.000		
36.85	15%	0%	0%	50%	3.333	100.000	3.333		
36.85	15%	0%	0%	60%	4.000	120.000	4.000		
36.58	7%	0%	0%	20%	2.857	40.000	2.857		
36.58	7%	0%	0%	20%	2.857	40.000	2.857		
35.63	7%	0%	0%	20%	2.857	40.000	2.857		
35.63	7%	0%	0%	20%	2.857	40.000	2.857		
35.48	15%	0%	0%	25%	1.667	50.000	1.667		
35.48	15%	0%	0%	25%	1.667	50.000	1.667		
35.23	10%	0%	0%	55%	5.500	110.000	5.500		
35.23	10%	0%	0%	55%	5.500	110.000	5.500		
35.00	10%	0%	0%	55%	5.500	110.000	5.500		
35.00	0%	0%	0%	35%	70.000	70.000	70.000		
14.33	20%	0%	0%	25%	1.250	50.000	1.250		
10.00	20%	0%	0%	25%	1.250	50.000	1.250		
9.63	7%	0%	0%	30%	4.286	60.000	4.286		
6.00	7%	0%	0%	30%	4.286	60.000	4.286		
6.00	1%	0%	0%	10%	10.000	20.000	10.000		
5.81	0%	0%	0%	0%	0.000	0.000	0.000		

CH-4 Binocular Microscope Mineralogy							
Depth (ft)	Biotite	Hornblende	Sulfides	FeO <sub>2</sub> %	Biotite-	Hornblende-	Total
	%	%	%	100x 70	oxide ratio	oxide ratio	Ratio
98.26	40%	0%	0%	5%	0.125	10.000	0.125
97.13	80%	5%	0%	2%	0.025	0.400	0.024
96.38	40%	5%	0%	1%	0.025	0.200	0.022
95.12	60%	7%	0%	2%	0.033	0.286	0.030
94.76	50%	0%	0%	20%	0.400	40.000	0.400
93.98	40%	0%	0%	10%	0.250	20.000	0.250
93.21	20%	0%	0%	1%	0.050	2.000	0.050
86.71	0%	75%	0%	0%	0.000	0.000	0.000
84.96	0%	60%	0%	0%	0.000	0.000	0.000
84.08	20%	45%	0%	1%	0.050	0.022	0.015
83.45	15%	3%	0%	0%	0.000	0.000	0.000
80.68	50%	0%	0%	2%	0.040	4.000	0.040
80.00	40%	0%	0%	7%	0.175	14.000	0.175
77.19	20%	0%	0%	3%	0.150	6.000	0.150
76.46	10%	0%	0%	1%	0.100	2.000	0.100
75.83	10%	20%	0%	0%	0.000	0.000	0.000
75.03	40%	0%	0%	15%	0.375	30.000	0.375
73.53	30%	0%	0%	2%	0.067	4.000	0.067
73.42	40%	0%	0%	0%	0.000	0.000	0.000
73.28	50%	0%	0%	25%	0.500	50.000	0.500
72.53	75%	3%	0%	1%	0.013	0.333	0.013
72.10	1%	0%	0%	0%	0.000	0.000	0.000
66.40	40%	0%	0%	15%	0.375	30.000	0.375
65.73	30%	0%	0%	15%	0.500	30.000	0.500
64.69	30%	2%	0%	15%	0.500	7.500	0.469
64.38	30%	0%	0%	15%	0.500	30.000	0.500
64.15	30%	0%	0%	20%	0.667	40.000	0.667
61.53	15%	0%	0%	15%	1.000	30.000	1.000
60.71	40%	0%	0%	2%	0.050	4.000	0.050
60.00	15%	0%	0%	7%	0.467	14.000	0.467
59.48	30%	2%	0%	0%	0.000	0.000	0.000
57.38	50%	0%	0%	0%	0.000	0.000	0.000
56.44	40%	0%	0%	2%	0.050	4.000	0.050
55.25	70%	0%	0%	0%	0.000	0.000	0.000
54.81	60%	0%	0%	1%	0.017	2.000	0.017
52.88	25%	0%	0%	10%	0.400	20.000	0.400
52.46	25%	0%	0%	10%	0.400	20.000	0.400
51.52	30%	0%	0%	25%	0.833	50.000	0.833
50.79	25%	0%	0%	5%	0.200	10.000	0.200

CH-4 Binocular Microscope Mineralogy							
Depth (ft)	Biotite	Hornblende	Sulfides	FeO <sub>2</sub> %	Biotite-	Hornblende-	Total
Deptii (it.)	%	%	%	1 CO <sub>X</sub> 70	oxide ratio	oxide ratio	Ratio
50.00	20%	0%	0%	25%	1.250	50.000	1.250
49.43	0%	0%	0%	0%	0.000	0.000	0.000
47.79	10%	0%	0%	3%	0.300	6.000	0.300
47.78	50%	0%	0%	15%	0.300	30.000	0.300
46.69	40%	0%	0%	20%	0.500	40.000	0.500
45.48	1%	0%	0%	1%	1.000	2.000	1.000
45.44	0%	0%	0%	1%	2.000	2.000	2.000
45.17	10%	0%	0%	5%	0.500	10.000	0.500
44.91	5%	0%	0%	3%	0.600	6.000	0.600
43.31	2%	0%	0%	10%	5.000	20.000	5.000
42.93	25%	0%	0%	3%	0.120	6.000	0.120
41.69	50%	0%	0%	30%	0.600	60.000	0.600
41.69	25%	0%	0%	15%	0.600	30.000	0.600
40.00	75%	0%	0%	7%	0.093	14.000	0.093
40.00	75%	0%	0%	7%	0.093	14.000	0.093
37.07	2%	0%	0%	20%	10.000	40.000	10.000
37.07	2%	0%	0%	20%	10.000	40.000	10.000
37.02	40%	0%	0%	30%	0.750	60.000	0.750
37.02	40%	0%	0%	30%	0.750	60.000	0.750
36.75	75%	0%	0%	20%	0.267	40.000	0.267
36.75	75%	0%	0%	20%	0.267	40.000	0.267
36.38	30%	0%	0%	60%	2.000	120.000	2.000
36.38	30%	0%	0%	60%	2.000	120.000	2.000
36.08	90%	0%	0%	1%	0.011	2.000	0.011
36.08	90%	0%	0%	1%	0.011	2.000	0.011
35.65	30%	0%	0%	60%	2.000	120.000	2.000
35.65	30%	0%	0%	60%	2.000	120.000	2.000
35.63	40%	0%	0%	25%	0.625	50.000	0.625
35.63	40%	0%	0%	25%	0.625	50.000	0.625
35.38	30%	0%	0%	20%	0.667	40.000	0.667
35.38	60%	0%	0%	20%	0.333	40.000	0.333
35.00	3%	0%	0%	0%	0.000	0.000	0.000
35.00	60%	0%	0%	20%	0.333	40.000	0.333
34.73	60%	0%	0%	10%	0.167	20.000	0.167
34.73	60%	0%	0%	10%	0.167	20.000	0.167
34.33	40%	0%	0%	15%	0.375	30.000	0.375
34.33	30%	0%	0%	25%	0.833	50.000	0.833
34.19	70%	0%	0%	0%	0.000	0.000	0.000
34.19	70%	0%	0%	0%	0.000	0.000	0.000

CH-4 Binocular Microscope Mineralogy							
Denth (ft)	Biotite	Hornblende	Sulfides	FeO <sub>x</sub> %	Biotite-	Hornblende-	Total
	%	%	%	100,70	oxide ratio	oxide ratio	Ratio
33.88	40%	0%	0%	30%	0.750	60.000	0.750
33.88	60%	0%	0%	25%	0.417	50.000	0.417
33.21	40%	0%	0%	50%	1.250	100.000	1.250
33.21	60%	0%	0%	30%	0.500	60.000	0.500
33.17	25%	0%	0%	40%	1.600	80.000	1.600
33.17	30%	0%	0%	50%	1.667	100.000	1.667
31.60	30%	0%	0%	20%	0.667	40.000	0.667
31.60	30%	0%	0%	20%	0.667	40.000	0.667
30.50	10%	0%	0%	0%	0.000	0.000	0.000
30.50	10%	0%	0%	0%	0.000	0.000	0.000
30.17	40%	0%	0%	10%	0.250	20.000	0.250
30.17	50%	0%	0%	10%	0.200	20.000	0.200
30.08	25%	0%	0%	10%	0.400	20.000	0.400
30.08	25%	0%	0%	10%	0.400	20.000	0.400
30.00	10%	0%	0%	5%	0.500	10.000	0.500
30.00	70%	0%	0%	0%	0.000	0.000	0.000
29.83	50%	0%	0%	15%	0.300	30.000	0.300
29.83	50%	0%	0%	15%	0.300	30.000	0.300
29.65	40%	0%	0%	20%	0.500	40.000	0.500
29.65	40%	0%	0%	20%	0.500	40.000	0.500
29.21	20%	0%	0%	70%	3.500	140.000	3.500
29.21	15%	0%	0%	75%	5.000	150.000	5.000
29.17	3%	0%	0%	70%	23.333	140.000	23.333
29.17	30%	0%	0%	50%	1.667	100.000	1.667
29.15	40%	0%	0%	15%	0.375	30.000	0.375
29.15	40%	0%	0%	15%	0.375	30.000	0.375
29.10	70%	0%	0%	7%	0.100	14.000	0.100
29.10	70%	0%	0%	7%	0.100	14.000	0.100
29.04	20%	0%	0%	40%	2.000	80.000	2.000
29.04	20%	0%	0%	40%	2.000	80.000	2.000
28.99	15%	0%	0%	40%	2.667	80.000	2.667
28.99	25%	0%	0%	25%	1.000	50.000	1.000
28.85	30%	0%	0%	25%	0.833	50.000	0.833
28.85	20%	0%	0%	50%	2.500	100.000	2.500
28.77	20%	0%	0%	50%	2.500	100.000	2.500
28.77	20%	0%	0%	50%	2.500	100.000	2.500
28.71	20%	0%	0%	50%	2.500	100.000	2.500
28.71	20%	0%	0%	50%	2.500	100.000	2.500
28.67	3%	0%	0%	50%	16.667	100.000	16.667

CH-4 Binocular Microscope Mineralogy											
Donth (ft)	Biotite	Biotite Hornblende			Biotite-	Hornblende-	Total				
Depth (ft.)	%	%	%	reO <sub>x</sub> %	oxide ratio	oxide ratio	Ratio				
28.67	7%	0%	0%	80%	11.429	160.000	11.429				
28.52 7% 0% 0% 80% 11.429 160.000 11.429											

CH-2 pXRF Results (ppm)								
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr	
99.00	233,437	9,886	507	42,200	119	98	116	
98.13	224,722	19,941	460	58,829	60	194	76	
98.13	283,221	10,372	527	58,052	143	109	214	
98.10	248,975	6,816	550	82,250	187	66	137	
98.10	222,577	6,331	653	71,885	147	63	194	
97.46	348,619	21,924	297	40,579	82	200	193	
96.82	222,387	10,194	472	107,066	289	43	363	
96.82	179,374	8,501	0	78,992	192	45	219	
96.78	245,545	9,011	0	42,364	84	131	93	
96.78	171,278	10,557	0	64,407	147	153	285	
96.58	241,828	16,258	0	33,389	64	201	111	
96.58	223,720	13,007	0	57,623	144	109	90	
96.54	310,961	26,653	0	35,264	41	255	21	
96.54	206,639	11,992	0	59,008	148	122	89	
95.92	224,345	8,170	240	49,657	101	95	137	
95.92	229,528	16,577	498	70,404	107	244	106	
95.17	223,932	10,562	733	44,532	151	262	172	
95.17	207,038	8,054	823	46,169	164	276	147	
94.63	220,962	9,027	1,602	60,781	144	137	151	
94.63	228,878	8,154	303	53,008	160	163	247	
93.91	376,632	26,574	0	22,382	68	261	102	
93.20	350,695	16,313	0	27,034	101	303	177	
92.48	227,089	20,971	294	55,705	145	148	208	
92.48	244,801	16,204	465	60,911	185	164	228	
91.60	338,009	10,144	0	12,174	39	165	101	
91.60	260,237	16,947	0	46,230	140	196	223	
90.85	228,475	42,027	1,554	52,605	167	91	196	
90.85	233,551	12,027	408	42,656	133	124	134	
90.00	232,384	13,796	398	43,673	136	124	196	
90.00	200,498	15,236	366	46,164	153	130	179	
89.31	220,508	19,920	290	42,223	164	125	262	
89.31	233,318	18,525	347	41,874	175	125	314	
88.38	253,448	11,330	0	33,713	122	94	157	
88.38	306,366	9,653	0	44,735	134	157	283	
87.58	239,824	9,644	277	37,861	112	119	362	
87.58	209,759	10,108	226	51,407	143	189	279	
87.50	246,805	10,032	391	58,121	180	233	194	

APPENDIX C: Tabular pXRF Results

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
87.50	238,181	8,373	393	57,695	135	73	363		
87.42	212,597	8,624	615	84,390	249	116	513		
87.42	238,896	10,206	434	60,797	179	107	323		
87.31	256,058	27,867	662	49,311	102	1,064	184		
87.31	291,317	40,212	0	49,456	86	1,350	183		
87.29	276,320	58,339	1,073	36,732	0	2,519	215		
87.29	144,922	186,003	0	30,767	33	2,540	111		
87.09	166,864	152,091	0	46,930	69	3,118	151		
87.09	162,766	185,440	0	26,288	33	3,623	188		
86.47	278,851	127,591	0	33,400	123	2,382	208		
85.84	194,210	18,626	0	60,787	176	401	493		
85.84	203,476	11,215	0	39,598	107	221	289		
85.56	212,288	5,066	0	17,412	39	24	494		
85.56	229,003	8,699	1,543	96,567	342	18	20		
85.46	302,947	2,363	0	15,272	21	0	456		
85.46	286,465	6,086	0	36,268	59	5	420		
85.00	286,465	6,086	0	36,268	59	5	420		
85.00	259,887	30,927	589	72,186	70	150	16		
84.98	281,768	21,711	508	46,542	168	267	227		
84.98	243,700	36,190	383	59,167	15	141	16		
84.96	200,123	32,803	778	68,875	29	83	20		
84.96	249,850	37,038	935	66,997	23	150	20		
84.88	212,233	13,006	499	75,344	213	91	19		
84.88	183,825	10,905	0	67,921	217	153	9		
84.75	189,970	14,954	335	44,078	100	350	84		
84.75	163,024	12,586	1,183	101,267	310	64	70		
84.04	284,336	7,800	573	39,485	50	152	620		
84.04	157,122	8,404	519	53,660	54	179	231		
83.96	207,277	23,719	571	41,503	47	166	42		
83.96	306,749	34,386	0	31,406	9	212	46		
83.88	262,973	10,149	831	55,543	84	229	196		
83.88	194,980	18,593	0	48,538	112	173	13		
83.75	165,821	12,900	0	16,041	29	173	21		
83.75	208,229	12,705	3,351	43,431	79	187	107		
83.17	164,547	28,292	375	54,139	43	95	26		
83.17	215,682	25,843	0	39,864	34	400	24		
82.83	198,049	22,272	0	37,850	53	317	333		
82.83	218,239	40,965	818	59,335	61	144	22		
82.42	184,951	12,986	1,061	78,398	88	188	92		
82.42	234,220	45,056	1,096	61,200	42	155	25		

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Са	Mn	Fe	Rb	Sr	Zr		
82.27	180,581	19,776	758	68,023	226	131	28		
82.27	182,120	22,695	474	62,268	233	125	48		
82.23	211,977	18,415	464	30,374	69	147	193		
82.23	197,356	19,574	0	22,907	57	158	238		
81.62	334,312	37,006	690	50,584	81	218	227		
81.00	161,198	8,354	365	64,454	133	58	94		
81.00	202,765	10,542	665	64,900	154	134	221		
80.00	287,391	16,713	0	40,005	68	214	229		
80.00	192,757	13,112	391	71,231	122	106	631		
79.06	215,436	9,365	0	52,942	234	68	1,572		
79.06	220,563	9,732	0	43,861	223	68	1,590		
78.53	301,117	43,188	464	78,456	66	305	171		
78.00	183,877	25,103	0	69,053	69	110	125		
78.00	204,966	23,807	594	87,663	94	126	152		
77.67	187,365	16,633	0	65,401	83	137	166		
77.67	218,193	18,734	0	62,307	81	206	227		
76.98	344,504	15,180	408	40,217	53	412	264		
76.28	273,027	53,265	521	101,190	73	242	187		
75.58	138,613	44,451	0	40,927	85	52	95		
75.58	167,183	86,098	0	51,517	49	68	28		
75.00	190,557	49,772	682	64,159	43	133	19		
75.00	154,344	50,200	0	34,924	16	81	13		
74.58	159,487	8,140	0	58,543	158	53	45		
74.58	187,091	29,767	0	55,050	96	158	162		
73.96	251,808	64,455	585	81,353	17	85	14		
73.33	179,236	30,688	542	80,484	167	115	281		
73.33	163,475	29,606	0	89,597	97	147	212		
72.58	185,240	15,000	766	83,488	76	126	20		
72.58	179,839	24,035	777	86,131	31	59	17		
71.64	277,821	61,793	974	82,456	6	279	20		
70.69	179,491	12,939	0	54,248	175	92	143		
70.69	158,496	19,379	0	33,600	83	199	16		
70.52	156,806	34,949	0	29,113	0	170	19		
70.52	229,900	43,535	0	33,838	0	198	16		
70.00	167,663	22,165	0	48,255	132	136	17		
70.00	196,293	43,617	724	67,226	135	108	87		
69.46	259,718	53,160	1,015	50,332	17	167	24		
69.46	225,777	35,876	855	59,170	64	132	15		
69.35	240,981	26,876	875	73,794	173	157	30		
69.35	198,863	45,762	1,239	58,765	19	172	17		

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
69.27	281,600	59,050	1,153	52,090	22	222	15		
69.27	192,839	36,556	0	37,028	20	139	10		
69.08	218,282	45,038	1,997	45,043	8	154	12		
69.08	198,527	40,486	1,139	38,120	10	178	9		
68.96	202,161	37,929	805	34,308	10	179	12		
68.96	258,080	53,025	1,212	50,152	12	198	11		
68.60	191,631	13,502	775	56,582	145	148	59		
68.60	214,911	13,223	1,415	78,906	197	154	270		
68.00	230,230	17,007	0	27,656	57	373	43		
68.00	282,527	16,541	1,380	40,691	92	318	12		
67.50	235,664	21,174	853	72,726	196	253	230		
67.50	224,728	30,412	0	38,795	87	306	197		
67.42	202,320	36,668	3,023	58,743	31	117	10		
67.42	217,754	45,238	1,186	86,282	9	104	12		
67.13	270,273	10,100	0	62,457	124	177	604		
67.13	194,494	9,530	0	38,164	34	150	374		
66.92	220,162	14,784	649	44,318	75	68	188		
66.92	211,864	5,480	0	37,745	104	10	84		
66.75	240,368	7,609	0	91,647	91	50	153		
66.75	174,936	8,612	589	57,429	144	22	77		
66.54	215,949	4,895	1,015	47,800	123	14	215		
66.54	214,521	8,632	766	67,008	184	23	123		
66.29	230,809	21,004	422	70,201	124	110	203		
66.29	227,409	15,047	401	76,723	121	63	183		
66.21	176,676	16,179	0	36,196	140	116	151		
66.21	265,168	15,644	3,268	72,576	309	95	189		
65.96	250,531	8,647	1,181	86,973	643	60	24		
65.96	235,559	14,270	547	92,591	246	147	183		
65.50	254,394	7,872	1,160	78,842	367	42	38		
65.50	285,219	12,287	0	57,702	152	141	184		
65.00	272,906	25,091	0	58,990	123	124	163		
65.00	239,960	21,813	0	51,227	150	204	221		
64.00	177,965	9,645	1,221	125,393	55	98	98		
64.00	209,495	25,243	0	57,784	70	78	121		
62.60	258,321	43,825	0	31,886	25	300	444		
62.60	237,308	38,812	0	39,576	30	286	448		
61.60	207,408	10,817	568	74,161	219	62	217		
61.60	190,540	11,097	0	55,031	151	131	209		
60.60	206,388	14,657	0	47,612	109	169	164		
60.60	243,356	15,534	0	40,717	118	156	251		

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
59.65	336,920	12,734	0	20,267	6	30	14		
59.65	280,093	9,213	0	30,458	11	19	32		
59.54	260,231	57,794	474	42,794	35	258	100		
59.54	281,308	44,505	0	40,839	25	162	83		
59.48	233,531	21,137	844	36,628	69	143	85		
59.48	177,037	14,625	0	62,085	113	102	181		
59.23	195,015	13,653	1,044	77,621	127	57	191		
59.23	168,480	8,424	299	81,506	90	58	130		
59.08	165,691	5,972	218	97,074	114	40	151		
59.08	207,931	17,627	411	79,683	212	261	208		
58.71	201,373	16,606	0	9,041	0	282	9		
58.71	189,650	18,179	0	21,629	7	293	10		
58.58	249,430	49,260	540	64,366	22	391	119		
58.58	229,235	44,157	690	65,154	20	396	120		
58.35	180,008	18,985	0	42,769	95	233	183		
58.35	198,260	21,127	0	52,442	88	241	262		
58.15	226,783	10,756	0	40,949	141	215	156		
58.15	232,683	9,985	0	46,469	186	197	139		
58.02	213,457	18,909	0	31,827	69	246	311		
58.02	148,244	14,070	0	31,082	56	167	342		
57.58	175,565	8,402	0	50,500	148	125	99		
57.58	208,789	23,028	346	55,232	63	285	128		
57.38	247,653	40,679	1,421	80,240	31	422	149		
57.38	174,856	35,927	697	62,198	34	422	164		
57.23	191,430	39,115	1,052	60,446	26	485	129		
57.23	208,704	39,256	0	68,675	31	368	109		
57.15	271,062	51,499	909	83,475	25	376	162		
57.15	236,882	50,872	593	81,922	21	301	129		
56.96	233,228	32,589	598	62,412	43	358	116		
56.96	234,622	45,509	1,041	88,371	19	290	118		
56.92	257,017	29,359	890	72,197	61	359	139		
56.92	256,938	39,863	1,468	70,648	23	324	127		
56.90	197,993	34,228	0	51,233	26	294	101		
56.90	239,347	37,540	1,271	116,806	18	378	147		
56.87	155,945	16,114	2,743	210,495	32	319	74		
56.87	239,955	44,105	1,075	76,166	18	347	135		
56.85	270,623	44,650	1,023	67,570	41	578	69		
56.85	220,598	41,151	846	65,774	20	288	104		
56.83	228,688	32,855	613	62,092	31	349	124		
56.83	238,884	34,387	1,530	82,485	51	310	121		
CH-2 pXRF Results (ppm)									
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Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
56.58	254,311	25,093	0	33,931	51	341	214		
56.58	177,040	14,254	0	46,108	92	195	138		
55.75	210,806	10,135	0	54,442	208	115	108		
55.75	162,173	9,120	0	46,717	177	123	188		
55.00	194,912	12,579	352	41,776	135	138	129		
55.00	244,732	21,083	884	40,510	74	293	81		
54.75	203,295	12,536	0	49,289	138	160	270		
54.75	218,393	16,266	1,079	72,477	103	223	126		
54.38	176,399	12,947	0	42,627	95	166	271		
54.38	193,199	14,134	0	49,625	107	195	113		
54.17	295,072	29,737	741	73,618	43	272	151		
54.17	240,211	32,924	0	63,806	25	231	119		
54.08	244,149	31,057	707	66,045	37	225	130		
54.08	180,784	28,318	579	72,279	32	270	135		
53.88	226,667	34,257	1,123	49,417	15	249	82		
53.88	243,435	16,300	487	67,125	183	230	117		
53.71	213,715	17,908	0	66,395	74	327	224		
53.71	241,884	7,846	0	41,072	95	147	96		
53.25	234,977	19,723	306	70,360	127	398	193		
53.25	200,457	25,771	3,896	109,878	114	455	82		
52.58	261,985	25,093	0	54,786	97	462	120		
52.58	256,584	10,266	0	42,902	110	361	136		
52.21	198,687	50,805	2,150	51,317	0	397	68		
52.21	241,194	12,253	0	46,150	106	355	274		
52.17	178,410	9,485	640	51,393	206	251	171		
52.17	280,664	13,652	0	56,478	141	294	132		
52.00	263,658	10,334	0	49,275	120	296	335		
52.00	239,428	10,390	571	53,996	130	276	277		
51.65	193,061	10,373	0	43,453	89	446	205		
51.65	249,152	13,021	463	64,818	160	406	259		
51.48	193,268	10,012	0	25,386	68	693	194		
51.48	204,861	9,737	0	47,015	170	397	107		
51.21	176,600	11,706	0	30,776	83	287	435		
51.21	287,802	14,730	0	39,499	74	302	443		
50.92	261,343	37,133	0	12,713	26	475	64		
50.92	244,875	30,377	0	22,227	43	327	122		
50.75	305,609	13,919	0	42,021	88	230	277		
50.75	160,442	10,307	0	54,674	145	226	274		
50.50	229,907	13,329	0	34,138	67	312	323		
50.50	180,554	11,293	0	42,358	120	253	417		

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
50.25	197,854	11,313	783	53,210	50	176	470		
50.25	254,799	13,593	592	37,557	30	139	504		
50.00	221,181	12,476	0	37,252	101	392	260		
50.00	180,867	9,846	454	49,808	121	272	231		
49.67	301,960	12,950	732	26,314	42	266	292		
49.67	315,530	19,039	450	15,811	26	379	323		
49.58	212,252	7,558	2,979	86,734	117	186	150		
49.58	276,384	13,052	364	71,200	234	365	160		
49.50	190,362	8,076	0	64,770	65	76	278		
49.50	215,795	6,236	0	52,481	34	39	76		
49.21	195,736	9,208	0	66,745	85	190	225		
49.21	288,322	4,616	0	39,910	51	72	43		
48.90	306,242	11,857	0	36,989	72	239	295		
48.90	226,258	11,670	0	44,258	73	217	243		
48.67	227,773	11,281	0	40,514	108	230	279		
48.67	259,071	10,553	363	40,814	81	234	416		
48.38	249,766	15,245	357	56,890	109	244	261		
48.38	189,904	8,158	0	46,811	159	119	147		
48.21	280,787	11,598	0	29,756	60	298	56		
48.21	190,866	19,546	0	32,883	98	293	141		
48.00	300,858	13,988	0	46,201	111	235	410		
48.00	240,922	8,447	439	50,111	184	304	199		
47.75	247,480	14,049	727	39,313	97	256	297		
47.75	230,501	10,929	1,088	53,996	170	226	264		
47.56	199,532	24,767	0	32,067	88	461	361		
47.56	235,506	14,423	0	47,008	172	312	223		
47.40	187,739	24,931	0	39,404	101	990	169		
47.40	242,785	19,610	0	28,194	70	692	159		
47.08	199,552	17,081	0	25,475	89	693	541		
47.08	199,088	16,415	0	42,637	92	811	256		
46.56	219,717	11,587	259	41,426	111	389	302		
46.56	269,936	17,136	0	64,631	221	851	317		
46.33	207,401	15,409	0	45,052	113	885	272		
46.33	242,051	23,828	0	41,326	94	1,082	267		
45.92	212,659	7,378	0	10,531	127	313	25		
45.92	260,820	7,685	0	8,771	85	271	12		
45.67	229,133	7,914	0	20,488	166	278	17		
45.67	205,250	21,292	277	57,662	128	1,103	102		
45.38	205,890	16,389	0	53,274	137	1,155	100		
45.38	187,844	8,374	618	51,339	209	626	211		

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Са	Mn	Fe	Rb	Sr	Zr		
45.00	215,404	6,330	582	49,576	173	537	251		
45.00	235,667	3,754	592	44,247	143	444	282		
44.79	131,798	4,017	875	38,757	134	477	260		
44.79	182,524	4,271	0	43,558	161	590	288		
44.67	198,686	5,286	1,090	42,251	190	559	420		
44.67	224,185	6,232	3,701	62,174	252	807	340		
44.46	205,319	6,150	460	43,885	141	529	257		
44.46	208,037	5,738	0	27,939	125	670	443		
44.25	143,514	9,503	0	33,207	166	814	181		
44.25	182,219	9,893	330	50,175	183	760	200		
43.90	181,649	11,228	377	51,383	340	935	118		
43.90	253,664	9,519	0	40,550	180	742	299		
43.73	172,704	11,686	0	54,342	225	904	108		
43.73	258,488	3,006	0	26,293	153	372	90		
43.00	293,044	4,089	318	38,043	153	819	205		
43.00	153,826	6,539	0	21,288	94	490	173		
42.50	181,672	9,054	967	70,251	219	1,038	126		
42.50	176,414	2,993	824	48,179	146	93	339		
42.21	178,340	2,447	0	49,987	122	183	189		
42.21	151,003	2,915	0	35,269	141	345	116		
42.04	142,674	2,253	4,322	92,819	98	386	120		
42.04	182,452	2,246	1,172	52,942	141	461	351		
41.85	273,175	0	0	49,072	178	583	258		
41.85	206,377	0	2,386	41,784	176	721	338		
41.65	182,954	2,843	0	29,434	166	593	319		
41.65	200,353	2,460	0	33,602	119	481	358		
41.40	163,249	2,633	0	25,252	96	335	299		
41.40	254,849	0	0	11,678	205	954	493		
40.75	185,079	2,119	360	56,340	206	809	237		
40.75	220,679	0	492	32,986	108	447	378		
40.00	192,939	4,142	643	42,694	171	481	328		
40.00	155,136	2,953	0	42,566	177	17	173		
39.83	191,378	2,025	0	39,357	126	12	455		
39.83	203,555	0	0	50,517	141	16	379		
39.58	182,326	2,564	0	29,802	115	24	221		
39.58	250,410	0	0	36,640	78	16	332		
39.25	194,269	2,510	0	34,567	148	21	163		
39.25	146,474	2,768	0	34,851	107	76	135		
38.98	150,098	2,331	0	41,882	137	14	271		
38.98	166,904	2,176	0	58,637	118	11	252		

CH-2 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
38.58	170,969	2,796	0	38,289	132	34	212		
38.58	161,526	2,437	0	40,269	140	9	107		
38.15	211,759	0	2,357	54,545	123	4	360		
38.15	222,351	2,335	779	43,521	159	6	290		
37.83	252,585	0	1,119	65,978	230	35	321		
37.83	189,364	2,498	0	45,182	157	203	211		
37.63	203,787	3,115	0	52,275	155	345	154		
37.63	267,068	0	0	36,423	173	657	419		
37.50	197,071	3,204	1,432	42,188	238	888	197		
37.50	197,672	0	1,347	92,132	65	14	195		
37.33	154,934	2,105	1,132	91,398	20	0	181		
37.33	197,860	0	13,176	66,101	89	3	96		
37.10	216,097	0	0	60,147	107	6	181		
37.10	193,539	1,947	0	53,070	97	4	163		
36.98	221,188	0	0	3,524	21	33	45		
36.98	268,880	0	0	14,352	32	102	44		
36.85	191,200	2,374	0	42,816	111	29	342		
36.85	248,384	0	614	69,509	244	20	687		
36.58	287,862	0	0	42,324	186	21	557		
36.58	265,416	0	0	45,251	184	23	396		
35.63	313,947	0	2,680	34,669	72	5	585		
35.63	272,426	0	532	46,704	35	2	259		
35.48	283,571	0	484	57,191	229	25	299		
35.48	253,077	0	636	57,862	209	18	232		
35.23	196,367	2,831	0	36,128	154	16	319		
35.23	274,403	0	483	71,083	281	23	245		
35.00	220,781	0	448	52,327	173	5	216		
35.00	320,442	0	1,482	76,216	93	9	27		
30.00	185,310	2,783	401	112,472	22	4	132		
30.00	202,946	0	612	50,069	158	18	186		
25.00	181,286	2,283	1,251	68,782	155	22	269		
20.00	242,597	0	531	41,387	77	21	277		
15.00	217,796	0	967	43,639	85	21	330		
15.00	177,335	2,408	0	49,286	109	30	275		
14.33	177,357	2,455	0	46,091	62	26	277		
14.33	271,744	0	583	70,841	123	21	217		
10.00	195,310	2,147	0	54,477	142	9	221		
10.00	257,467	0	6,540	89,599	217	20	449		
9.63	188,688	2,044	16,674	57,220	166	29	234		
9.63	189,850	2,210	0	55,420	132	31	211		

CH-2 pXRF Results (ppm)										
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr			
6.00	194,298	0	1,962	50,862	106	80	132			
6.00	203,155	0	1,283	50,895	111	14	119			
5.81	249,875	0	0	44,916	104	21	135			
5.81	177,041	0	0	20,928	38	13	62			
5.00	196,946	0	689	74,095	148	0	395			
3.00	192,185	2,416	0	41,958	66	39	327			
1.50	207,099	0	0	63,001	73	27	299			
0.00	173,833	0	0	71,974	77	10	176			

CH-4 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
100.00	222,509	57,394	756	80,797	25	86	15		
99.00	192,000	24,457	0	4,329	15	227	35		
98.26	176,982	11,797	0	54,427	151	18	25		
98.26	223,763	10,373	0	49,239	121	118	23		
98.00	216,403	30,876	0	4,903	12	349	17		
97.13	208,092	39,078	629	113,430	44	97	228		
97.13	201,657	29,350	0	88,573	84	153	235		
97.00	147,789	27,939	0	36,543	17	393	75		
96.38	280,116	26,316	0	19,519	0	799	45		
96.38	256,595	66,861	591	92,871	8	341	248		
96.00	153,377	62,595	917	90,288	25	138	173		
95.12	265,846	42,114	900	93,463	127	170	223		
95.12	235,963	24,781	560	98,235	201	25	184		
95.00	191,414	24,769	2,703	51,716	49	178	126		
94.76	251,679	23,073	534	67,715	76	105	243		
94.76	234,005	16,989	0	84,239	138	94	352		
94.00	212,685	15,013	0	14,557	16	184	35		
93.98	321,016	5,964	0	39,790	19	54	36		
93.98	269,126	28,339	0	39,795	26	98	77		
93.21	186,092	60,066	970	66,835	0	385	129		
93.21	207,782	44,459	973	69,885	14	367	127		
93.00	184,464	30,271	0	41,710	41	208	307		
92.00	149,969	46,438	0	60,522	48	540	104		
91.71	231,324	33,909	1,824	100,811	128	84	353		
91.71	196,689	18,793	0	50,113	51	275	79		
91.00	186,061	22,389	0	10,646	29	320	505		
90.00	213,162	66,086	873	67,905	12	143	20		
90.00	243,620	56,555	0	50,738	11	196	20		
89.00	251,507	62,811	951	69,247	11	131	26		
88.00	232,076	64,881	951	67,045	11	187	26		
87.71	219,332	97,818	757	68,150	15	158	24		
87.71	230,484	102,272	1,031	74,186	16	146	26		
86.71	179,527	83,104	0	77,141	14	57	25		
86.71	229,688	73,663	0	89,952	13	105	27		
85.84	277,535	61,021	560	68,011	13	127	33		
84.96	238,610	71,389	709	64,936	12	126	17		
84.96	215,242	62,485	774	57,869	13	129	20		
84.08	195,920	67,024	0	59,405	12	66	18		
84.08	236,641	88,580	918	70,086	13	107	21		
83.45	247,643	29,080	0	3,529	11	309	17		

CH-4 pXRF Results (ppm)									
Depth (ft.)	Si	Са	Mn	Fe	Rb	Sr	Zr		
83.45	286,118	27,133	0	7,631	22	327	17		
82.62	259,323	66,213	659	66,050	11	203	24		
81.79	242,516	15,644	889	98,543	384	8	15		
81.79	197,146	11,535	572	89,713	356	14	18		
81.24	273,304	37,364	0	35,323	10	603	93		
80.68	223,001	85,611	0	36,816	78	404	109		
80.68	252,278	74,922	0	41,311	107	446	174		
80.00	291,846	5,568	0	38,264	59	58	177		
80.00	183,420	16,115	0	56,179	125	227	171		
79.00	259,872	20,869	0	44,700	88	238	145		
78.00	277,821	30,069	0	52,275	122	205	146		
77.19	226,694	100,923	881	65,547	38	170	36		
77.19	257,093	44,382	0	39,778	33	274	82		
76.46	344,819	25,339	0	7,053	21	354	53		
76.46	299,028	25,505	0	10,922	30	348	59		
75.83	232,684	95,893	0	36,012	12	385	77		
75.83	218,532	103,860	733	55,457	21	380	135		
75.03	199,098	9,940	0	73,230	190	106	167		
75.03	231,837	38,501	0	53,923	181	117	242		
74.25	318,230	29,035	0	40,379	85	270	230		
73.53	241,108	9,550	0	49,296	158	291	151		
73.53	242,253	17,461	750	39,109	52	407	319		
73.42	189,870	6,718	0	44,977	47	92	74		
73.42	232,484	14,236	0	57,503	173	310	217		
73.28	226,580	9,947	0	61,169	152	841	203		
73.28	247,147	12,434	0	70,249	183	910	164		
72.53	263,615	17,507	0	56,798	198	719	25		
72.53	222,033	15,403	0	65,485	243	606	54		
72.10	184,871	208,323	0	32,180	87	2,319	120		
72.10	162,714	201,036	0	26,897	88	2,015	95		
72.00	299,897	104,648	0	24,102	105	1,409	216		
71.00	327,885	77,346	0	18,194	84	997	334		
70.00	300,377	93,164	0	3,649	64	742	271		
70.00	271,336	93,374	0	8,047	96	1,032	209		
69.00	252,102	120,836	0	20,589	101	1,662	304		
68.00	191,737	150,296	0	26,959	85	1,717	175		
67.00	285,979	27,348	0	36,337	123	387	225		
66.40	323,744	32,089	0	38,757	101	432	237		
66.40	273,490	36,607	0	22,578	100	339	266		
65.73	209,548	12,057	0	52,641	209	69	265		

CH-4 pXRF Results (ppm)									
Depth (ft.)	Si	Са	Mn	Fe	Rb	Sr	Zr		
65.73	236,959	16,363	0	61,426	145	289	192		
65.21	268,560	25,896	0	50,327	155	379	241		
64.69	206,369	18,775	883	95,250	125	179	207		
64.69	277,615	20,847	0	36,623	83	361	518		
64.38	215,970	15,223	0	52,152	179	115	251		
64.38	274,815	18,589	0	51,219	161	228	356		
64.15	249,295	23,151	536	73,850	193	200	328		
64.15	194,952	19,599	561	63,975	171	145	320		
63.50	301,663	29,552	0	17,941	38	398	96		
62.93	198,933	24,910	0	70,240	53	105	29		
62.93	255,750	31,708	627	69,457	42	196	28		
62.25	272,780	33,170	0	4,458	29	353	33		
61.53	348,560	16,147	0	3,449	18	301	28		
61.53	280,555	18,091	0	7,696	32	311	48		
60.71	337,523	6,098	0	17,217	54	163	22		
60.71	319,444	3,255	0	30,971	56	50	19		
60.00	325,084	12,009	0	6,295	17	151	24		
60.00	364,272	22,085	0	4,860	15	360	21		
59.48	276,829	20,572	0	53,778	153	403	330		
59.48	252,798	18,147	0	50,141	116	335	283		
59.00	305,869	19,106	0	9,312	12	339	42		
58.00	254,880	13,309	3,616	112,315	200	180	500		
57.38	205,354	26,979	2,291	105,953	173	9	335		
57.38	258,975	19,587	928	53,986	80	219	186		
56.44	387,269	17,134	0	12,502	45	618	94		
56.44	307,699	13,989	0	38,090	99	519	138		
56.00	232,766	7,726	1,584	80,919	139	164	195		
55.25	242,885	13,655	0	90,319	257	41	197		
55.25	255,241	3,072	0	64,847	178	2	216		
54.81	229,875	7,307	0	67,132	166	152	359		
54.81	221,479	4,786	0	71,708	152	38	526		
53.81	292,497	12,475	771	61,374	142	277	237		
52.88	242,810	4,523	0	60,617	180	130	255		
52.88	337,224	7,886	0	17,119	122	234	39		
52.46	372,270	10,458	0	21,818	38	112	65		
52.46	295,813	12,425	0	54,442	119	165	233		
51.52	228,170	2,590	0	73,824	143	52	254		
51.52	214,392	2,672	0	70,954	110	0	107		
50.79	291,907	17,569	0	42,604	106	51	167		
50.79	215,077	28,178	0	82,516	162	8	220		

CH-4 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
50.00	214,330	5,935	0	61,592	156	107	213		
50.00	298,881	10,322	560	51,545	147	330	231		
49.43	362,889	7,870	0	3,869	47	262	20		
49.43	378,146	7,925	0	4,673	48	327	19		
48.50	398,787	3,992	0	1,676	11	237	18		
47.79	216,562	4,856	0	49,272	94	147	95		
47.79	286,033	8,043	0	44,132	59	216	72		
47.78	247,125	20,256	0	57,237	113	263	250		
47.78	298,159	5,071	0	41,515	87	106	80		
47.24	313,811	4,792	1,371	62,051	121	266	149		
46.69	294,973	3,077	0	20,657	72	43	16		
46.69	331,668	18,315	0	12,748	72	68	17		
46.09	363,130	12,535	0	2,862	19	380	21		
45.48	382,295	0	0	9,674	38	21	17		
45.48	394,341	0	0	2,133	11	172	19		
45.44	354,537	7,642	0	2,240	97	358	17		
45.44	262,848	10,595	0	1,608	28	296	22		
45.17	313,906	3,637	0	6,335	24	114	19		
45.17	319,657	10,338	0	8,529	28	334	17		
44.91	374,643	12,384	0	1,476	22	379	19		
44.91	337,686	9,331	0	1,728	15	286	18		
44.11	377,694	7,856	0	3,570	55	320	20		
43.31	342,767	8,022	0	4,939	44	272	20		
43.31	286,094	8,473	0	5,591	36	234	23		
42.93	360,822	10,313	0	11,723	32	165	17		
42.93	311,453	8,123	0	18,776	50	176	33		
42.31	272,863	23,472	0	45,259	132	181	263		
41.69	260,756	31,843	0	55,467	143	156	272		
41.69	245,317	29,261	0	28,030	24	1	34		
40.85	320,647	29,891	0	17,098	51	338	89		
40.00	218,388	4,555	794	72,260	183	16	379		
40.00	190,795	5,654	0	77,339	237	42	474		
39.00	282,940	3,150	0	59,493	148	191	168		
38.00	384,651	0	0	13,259	34	82	68		
37.07	285,234	4,491	1,325	68,596	224	175	179		
37.07	240,703	4,868	798	45,708	146	178	97		
37.02	241,277	4,916	0	34,570	129	241	71		
37.02	221,143	5,115	800	40,382	126	198	39		
36.75	197,127	4,117	544	84,576	192	34	174		
36.75	215,185	5,682	0	82,517	199	103	218		

CH-4 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
36.38	158,889	6,205	859	84,269	132	103	169		
36.38	178,730	6,907	0	82,777	182	107	257		
36.08	247,851	10,354	0	67,501	153	138	285		
36.08	272,690	20,473	0	39,946	106	244	191		
35.65	191,193	5,517	2,094	115,321	151	60	128		
35.65	196,433	8,825	0	93,974	157	144	330		
35.63	229,867	4,369	1,946	78,041	159	24	259		
35.63	193,513	7,862	462	107,287	130	155	258		
35.38	244,922	7,122	476	59,931	92	111	206		
35.38	202,611	11,151	0	2,981	0	188	22		
35.00	134,975	2,475	0	9,872	13	42	8		
35.00	216,460	5,165	0	44,774	84	72	266		
34.73	204,666	4,928	496	32,841	72	215	65		
34.73	221,274	9,004	1,457	68,034	141	235	315		
34.33	232,020	6,828	0	55,146	110	119	287		
34.33	218,329	9,313	1,751	62,480	134	119	275		
34.19	259,489	6,125	0	61,903	140	136	251		
34.19	194,381	5,649	0	56,597	134	61	318		
33.88	167,407	4,912	2,596	103,970	158	51	288		
33.88	187,972	4,215	692	101,196	197	15	298		
33.21	212,424	3,672	459	75,808	180	28	231		
33.21	195,960	5,104	807	75,270	147	91	177		
33.17	201,158	5,057	4,973	84,376	213	63	226		
33.17	155,820	4,330	559	45,528	107	96	109		
32.39	297,758	4,966	0	57,554	116	154	213		
31.60	156,727	4,113	2,309	66,558	113	23	124		
31.60	196,046	5,023	4,213	86,630	199	71	262		
31.05	301,685	4,332	797	64,052	144	145	210		
30.50	243,442	3,149	0	56,832	59	189	112		
30.50	221,194	4,271	0	64,152	111	152	218		
30.17	296,416	7,431	699	62,423	164	211	210		
30.17	210,782	4,833	0	40,265	88	191	77		
30.08	230,399	3,564	0	29,206	69	99	22		
30.08	241,400	4,825	0	28,152	52	112	31		
30.00	316,650	8,810	0	6,681	31	344	21		
30.00	263,735	3,878	837	71,351	143	193	127		
29.83	234,223	6,609	0	59,366	152	177	295		
29.83	246,601	3,584	1,692	89,443	207	29	326		
29.65	252,391	4,147	718	88,362	206	29	235		
29.65	214,930	4,524	0	54,424	131	79	353		

CH-4 pXRF Results (ppm)									
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr		
29.21	185,244	4,897	805	79,030	106	135	294		
29.21	217,306	0	0	8,900	17	2	50		
29.17	195,642	0	0	12,867	12	2	65		
29.17	175,019	6,894	0	25,707	42	194	113		
29.15	151,872	4,720	0	55,296	124	99	240		
29.15	150,003	5,839	1,345	59,528	105	122	303		
29.10	172,733	6,545	0	37,169	71	177	181		
29.10	179,306	6,620	0	49,753	130	116	458		
29.04	166,229	6,235	0	38,744	99	200	130		
29.04	194,565	7,447	2,105	61,863	119	181	188		
28.99	206,827	4,598	4,644	85,296	132	129	177		
28.99	157,876	5,529	2,533	65,151	110	89	170		
28.85	159,994	8,336	0	47,980	110	247	231		
28.85	145,786	6,470	0	35,229	73	207	153		
28.77	157,363	6,018	1,736	55,146	128	170	197		
28.77	134,183	2,256	0	12,982	0	10	32		
28.71	132,982	2,003	0	11,383	0	3	20		
28.71	164,215	6,243	677	65,796	103	159	257		
28.67	178,146	5,832	2,920	49,277	112	103	314		
28.67	139,077	2,829	0	15,545	23	22	51		
28.52	133,730	2,184	0	13,079	11	7	30		
28.00	127,235	7,609	0	37,960	53	52	74		
27.00	128,735	3,990	2,038	82,002	101	44	257		
26.00	199,308	3,417	2,281	69,153	171	31	921		
25.00	160,577	4,132	1,103	82,022	132	37	371		
24.00	129,122	6,090	1,025	45,255	14	18	27		
23.00	140,115	10,536	2,956	71,118	20	16	25		
22.00	140,667	3,835	2,670	58,625	50	19	74		
21.00	149,365	14,975	4,053	64,016	16	26	26		
20.00	196,843	0	0	5,136	30	32	148		
19.00	176,312	0	0	6,140	16	17	60		
18.00	178,397	3,348	0	36,423	129	32	34		
17.00	131,783	2,871	0	44,737	160	13	232		
16.00	174,703	2,111	970	89,788	198	8	222		
15.00	174,268	2,123	0	48,332	169	8	239		
14.00	152,641	2,462	0	43,118	109	7	232		
13.00	151,925	2,464	0	38,614	105	4	120		
12.00	159,226	2,258	916	53,964	140	41	293		
11.00	159,095	0	1,824	52,064	99	498	277		
10.00	228,150	0	557	52,759	79	161	394		

	CH-4 pXRF Results (ppm)										
Depth (ft.)	Si	Ca	Mn	Fe	Rb	Sr	Zr				
9.00	145,196	0	1,230	70,107	60	52	168				
8.00	164,869	0	1,132	33,166	46	5	406				
7.00	141,804	2,117	560	63,929	50	216	248				
6.00	141,141	2,583	646	109,796	18	60	171				
5.00	200,357	0	0	74,038	41	28	689				
4.00	175,122	0	0	82,244	70	70	255				
3.00	213,645	0	1,589	66,505	37	41	318				
2.00	231,389	0	726	55,356	75	63	547				
1.00	207,175	0	858	76,184	29	58	570				
0.00	240,163	0	998	39,485	78	52	473				