METHODOLOGICAL DEVELOPMENTS FOR THE GEOCHEMICAL ANALYSIS OF OCHRE FROM ARCHAEOLOGICAL CONTEXTS: CASE STUDIES FROM BRITISH COLUMBIA AND ONTARIO, CANADA

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By

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ABSTRACT

Ochre is a culturally significant material that is commonly recovered from archaeological sites. However, despite its ubiquity it has yet to realize its full interpretive potential as an artifact of archaeological inquiry, specifically in the context of geochemical characterization studies. Studies of this type, often referred to as ‘sourcing’ studies, involve the application of techniques in radiation physics to determine the elemental composition of artifacts and raw materials. These data are then used interpret patterns of behaviour in the procurement, movement, and trade of different artifact classes such as obsidian, chert, or ceramic. By comparison, geochemical characterization studies centred on ochre-related activities are fewer in number.

This thesis consists of three case studies that developed methodological foundations for the geochemical study of ochre in regions of British Columbia and Ontario, Canada, respectively. Using instrumental neutron activation analysis and X-ray fluorescence, ochre from geologic outcrops and archaeological sites were analysed to determine their elemental composition. Multivariate statistical tests, including principal components and canonical discriminant analyses, were conducted to explore patterns and variability in ochre geochemistries. The results described in the following papers demonstrate the challenges and limitations for characterization studies of ochre, and present considerations for expanded research in these geographic regions. This thesis offers contributions to broader topics of discussion in archaeological sciences, such as the accurate and precise acquisition of geochemical data, the role of geologic scales and diagenetic processes on the chemistries of iron oxides, how to identify and interpret patterns in elemental data sets, and the utility and limitations of portable analytical technologies.

This research has established important methodological foundations for the study of ochre in British Columbia and Ontario, and has demonstrated the potential for expanded analysis of materials from additional archaeological sites and geologic outcrops. This will enable the future interpretation and regional synthesis of patterns and networks of ochre-related activities, including quarrying and procurement, trade and exchange, and variability in use contexts.

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All errors and omissions are my own.

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CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Ochre is a red mineral pigment that was, and continues to be, a key component of social and ceremonial practices. The use of ochre has been well documented, and it has long been known for its use for a range of purposes: in medicines (Velo 1984, 1986, Mahaney *et al* 1993), for decoration or body painting (Capel *et al* 2006), as a component of mortuary ritual (Ames and Maschner 1999: 186), and as pigment for creating pictographs (Rajnovich 1994; Williams 2006). It has continued to draw archaeological attention for its analytical potential as a material for determining patterns of resource procurement (Taçon 2004), trade and exchange (Smith *et al* 1998), population migration (Stafford *et al* 2003, Tankersley *et al* 1995), and its specific patterns of use (Schmandt-Besserat 1980). Despite its widespread presence, it is difficult to interpret its significance without first understanding the nature of its procurement, distribution, and use contexts. The purposes of this thesis were twofold: to develop a methodological foundation for ochre-centred research by establishing protocols for its geochemical analysis and interpretation; and, to use those techniques to explore its use and significance in multiple archaeological contexts in British Columbia and Ontario, Canada, respectively. The theme that connects the papers in this thesis is the analysis of ochre from archaeological contexts to better understand patterns of its use. In the three papers that comprise this thesis, I applied techniques in radiation sciences, including neutron activation analysis (NAA) and x-ray fluorescence (XRF), to assess geochemical trends and patterns in ochre from sources, archaeological sites, and pictographs. Chapters 2 and 3 are studies that involved the geochemical characterization of ochre from sites and sources in central and southern British Columbia, Canada using NAA. Chapter 4 consists of a pilot study of the chemistry of ochre sources and pigments used at pictograph sites in the lower Canadian Shield region of northern Ontario, Canada. The results from these studies demonstrate the interpretive potential for ochre-centred research using techniques in geochemistry and radiation sciences.

1.2 CONCEPTUAL FRAMEWORK

The conceptual framework of this research is based on the notion that ochre was a culturally significant material that was used for symbolic and utilitarian purposes, and that the places from which it came and the networks of its movement were important locations and pathways within a landscape. The geographic extent to which ochre moved via acquisition, trade or transport, and the networks and contexts of its use, reveal patterns of information on how it was valued by individuals and communities. Case studies have shown that the places from which it came were unique locations known to people within a community, deliberately and repeatedly accessed and utilized over long periods of time (e.g. see Smith *et al* 1998). Ochre sources vary significantly in size, the quality of pigment they offer, their location and accessibility, and the frequency of their use. The decisions people made regarding where, when, and how often to access different sources, and the contexts within which those pigments were used, have the potential to reveal detailed information on elements of its social significance.

These ochre-related activities were interwoven in the fabrics of local traditions, histories, and engagement with places.

Archaeologists have begun to recognize the importance and role of ochre and its associated activities as a way of understanding human group interactions, and ideas about places, mythological beings, and symbolic landscapes. It has been described as a material through which we can explore and understand human engagement with the mineral world (Boivin 2004). Ochre and other minerals have historically been viewed as symbolically meaningful, ritually powerful, and deeply embedded within social, mythological and material elements of human experience. The relationships that humans have with the mineral world influence their actions and perceptions. As archaeologists, we are able to gain perspective on those beliefs by better understanding patterns and changes over time in procurement, transport, exchange, manipulation, and use contexts of the raw materials. With these concepts in mind, this thesis has aimed to develop methodological foundations for the elemental analysis and interpretation of ochres to enable the tracing of patterns in ochre acquisition, movement, and use over time and space.

1.3 PREVIOUS OCHRE RESEARCH

The study of ochre from a geochemical perspective has seen a range of applications internationally. Studies of this kind typically involve the elemental or chemical characterization of ochres from various contexts to determine their chemical 'fingerprint', and to match raw materials to their geologic origins. Results from these approaches have demonstrated how ochre was valued as a raw material, where it was traded and used, and how it was accessed. Capel *et al*

(2006) conducted an x-ray diffraction (XRD) study of ochre used to decorate vessels being traded in the Spanish Neolithic. Mioč *et al* (2004) conducted an XRD study of red pigments on and in Neolithic pottery in Serbia to differentiate cinnabar and ochre residues. Mooney *et al* (2003) used magnetic resonance techniques to determine the magnetic characteristics of ochre from a quarry in Australia. Smith and Pell (1997) analyzed the oxygen isotope ratios of ochre quarry materials from Australia and found that sources could be differentiated on the basis of those ratios. Weinstein-Evron and Ilani (1994) used a combination of XRF, ICP-AES (inductively coupled plasma – atomic emission spectroscopy) and SEM-EDS (scanning electron microscopy – electron dispersive spectroscopy) to match ochre source materials to finds from a Natufian rockshelter site (13,000 BP), in Mt. Carmel, Israel. Tankersley *et al* (1995) characterized ochre from the Hell Gap site in Wyoming (US), matching that source to the Powars II site, a Palaeoindian ochre mine (later described by Stafford *et al* 2003). A study by Smith *et al* (1998) showed evidence of preferential selection of ochre sources and long distance trade networks spanning intermittently over 32,000 year period at the Puritijarra rockshelter deposits in Central Australia. That there was preference for some ochre sources over others (despite local availability of other materials), and that it would have travelled such great distances over trade networks for long durations of time indicates that it was a highly valued material. Examples such as these, which are all based on geochemical evidence, demonstrate the interpretive potential of ochre and that it is possible to explore its associated activities and derive meaningful interpretations on how humans interacted with their natural and supernatural surroundings through ceremony, trade, and rock paintings.

1.4 RESEARCH OBJECTIVES

This thesis consists of three case studies that explore different methods and applications for the geochemical characterization of ochre, and each has regionally specific implications concerning the nature of its use. The foundation of this work has focused on determining whether ochre geochemistry satisfies the *provenance postulate* (Weigand *et al* 1977), a fundamental concept for the chemical characterization and differentiation of materials of archaeological interest (described in more detail in section 1.5.1), and this theme appears in each case study. The ochres studied for this thesis came from archaeological sites and one source located on the central coast of British Columbia, from ochre sources in coastal and interior contexts of southern British Columbia, and from sources and pictographs in the northern Ontario region of the Canadian Shield (described in section 1.6). Methods including NAA and portable XRF were used to geochemically characterize the ochres, and multivariate statistics were used to analyze patterns and trends in their geochemistries. The following sections describe these contexts in more detail.

1.5 MATERIALS AND METHODS

1.5.1 Ochre Geochemistry, Sources, and the Provenance Postulate

Ochre is an iron oxide-rich material that was selected and used by people based on criteria such as colour, texture, mineral inclusions, and its suitability as a prepared pigment. Red, purple, and brown ochre is derived primarily from the mineral hematite (Fe_2O_3), while orange and yellow variations are derived from the minerals goethite [FeO(OH)], and limonite [$FeO(OH) . nH_20$]. It forms in sedimentary, metamorphic, and igneous rock forming conditions; however, most commonly is derived from weathered and oxidized sedimentary contexts. Its chemistry can range from 5-70% iron (Fe), with components of oxygen (O), calcium (Ca), silica (Si), aluminum (Al), manganese (Mn), and a range of other minor and trace elements whose concentrations are unique to its diagenetic history. Expanded descriptions of geologic conditions for ochre formation can be found in Chapter 2 (section 2.1.2), and Chapter 3 (section 3.3). A concept at the core of this thesis, which is applicable to the geochemical characterization of any geologic materials of archaeological interest (such as obsidian, chert, clay, metal ore, or trade glass), is that of the *provenance postulate*. This term, first described by Weigand *et al* (1977: 24), that 'chemical variability between sources must be greater than the variability within any one given source', is a concept fundamental to any characterization study. As the range of methods used to characterize materials has broadened to include isotopic and mineralogical techniques, Neff expanded this definition to include 'qualitative or quantitative chemical or mineralogical differences between natural sources that exceeds qualitative or quantitative variation within each source' (2000: 108). The ability for the elemental chemistry of a geologic source of any raw material to satisfy the provenance postulate relies on a number of factors such as the nature of the source (size, extent, diagenetic history), its spatial distribution, chemical homogeneity, treatment or preparation by humans, and intra- and inter-source chemical variability. The results of the following studies demonstrate that under the appropriate circumstances and using suitable methods for analysis, ochre source chemistry satisfies the provenance postulate.

1.5.2 Methods of Analysis: NAA and XRF

For the following case studies NAA and XRF were used to characterize ochre samples elementally. Ochre is a geochemically heterogeneous material, and as a result it is necessary to obtain elemental concentration data on major, minor, and trace elements, and to explore trends in those concentrations using multivariate statistics. Other examples of approaches to this include Erlandson *et al* (1999), Popelka-Filcoff *et al* (2007, 2008), Smith and Pell (1997), Smith *et al* (1998), Stafford *et al* (2003). NAA was chosen for this application as it is capable of measuring the abundances of 30+ elements at relatively low detection limits and with a high degree of precision and accuracy. Furthermore, it is well suited to measure transition metals and rare earth elements, which are typically diagnostic for differentiating chemical source groups of ochre. It is a method whereby samples are exposed to neutrons from a nuclear source, and a fraction of the nuclei from each element within the ochre sample transforms into unstable isotopes that decay with characteristic half-lives. Those radioisotopes emit gamma rays characteristic of each isotope, which are subsequently measured by a high-purity germanium (HPGe) detector-based gamma ray spectrometer. The detector signals are amplified and sorted into channels measured in keV using a multi-channel analyzer, and the resulting peaks that form are qualitative and quantitative representations of those elements. Sample preparation methods, irradiation protocols, and statistical treatment of data are described in further detail in section 2.4.1. Other detailed descriptions of NAA theory have been described elsewhere (Neff 2000; Glascock and Neff 2003; Pollard *et al* 2007). This method was applied in the case studies in Chapters 2 and 3, and was conducted at the Centre for Neutron Activation Analysis at the McMaster Nuclear Reactor with the support and supervision of A. Pidruczny and R.G.V. Hancock.

X-ray fluorescence is a non-destructive, near-surface, elemental analytical technique used widely in archaeological sciences for the study of materials such as obsidian, chert, clay, pigments, metals, and glass. A small area on the object of study is targeted with a beam of high-energy x-rays that are powerful enough to temporarily transform atoms at the surface by dislodging inner K-shell electrons from their respective shell configurations. The target atoms become unstable and the outer L- and M-shell electrons replace the inner-shell vacancies until the atom is charge satisfied. The energy that is emitted, or fluoresced, during this process is an incident x-ray that is characteristic of that element. Those emitted x-rays are measured by detectors and subsequently calculated to elemental concentrations. For the case study described in Chapter 4, an Olympus Innov-X Delta Premium model field portable XRF was used to analyze pictographs and ochre source materials in northern Ontario, Canada. A full description of the protocol for this equipment is in section 4.3. This system was generously provided by J. O'Meara (Department of Physics, University of Guelph).

1.6 STUDY AREAS

1.6.1 Coastal British Columbia, Canada

Two of the three chapters in this thesis have a geographical focus on coastal British Columbia, Canada. The archaeological sites included in these studies can be generally described as hunter-gatherer villages and camps, some occupied continuously and others as part of a seasonal round of migration. While occupations of some of the sites date to 9000 BC, only materials from the most recent 2800 years of occupation were targeted. Ochre use in the context of coastal British Columbia has been documented archaeologically and ethnographically as an element of ceremonial practice and face painting (Bouchard and Kennedy 1986: 246), and as a trade item (Matthews 1995: 47; Mitchell and Donald 1988: 237; Olson 1955). Ames (2005) describes ochre use as part of mortuary ritual and in association with burials, and Carlson (1993, 1994), and Williams (2006) describe its use for pictographs across the region. Erlandson *et al* (1999), and Mrzlack (2003) offer the nearest examples on the northwestern coast of North America of geochemical studies of ochre. It is commonly recovered from archaeological sites in the region, however prior to this research very little has been known about its geochemistries, procurement, and distribution.

The ochre artifacts described in Chapter 2 were recovered from ten archaeological sites and one geologic outcrop in traditional Heiltsuk, Wuikinuxv (Oweekeno), and Nuxalk territories on the central coast of British Columbia. The materials from archaeological sites located in Heiltsuk and Oweekeno territories were collected by A. Cannon as part of a regional-scale project focused on settlement patterns and resource use (Cannon 2000, 2002). Ochre samples analyzed from Nuxalk territory were acquired during excavations led by Hobler and Bedard (1988), and analyzed with the permission of R. Carlson from Simon Fraser University, facilitated by Dr. B. Winter and S. Wood. Ochre source materials from Sagar Lake were collected in 2009 by B. MacDonald, A. Cannon, M Burchell of McMaster University, and E. White of Heiltsuk First Nation. A total of 64 samples were characterized using NAA to determine if ochre artifacts from unknown sources could be differentiated on the basis of their elemental composition. Table 2.1 (Chapter 2) summarizes the sites, dates, and number of ochre samples analyzed. The results from this study showed statistical trends indicating that there were four different ochre geochemical groups within the sample set, with only one or two of those groups being present at any given archaeological location. Source materials from Sagar Lake were only recovered from sites in the immediate vicinity of the source, while the other three groups of unknown origin were distributed in other clusters (see Figure 2.7). This pattern of acquisition and use persisted over a ~2000 year period, with no variability in the sources accessed. This indicates a model of highly localized, preferential, long-term ochre acquisition practices. Other evidence has suggested highly localized procurement of subsistence resources (Cannon *et al* 2008, 2011), with the exception of obsidian, which was traded extensively (Carlson 1994), and fish oil. However, on the basis of these results, ochre does not appear to be a component of those trade networks. The absence of ochre trade in the presence of existing trade networks suggests that there may have been no need or desire to share or trade this resource.

Chapter 3 describes a case study analyzing ochre from three deposits (each with two sub-outcrops) in southern coastal British Columbia, located near Mt. Garibaldi in traditional Squamish First Nation territory, and in the Tulameen Ochre Bluffs in Upper Similkameen First Nation traditional territory. A critical step toward understanding the nature of ochre geochemistry and its potential use as archaeological evidence of procurement and trade is to determine intra-source and regional variability in outcrop chemistry. This study tested a total of 81 samples from the ochre sources Paul Ridge and Chichen Stenach (DkRs-14), from the Mt. Garibaldi highlands, Pilchuck Creek (A and B) in the Squamish lowlands, and the Tulameen Ochre Bluffs in the British Columbia interior. All materials were collected during field visits by MacDonald and Reimer, with the exception of Tulameen ochre which was provided by Reimer. Results of this study demonstrate the implications that geological and geographical scales have on research design, methodological application, and statistical treatment of data. Moreover, results show that ochre source geochemistry in the southern coast area satisfies the provenance postulate. This project set the ground work for anticipated future study of ochre artifacts from archaeological sites in the region to link networks of acquisition and use.

1.6.2 The Canadian Shield and Northern Ontario, Canada

Chapter 4 of this thesis has a geographical focus on pictographs and ochre sources located in the southern Canadian Shield region in northern Ontario, Canada. The areas targeted in this study are: the Greater Temagami Area (Lake Temagami, Lake Obabika, Diamond Lake, Anima-Nipissing Lake, Yorston River ochre source), located in Temagami First Nations traditional territory, the north shore of Lake Huron (Spanish River, Granary Lake, Quirke Lake) in Serpent River and Sagomok First Nation territory, and on the French River in Henvey Inlet First Nation territory, respectively. Research on the geochemical characterization of ochre in this area is virtually non-existent, however, a long tradition of field surveys and aesthetic interpretations of pictograph imagery do exist (Arsenault 2004a, 2004b; Colson 2007; Conway, 1993, Dewdney 1959, 1970; Molyneaux 1981; 1987; Rajnovich 1994, Zawadzka 2009, 2013). Human occupation of the Ontario Shield Woodland area by traditional hunter-gatherer societies has been dated to 7,000 BP (Aubert *et al* 2004). Gordon (2013) offers an extensive review of Lake Temagami area archaeological history. Historical information suggests that the majority of the rock paintings were painted within the last 2,000 years (Rajnovich 1994: 34). A total of 62 pictographs were analyzed in the field by MacDonald and Cooper from 2011to 2013, and results show that multiple ochre sources were used to create the pictographs, and that the patterns of locations of their use within the study are complex and variable.

1.7 Description of thesis format

This thesis follows a 'sandwich' format that includes an introduction, three papers, and a concluding chapter. Chapters 2 and 3 consist of papers that are already published in print, and references appear at the end of each chapter according to the style guidelines for the journals to which the papers were submitted. References cited for Chapters 1 and 5 appear at the end of Chapter 5. Chapter 4 is a manuscript in preparation for submission in *Archaeometry* and is formatted to those style guidelines. The reader will note that there is some overlap between the chapters with regard to literature on previous ochre research as well as descriptions of some of the techniques and statistical applications employed for the analysis of ochre. The following is a brief summary of each of the papers, their purpose, and author contributions.

Paper 1: Geochemical characterization of ochre from central coastal British Columbia, Canada.

Authors: B.L. MacDonald, R.G.V. Hancock, A. Cannon, A. Pidruczny.

This paper presents the results of a geochemical study of ochre recovered from archaeological sites located in the central coast region of British Columbia, Canada. It is published in *Journal of Archaeological Science* (2011, 38: 3620-

3630), and is co-authored by B.L. MacDonald, R.G.V. Hancock, A. Cannon, and A. Pidruczny. B.L. MacDonald collected and analyzed the data, and wrote all original drafts. R.G.V. Hancock assisted with statistical analysis and interpretation of geochemical data. A. Cannon provided ochre materials from previous field excavations, funding, and assisted with figures and editing. A. Pidruczny provided lab facilities, technical support, and funding.

The purpose of this study was to determine the potential for differentiating ochre source chemistry using elemental data and multivariate statistical methods. It offers an original contribution to research related to ochre sourcing and geochemistry both methodologically and in its geographic reach. Typically, ochre sourcing studies place emphasis on the long-distance movement or trade of raw materials. However, this example is unique in its application of these methodologies to materials recovered from a relatively restricted geographic context of archaeological sites. Determining trends in ochre geochemistry through the application of statistical calculations such as principal components analysis, canonical discriminant analysis, and bivariate exploration of data, is of value as a case study to inform others studying ochre in any other geographic context. This study provides an example of how to apply multivariate statistics to chemically complex raw materials. Furthermore, by creating a database of elemental ‘fingerprints’ of multiple geologic source groups of ochre in central coastal British Columbia, this work has created a foundation and comparative basis for future ochre-centred work of this kind.

Paper 2: Elemental analysis of ochre outcrops in southern British Columbia, Canada.

Authors: B.L. MacDonald, R.G.V. Hancock, A. Cannon, F. McNeill, R. Reimer, A. Pidruczny

This paper describes the results of a systematic survey and characterization of geologic ochre sources in southern coastal British Columbia. It is published in *Archaeometry* (2013, 55[6]: 1020-1033), and is co-authored by B.L. MacDonald, R.G.V. Hancock, A. Cannon, F. McNeill, R. Reimer, and A. Pidruczny. B.L. MacDonald performed neutron activation analysis of the ochre materials and all statistical procedures, as well as wrote all original text. R.G.V. Hancock assisted with statistical interpretation of data. A. Cannon and F. McNeill both provided funding and editorial support. R. Reimer assisted in field collection of samples. A. Pidruczny provided lab facilities and funding. This paper offers an original contribution to research as it is the first to show systematic geochemical analysis of ochre sources at this scale in the southern British Columbia region. Prior to this, no studies in British Columbia existed that contextualized ochre chemistry within local geologic processes. Determining the chemistry of ochre sources in this study region has shown that ochre elemental composition satisfies the provenance postulate. Furthermore, this project has set a foundation for future research that could include analysis of ochre finds from archaeological sites and pictographs. This study also offered implications for how statistical exploration of data can be significantly affected by scales, both geographically and in the differentiation of chemical groupings.

Paper 3: Analysis of pictographs in the southern Canadian Shield: an example of the utility of portable x-ray fluorescence technology

Authors: B.L. MacDonald, M. Cooper, F. McNeill, J. O'Meara, R.G.V. Hancock, A. Cannon

This paper presents the results of a survey of 62 pictograph sites and two ochre sources in central Ontario in the Canadian Shield Woodland area. It is a manuscript prepared for submission to *Archaeometry*, and is co-authored by B.L. MacDonald, M. Cooper, F. McNeill, J. O'Meara, R.G.V. Hancock, and A. Cannon. B.L. MacDonald drafted all original text, performed x-ray fluorescence testing in the lab and field, and analyzed all of the data. M. Cooper guided field surveys, and provided regional expertise, funding, and editorial support. F. McNeill and J. O'Meara provided funding and analytical facilities. R.G.V. Hanccock and A. Cannon provided editorial guidance with writing and statistical analyses.

The goal of the study was to assess the feasibility of using p-XRF spectroscopy to analyze pigments used for the creation of pictographs *in situ*. Three components of the project were: 1) to assess the precision and accuracy of p-XRF technology via the analysis of standard reference materials and ochre sources of known chemistries; 2) to develop a testing framework for pictographs *in situ*, and for the differentiation of source groups of ochre used specific to the geographic area; 3) to gain insight into characteristics of ochre source use in northern Ontario. This paper offers a contribution to the ongoing and rigorous evaluation of p-XRF technologies that are evident in the literature (Goodale *et al* 2012, Nazaroff *et al* 2010, Shugar and Mass 2012). Moreover, it contributes a valuable case study in the analysis of ochre geochemistry, distribution, and use in northern Ontario, and offers a comparative foundation for future study of ochre distribution at archaeological sites in the region. This work will be of value to those studying Algonquian archaeology, and more broadly, those interested in methodologies for the analysis of ochre geochemistry and the application of portable technologies in the field.

CHAPTER 2

GEOCHEMICAL CHARACTERIZATION OF OCHRE FROM CENTRAL COASTAL BRITISH COLUMBIA, CANADA

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Abstract

The use of ochre and its presence in archaeological contexts is well documented archaeologically, ethnographically and historically. Elemental analysis of ochre is becoming increasingly common as a method for identifying ancient quarrying and mining practices, and for identifying patterns of resource use, trade and exchange. As this type of work has become more common it has become apparent that two critical issues need to be considered: 1) the need for systematic identification of trends and patterns in ochre geochemistry using appropriate statistical analyses, and, 2) consideration of geographic and geologic scale in relation to ochre chemistry. Because ochre is a heterogeneous material relative to other raw material types, it is necessary to apply multivariate and discriminant statistics to differentiate geochemical groups within a sample set. However, caution must be taken when interpreting statistical results at face value. Local geologic and geomorphologic conditions play a significant role in ochre chemistry and need to be taken into account when interpreting analytical results.

The purpose of this project was to determine if geochemically distinct groups of ochre could be distinguished through neutron activation analysis (NAA) of archaeological and geological ochres from the central coast of British Columbia, Canada. The results show that it is possible to satisfy the provenance postulate and to differentiate chemical groups through elemental characterization and using multivariate statistical methods.

2.1 Introduction

Ochre is common to archaeological sites around the world and is often considered to be a culturally significant material. It was and continues to be used in a variety of contexts, as pigment for rock art and body paint, medicinally, and as a component of ritual and mortuary practices. However, the nature of its acquisition is poorly understood. The elemental analysis of raw materials of all types is continually increasing in frequency and occurrence, and the analysis of ochre for the purpose of determining ancient resource use and trade and exchange practices is an area of growing interest (Manscalo, 1989; Popelka-Filcoff et al., 2005; Smith et al., 1998; Smith and Pell, 1997; Stafford et al., 2003; Tankersley et al., 1995). As this body of knowledge continues to expand it is apparent that a foundation of knowledge of ochre geochemistry and local geological conditions must be established to enable detailed interpretations of ochre-related practices. Ochre is common in archaeological sites in the region of coastal British Columbia, yet no systematic study of its geochemistry, acquisition and distribution currently exists. The focus of this study was to assess the range of geochemical variability within regionally restricted assemblages of archaeological ochres, and to determine if their geochemistry satisfies the provenance postulate:

that the geochemical variability between different sources of materials must be greater than the internal variability within any one source (Glascock and Neff, 2003; Weigand et al., 1977). With the exception of one sampled geological source at Sagar Lake the samples included in this study are from archaeological contexts and their geological source(s) locations are unknown. The results of this project are an example of the interpretive potential of the elemental analysis of ochre.

2.1.2 Definition of Ochre

The term 'ochre' broadly refers to earth pigments that range in colour from red to brown to yellow to purple. Most often these pigments are various forms of mineralogical admixtures containing iron oxides that provide produce its colour properties. For the purpose of this study we use the term ochre with reference to deposits of iron oxides found within the archaeological record that are suitable for use as pigment based on criteria such as colour richness, texture, friability and presence and type of mineral inclusions. Ochre can form in sedimentary, metamorphic, and igneous conditions, however the most common is derived from weathered sedimentary contexts. Red, brown and purple ochre come primarily from the mineral hematite (Fe_2O_3), while orange-yellow ochre is derived from the minerals goethite ($FeO(OH)$), and limonite $FeO(OH)\cdot nH_2O$). Hematite is composed primarily of 70% Fe and 30% oxygen (O), and forms in a variety of rock types. For example, it is found in red sandstones as the cementing material that binds quartz grains together, it forms in irregular masses and beds as the result of weathering and oxidation of iron-bearing rocks, it occurs as a sublimation product in connection with volcanic activities, and also in contact metamorphic deposits and as an accessory mineral in feldspathic igneous rocks such as granite (Klein, 2002, 281). Goethite is composed of Fe 63%, O 27% and H_2O 10%, with Mn sometimes present in amounts up to 5%, and is most commonly associated with other iron oxides such as limonite and hematite. Goethite is formed by the weathering or hydrothermal alteration of iron-bearing minerals in oxidizing conditions (Battey 1981, 213; Klein, 2002, 396). It also forms as a direct inorganic or biogenic precipitate from water, and is widespread as a deposit in bogs and springs (Battey, 1981, 213).

Characterization studies typically begin with the analysis of raw materials from local sources, or, with an archaeological assemblage in cases where source materials are not readily available (Shackley, 2008). Samples included in this study are primarily from archaeological contexts, with additional specimens from one geological deposit. In contrast to other ochre characterization studies (e.g. Erlandson et al., 1999), this study examined the geochemistry and distribution of ochre within a relatively restricted geographical extent, and from multiple contexts including villages, camps and a geological outcrop. Where other studies have emphasized long-distance procurement, this project has sought to explore the potential for determining ochre use and the nature of its procurement within a regional settlement system. Careful consideration has been given to the issue of geologic scale with respect to ochre geochemistry. It was expected that ochre outcrops in the central coast of the British Columbia region would be geochemically similar based on the formation processes of ochre and given the local geological conditions. Therefore, to assess the feasibility of attributing archaeological ochres to specific geological deposits within this territory, it was necessary to first identify trends in ochre geochemistry within the available archaeological and geological assemblage. While we use the terms ‘source’, ‘deposit’ or ‘outcrop’ interchangeably to refer to a geochemically characterized group of ochre, it is important to note that we are not referring to the ‘sourcing’ or attribution of archaeological ochre to a specific outcrop. We subscribe to Shackley’s description of ‘the sourcing myth’ (Shackley, 2008, 196), and use the term ‘source’ to describe a geochemically characterized group of ochre(s) that may be representative of one or more discrete geological deposit(s).

2.2 Brief Review of Ochre Research

References to ochre use exist within a broad range of ethnographic, historical and archaeological literature and such works illustrate the diversity of ochre use as a utilitarian, symbolic, artistic and medicinal material. It has been described as medicinally useful (Mahaney et al., 1993; Velo, 1984, 1986), symbolically charged (Marshack, 1981; Taçon, 2004), functionally valuable as a filler for adhesive (Lombard, 2005; Wadley, 2005), a preservative (Roper, 1991; Wadley, 2005), as well as pigment for rock art, as house floor deposits, as wall painting or pottery decoration, and in association with burials (Roper, 1991). Ochre use specific to British Columbia has been documented historically and ethnographically as an element of ceremonial practices (Bouchard and Kennedy, 1986, 246; Matthews, 1955, 47; Olson, 1955), and trade and exchange between culture groups (Mitchell and Donald, 1988, 327; and Williams, 2006). Archaeologically, ochre has been documented as a component of mortuary ritual (Ames, 2005; Burchell, 2003), as medium for pictographs (Williams, 2006) and has been found at numerous excavations.

Previous methodological research has played a critical role in determining what is analytically suitable for geochemical and mineralogical characterization of ochre. Notable examples include Popelka-Filcoff et al. (2008) who used NAA to characterize ochres from southern Arizona. Erlandson et al. (1999) were able to geochemically differentiate ochres from eight different locations in western North America using proton-induced x-ray emission analysis (PIXE). A study by Tankersley et al. (1995) showed that x-ray diffraction (XRD) could be used successfully to determine that ochre from the Hell Gap site in Wyoming was acquired from the Powars II ochre mine (see Stafford et al., 2003). Smith et al. (1998) also demonstrated that it was possible to match archaeological ochres to geological outcrops using a combination of inductively-coupled plasma mass spectrometry (ICP-MS) and SEM-EDS. Collectively, these studies have demonstrated that ochre can be heterogeneous and often difficult to differentiate into discrete geochemical groups without the use of multivariate statistics. Another consideration is that some of these studies analyzed ochre from various outcrops large geographic scales in relation to the present study (e.g. Erlandson et al., 1999; Smith et al., 1998). To build upon the foundation created by previous studies, this project sought to examine the geochemical variability and distribution of ochre at a smaller scale and within a relatively restricted geographical context.

2.3 Archaeological and Geological Background

The ochre samples analyzed for this study came from locations in traditional Heiltsuk, Wuikinuxv (Oweekeno), and Nuxalk territories in the central coast region of British Columbia. Collection of archaeological materials from sites in Heiltsuk and Oweekeno territories was conducted by Cannon as part of a regional-scale project focused on settlement patterns and resource use. Sites in Heiltsuk territory include two villages: Namu (ElSx-1), Kisameet (ElSx-3); one smaller residential base camp (ElSx-10), and one geologic deposit at Sagar Lake on King Island. The archaeological sites are described as villages and camps based on a variety of criteria including site size and the density and diversity of faunal remains (Cannon, 2000; Cannon, 2002, 320). Sagar Lake is a freshwater lake located in Codville Lagoon, and is the only known accessible ochre outcrop in the territory. Sites located in the Oweekeno territory include two villages: Cockmi (EjSw-1), and Katit (EkSt-1), and two small camps (EjSv-5 and EjSv-3). Materials from Heiltsuk and Oweekeno territories were collected by bucket auger, washed and sorted through 2mm mesh screen and analyzed microscopically (10x) to extract fish and shellfish remains, ochre and obsidian. Radiocarbon dates yielded from charcoal or shell from multiple core and auger locations and depths at each site have provided chronologies for the initial and terminal occupations. Samples chosen for analysis were all taken from contexts dating to the final 2000 years of occupation into the European contact period. Sample collection from the geological outcrop at Sagar Lake was completed in 2009 by MacDonald, Cannon, and E. White of Heiltsuk First Nation. Sites located in Nuxalk territory include three villages: Joashila (FaSu-19), Nut'l (FeSr-7) and Stskiutl (FeSq-8). Excavations at sites in Nuxalk territory were directed by Hobler (1988) and materials were acquired with permission from R. Carlson from Simon Fraser University, facilitated by Dr. Barbara Winter and Shannon Wood. See Figure 2.1 for a map of these sites. Table 2.1 shows a summary list of sites, dates and number of ochre samples analyzed. The samples chosen for analysis were primarily small in size and weight (approximately .5 to 2.0 g), with the exception of some cobble-sized chunks retrieved from one site. Across the sample set, the ochres exhibited variability in visual characteristics such as hue, presence of micaceous or sandy inclusions and relative grain size.

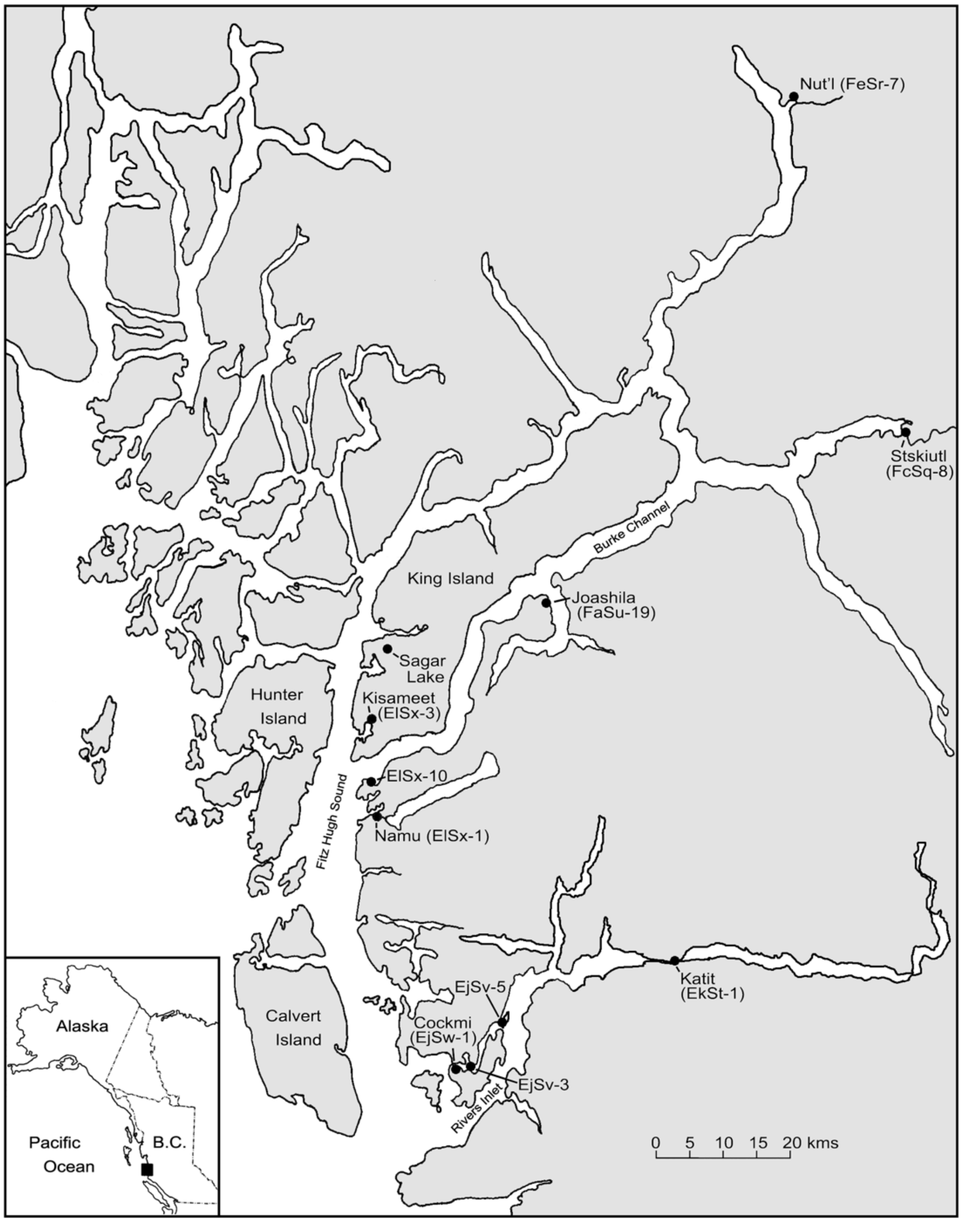

Figure 2.1: Map of sites within the study region of central coastal British Columbia, Canada.

Table 2.1
Summary List of Sites, Dates and Quantities of Ochre. (Radiocarbon dates taken from Cannon, 2000; Carlson, 1996; Hobler and Bedard, 1988; Hobler, 1982.)

Site name (Borden Number)	**Location / Territory**	**Site type**	**Date range (calibrated BC/AD)**	**Ochre pieces analyzed (n=)**
Namu (ElSx-1)	Fitz Hugh Sound / Heiltsuk	Village	[a]9000 BC – contact	14
Kisameet (ElSx-3)	Fitz Hugh Sound / Heiltsuk	Village	940 BC – contact	7
ElSx-10	Fitz Hugh Sound / Heiltsuk	Res. Camp	4315 BC- contact	2
Sagar Lake	Fitz Hugh Sound / Heiltsuk	Geologic Outcrop	N/A	3
Cockmi (EjSw-1)	Rivers Inlet / Oweekeno	Village	560 BC- AD 1230	13
Katit (EkSt-1)	Rivers Inlet / Owekeeno	Village	AD 1320- 1935	9
EjSv-5	Rivers Inlet / Oweekeno	Small Camp	2210 BC- AD 880	2
EjSv-3	Rivers Inlet / Oweekeno	Small Camp	AD 1260- 1650	1
Joashila (FaSu-19)	Bella Coola / Nuxalk	Village	3390 BC – AD 1500	1
Nut'l (FeSr-7)	Bella Coola / Nuxalk	Village	Unknown initial date – into contact period	7
Stskiutl (FcSq-8)	Bella Coola / Nuxalk	Village	Unknown initial date – into contact period	5
				Total: 64

[a] *While Namu dates to 9000 BC, only materials from the last 2800 years of occupation were included in this study.*

Geologically, the Coast Range Plutonic Complex consists primarily of Mesozoic and Tertiary deposits as interspersed sedimentary and volcanic rocks including basalt, grandiorite, quartz diorite, quartz monzonite, granite, syenite, diorite and gabbro (Geological Survey of Canada, 1969). The study area straddles the divide of two major Coast Range Mountain Complexes: Kitimat Ranges to the north of Bella Coola and King Island, and Pacific Ranges running from Bella Coola in the north to the Fraser River in the south. Highly detailed geological surveys of the area do not currently exist, however bedrock and geochemical information is available, albeit at low resolution. The area is, essentially, a sea of granite with interspersed occurrences of basalt that could potentially weather to give rise to iron oxide rich outcrops (Nelson, pers. comm.).

2.4 Description of Ochres and Sampling Rationale

2.4.1 Analytical Methods and Protocol

Ochre is a geochemically heterogeneous material in comparison to other raw materials such as obsidian and some clays, however, previous work on the characterization of ochre outcrops indicates that sufficient geochemical variability exists to satisfy the provenance postulate (Erlandson et al., 1999; Popelka-Filcoff et al., 2007; Popelka-Filcoff et al., 2008; Smith and Pell, 1997; Smith et al., 1998; Stafford et al., 2003; Weigand et al., 1977). Because there exists the potential for significant chemical variability in ochre, it is critical to obtain elemental concentration data on major, minor and trace elements and to explore trends among them through application of multivariate statistics. Elements that are diagnostic for differentiating chemical groups are typically transition metals and rare earth elements (Popelka-Filcoff et al., 2008). For this reason we chose to analyze the ochre using NAA as it is capable of measuring the abundances of 30+ elements at relatively low detection limits and with high degree of precision and accuracy. NAA is a method whereby samples are exposed to neutrons from a nuclear source, and a tiny fraction of the nuclei from each element within the sample is transformed into unstable isotopes that decay with characteristic half-lives. The radioisotopes emit gamma rays characteristic of each isotope. Those gamma ray energies are measured by a high-purity germanium (HPGe) gamma ray spectrometer, their signals amplified and sorted into channels along a spectrum measured in keV. The resulting peaks that form are the spectrometric end-products of elements that produce radioisotopes.

A total of 64 ochre samples were selected for analysis. Their surface colours ranged in colour from yellow to orange, red and purple and they were systematically chosen based on the quantity of materials available and the contexts from which they came. Effort was made to select samples from a range of contexts (villages, residential camps, small camps), from comparable time periods (primarily within last ~2000 years), and across sites and at variable depths at each site wherever possible. Specimens were washed with distilled water in an ultrasonic cleaner to remove dirt and shell residue. In the case of friable materials they were cleaned by hand with a clean wire brush or pick to remove the outer layer, rinsed with distilled water to remove any remaining surface impurities and dried in a low-temperature oven for 24 hours. Specimens were weighed to approximately 1g where possible, and heat-sealed in high-purity polyethylene vials.

Using facilities at the McMaster University Nuclear Reactor, two neutron irradiations were performed to acquire concentration data on elements that produce short-, medium- and long-lived isotopes. Multiple standard reference materials (SRMs) and control samples were run alongside each batch of samples including SRM 1632b Coal, SRM 1633b Fly Ash, SRM 688 Basalt, SRM 278 Obsidian Rock all issued by the National Institute of Standards and Technology (NIST), and Ohio Red Clay. For every 10-12 unknown samples analyzed, two of each SRM 1632b, SRM 1633b, and one of each SRM 278, SEM 688 and Ohio Red Clay were also tested. Non-certified elemental concentrations from the Ohio Red Clay were taken from Glascock et al. (2007). The samples were run through a pneumatic tube system and subjected to a 10-second thermal irradiation at a neutron flux of 5×10^{13} n cm^{-2} s^{-1}. Each sample was left to decay for 10 minutes and then measured by a HPGe detector for 5 minutes. The elements measured for the short-lived isotope procedure included Al, Ba, Br, Ca, Co, Cl, Dy, K, Mg, Na, Ti and V. The samples were left to decay for approximately 24 hours, after which a second 5-minute count was performed to collect concentration data on Eu, K, La, Mn, Na and Sm. The same samples were repackaged into high-purity quartz vials and irradiated for 8 hours at a neutron flux of 5×10^{13} n cm^{-2} s^{-1}. The samples were left to decay for 7-10 days after which they were counted for 15 minutes to measure concentrations of Au, As, Ba, Br, Fe, La, Na, Nd, Sb, Sm and Th. Approximately 14-16 days after the long irradiation the samples were counted for another 15 minutes to measure concentrations of Ce, Co, Cr, Cs, Eu, Hf, Lu, Sc, Tb, and Yb. Other elements measured but not included in statistical analyses include Ga, Pr, Rb and Zn. The data were calculated and calibrated using

GammaVision™ and PEAK software, and multivariate statistical analyses were performed using SAS JMP software. Table 2.2 (Appendix A) shows average reported values for all SRMs used for the duration of the project.

2.4.2 Elemental Concentration Data

Table 2.3 shows the summary elemental concentration data for four chemical groups found. The samples that comprise these four groups were determined based on the results of a principal components analysis (PCA), described in further detail below. In an unanticipated outcome, these chemical groupings also correspond closely to their geographic location, as indicated by cardinal direction. Even though large group standard deviations are associated with most means, there are major differences in means for selected elements. The most striking differences between groups are that of Al, Fe, Na, Ti, and the group of measured rare earth elements. Major element concentrations appear to distinguish between eastern and western sites, while trace and rare earth element concentrations highlight differences between all four groups. Samples that come from the west (Groups 1 and 4) have characteristically higher Al, Ca, Na, Nd, and Sm. Samples from the east (Groups 2 and 3) have significantly higher Fe content, suggesting different parent rock material, as well as high Eu and Sb. Exceptionally low Fe content for Groups 1 and 4 may be indicative of low quality pigments. Elements that further distinguish groups from each other are high Ti concentrations at northern sites (Groups 2 and 4), high Ta in southern sites (Groups 1 and 3), high Ba and Zn in the south west (Group 1), high Cs and Au in the south east (Group 3), high Cr in the north east (Group 2), and high Co in the north west (Group 4).

Table 2.3 Summary Table of Elemental Concentration Data for Geochemical Groups. High mean values are **bolded.**

Elemental Data		***Group 1 (n=32) *south west***	***Group 2 (n=14) *north east***	***Group 3 (n=8) *south east***	***Group 4 (n=10) *north west***
		Mean ± St.Dev	**Mean ± St.Dev.**	**Mean ± St.Dev.**	**Mean ± St.Dev.**
Al	**%**	**7 ± 2**	5 ± 3	3 ± 2	**12 ± 7**
Ca	**%**	5 ± 3	2 ± 1	2 ± 1	5 ± 4
Fe	**%**	4 ± 2	**21 ± 15**	**34 ± 17**	3 ± 2
Na	**%**	**2.7 ± 1.6**	0.9 ± 0.8	0.5 ± 0.5	**3 ± 1**
Cs	**ppm**	3.2 ± 2.3	1.9 ± 2.6	**20 ± 26**	0.5 ± 0.8
Ta	**ppm**	**1.2 ± 1.1**	0.2 ± 0.7	**1.3 ± 3.2**	0.3 ± 0.3
Co	**ppm**	8 ± 9	14 ± 9	11 ± 4.8	**19 ± 15**
Au	**ppm**	0.6 ± 1.0	0.01 ± 0.02	**2.1 ± 2.2**	0.8 ± 0.3
Ti	**ppm**	400 ± 240	**3400 ± 3600**	250 ± 160	**5900 ± 4000**
As	**ppm**	4 ± 6	**25 ± 43**	12 ± 14	14 ± 31
Cr	**ppm**	17 ± 24	**45 ± 60**	24 ± 28	8 ± 3
Eu	**ppm**	1.5 ± 1	**2.5 ± 1.8**	**2.8 ± 2.7**	1.0 ± 0.5
Zn	**ppm**	**740 ± 1490**	72 ± 47	65 ± 113	39 ± 32
Sc	**ppm**	16 ± 12	11 ± 6	7 ± 6	14 ± 11
Mn	**ppm**	846 ± 44	719 ± 368	893 ± 408	787 ± 435
Ba	**ppm**	**1100 ± 1800**	740 ± 420	700 ± 760	870 ± 500
Cl	**ppm**	250 ± 210	110 ± 100	**460 ± 300**	**570 ± 410**
Hf	**ppm**	2.9 ± 1.8	**6 ± 4.8**	1.7 ± 2.1	1.5 ± 0.5
Sb	**ppm**	0.4 ± 0.4	**1.2 ± 1.5**	**1.5 ± 1.7**	0.6 ± 1.1
Th	**ppm**	3.5 ± 2.9	4.8 ± 6.6	4.3 ± 7.7	4.7 ± 4.2
V	**ppm**	147 ± 106	186 ± 68	84 ± 53	181 ± 187
Ce	**ppm**	26 ± 15	23 ± 13	14 ± 18	24 ± 10
La	**ppm**	13 ± 9	22 ± 16	14 ± 7	10 ± 4
Lu	**ppm**	**0.8 ± 1.6**	0.2 ± 0.1	0.3 ± 0.3	0.2 ± 0.2
Nd	**ppm**	21 ± 26	14 ± 8	8 ± 19	15 ± 10
Yb	**ppm**	0.4 ± 0.6	0.9 ± 0.6	**1.8 ± 2.7**	**1.6 ± 1.4**
Tb	**ppm**	0.5 ± 0.3	0.7 ± 0.5	0.2 ± 0.5	0.5 ± 0.6
Sm	**ppm**	4.2 ± 2.3	3.0 ± 1.1	1.5 ± 1.4	4.8 ± 3.3
Dy	**ppm**	nm	3.9 ± 2.5	nm	4.2 ± 3.3

2.4.3 Statistical Treatment of Data

To identify geochemical trends in ochre we explored the data set using multivariate statistics including bivariate plotting, principal components analysis (PCA) and canonical discriminant analysis (CDA). Bivariate plotting of element pairs is useful as a first step towards determining positively and negatively correlated elements PCA is a statistical test for identifying how variable points are within a data set, and which variables drive that variance. CDA is similar to PCA as a means for determining which variables have the highest and lowest possible multiple correlation between groups.

Before the statistical tests were conducted we normalized all element concentrations (in parts per million) to the Fe content of each sample, also referred to as Fe normalization as described in Popelka-Filcoff et al. (2008). The Fe content of ochres can be highly variable, and this variability can potentially dilute or amplify the presence of other diagnostic elements, or where other minerals may substitute for Fe. The Fe-normalized values were then converted to a base-10 logarithmic format as part of standard statistical practice when the variability within a data set can be across several orders of magnitude (Baxter, 1994, 40). The results of a PCA depend on how the data are scaled, therefore, because PCA is scale dependent, the ppm (parts per million) concentration data were expressed on a logarithmic scale. These Fe-normalized, base-10 logarithmic values were then subjected to bivariate plotting, PCA and CDA. The PCA and CDA tests identified four discernible geochemical groups of ochre within the data set, to be described in further detail in sections 2.4.5 and 2.4.6. For all subsequent plots and figures those groups are identified by 80% confidence ellipses.

2.4.4 Bivariate Plotting

For this data set biviariate plotting of elements was used for determining positive or negative correlations between elements. Elemental groups such as first row transition metals (e.g. Sc, Ti, V, and Cr) or the rare earths (e.g. La, Ce, Pr, Nd, Sm, and Eu) are expected to behave similarly as they share similar chemical and physical properties. Substitutions of these elements for each other occur when, under specific geological conditions, multiple elements with similarly-sized atoms and charges replace each other within a crystal structure. Light and rare earth elements are substituted in variable quantities as a result of geological conditions, such as the temperature of mineral crystallization or through diagenetic processes. Therefore, by measuring the correlations between these element groups it is possible to identify potential variability in formation and diagenetic processes of ochre deposits. As a measure of the uniformity and reliability of the data set these correlations also indicate if there are any outliers or erroneous results. Figures 2.2-2.4 show positive correlations between elements of significance.

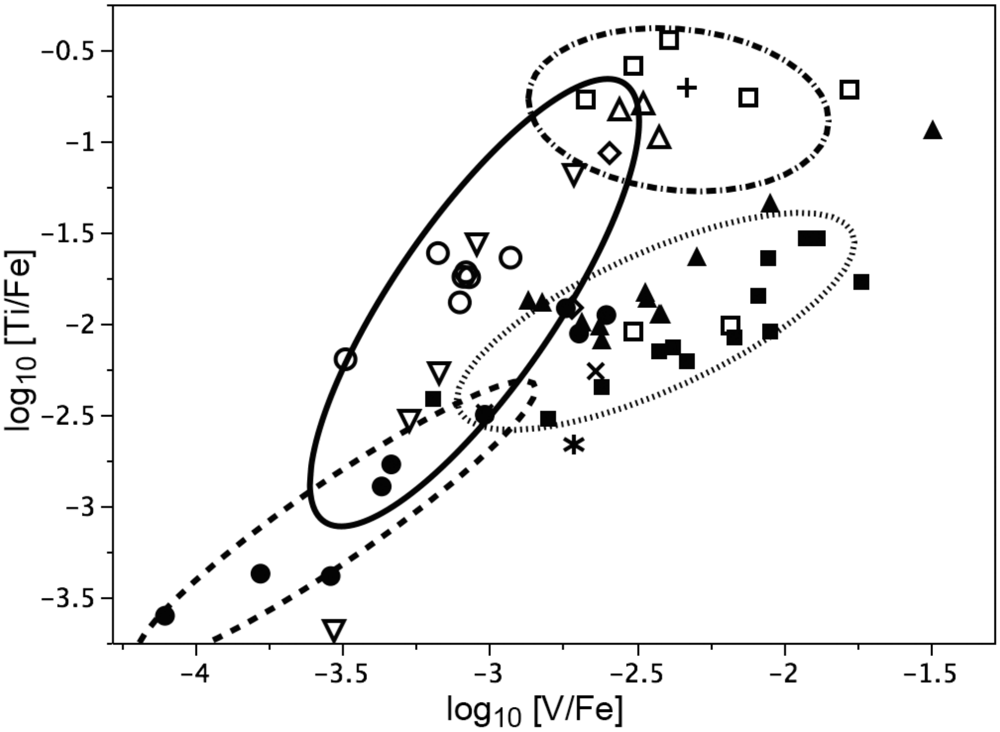

Figure 2.2: Bivariate plot of log$_{10}$ [Ti/Fe] versus log$_{10}$ [V/Fe]. Confidence ellipses refer to geochemical groups at 80% confidence. Legend: ◇ = Residential Camp (ElSx-10), ○ = Nut'l (FeSr-7), ✚ = Joashila (FaSu-19), ▽ = Stskiutl (FcSq-8), □ = Kisameet (ElSx-3), ■ = Cockmi (EjSw-1), ▲ = Namu (ElSx-1), ● = Katit (EkSt-1), △ = Sagar Lake, ✱ = Small Camp (EjSv-3), ✕ = Small Camp (EjSv-5).

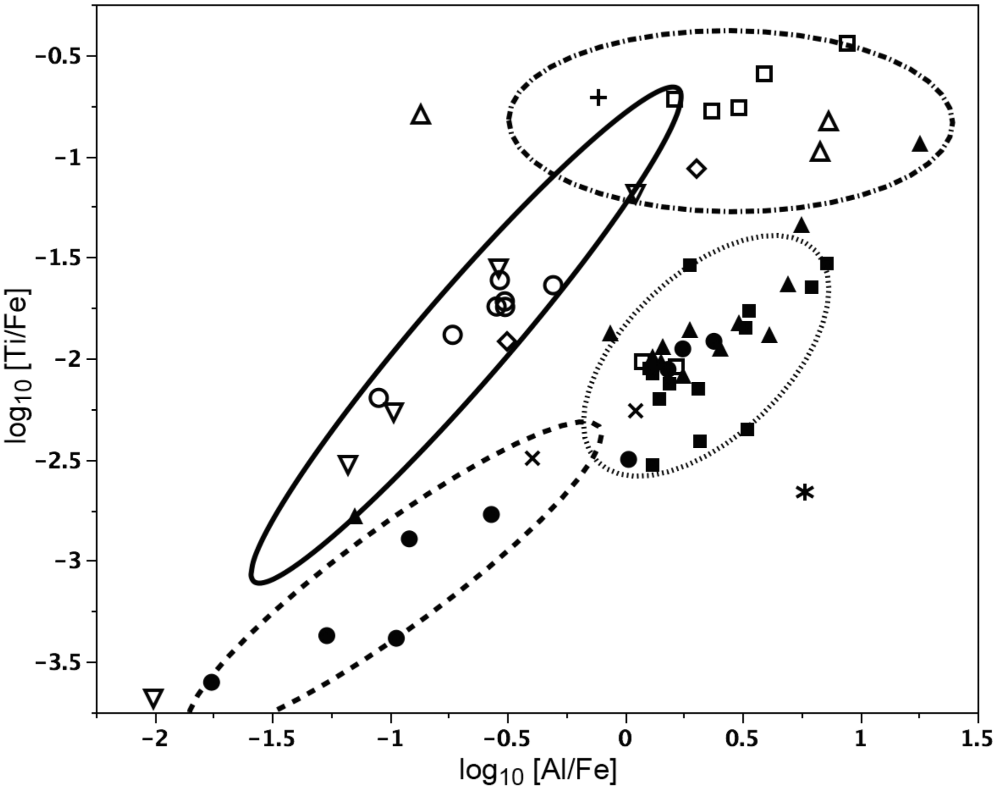

Figure 2.3: Bivariate plot of log$_{10}$ [Ti/Fe] versus log$_{10}$ [Al/Fe]. Confidence ellipses refer to geochemical groups at 80% confidence. Legend: ◇ = Residential Camp (ElSx-10), ○ = Nut'l (FeSr-7), ✚ = Joashila (FaSu-19), ▽ = Stskiutl (FcSq-8), □ = Kisameet (ElSx-3), ■ = Cockmi (EjSw-1), ▲ = Namu (ElSx-1), ● = Katit (EkSt-1), △ = Sagar Lake, ✱ = Small Camp (EjSv-3), ✕ = Small Camp (EjSv-5).

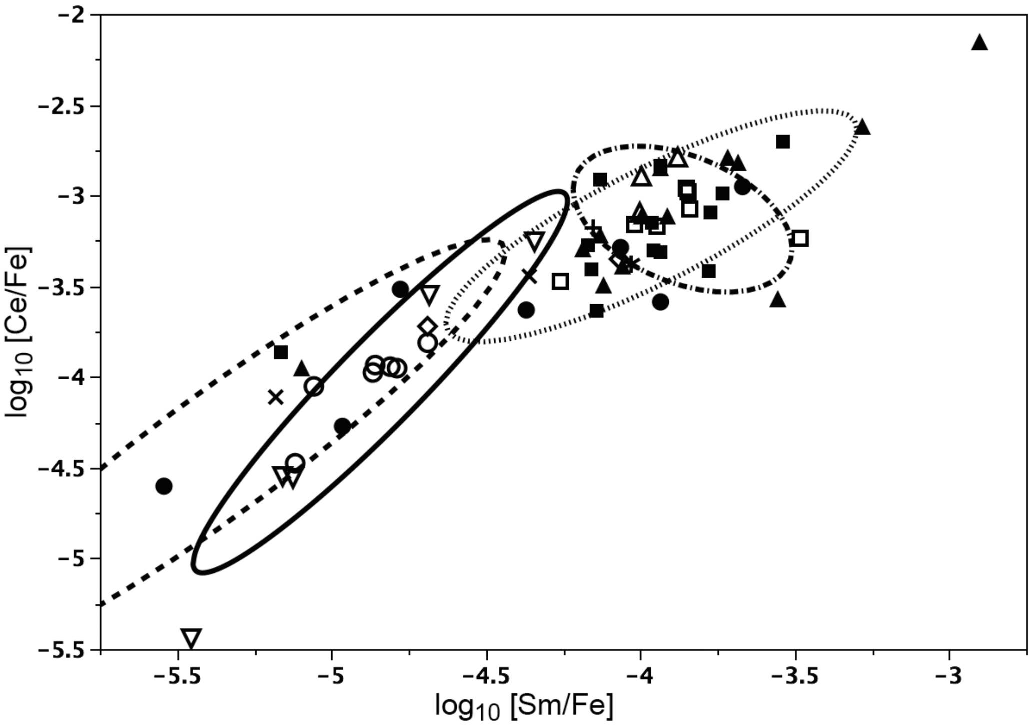

Figure 2.4: Bivariate Plot of $\log_{10}$ [Ce/Fe] versus $\log_{10}$ [Sm/Fe]. Confidence ellipses refer to geochemical groups at 80% confidence. Legend: ◇ = Residential Camp (ElSx-10), O = Nut'l (FeSr-7), ✚ = Joashila (FaSu-19), ▽ = Stskiutl (FcSq-8), ☐ = Kisameet (ElSx-3), ■ = Cockmi (EjSw-1), ▲ = Namu (ElSx-1), ● = Katit (EkSt-1), △ = Sagar Lake, ✱ = Small Camp (EjSv-3), ✕ = Small Camp (EjSv-5).

Figures 2.2 and 2.3 demonstrate the positive correlation between Fe-normalized concentrations of Ti and V, and Ti and Al, respectively. Positive correlations between these transition metals are expected as Ti and V can substitute for Fe. Samples at the highest end of that ratio come from Kisameet, Sagar Lake and ElSx-10. There are two groups at the mid-range of that ratio. One group with a slightly higher proportion of Ti includes samples from Nut'l, Joashila and Stskiutl. The other mid-range group has slightly higher proportions of V and Al and includes samples primarily from Namu and Cockmi, with a small number from Kisameet and Katit. The group with the lowest proportions include

Katit, Namu and EjSv-3. Figure 2.4 shows the positive correlation between Fe-normalized Ce and Sm. The pattern of REE enrichment is consistent with all measured, Fe-normalized light REEs (La, Ce, Nd, Sm and Eu). Overall, what these bivariate plots demonstrate is that there is a trend whereby as one moves from sites located in the eastern most area of the study region towards the western most area there is an increasing substitution of other materials for iron, and an increase in the presence of REEs relative to iron. We believe that these element substitutions and enrichments are directly associated with the Fe oxide matrix reflecting the geologic origins of the iron content, as well as variable degrees of post-depositional and diagenetic processes acting on these deposits. Further mineralogical testing using x-ray diffraction and petrographic analysis would verify these assumptions. This pattern of transition metal substitution and REE enrichment also correlates roughly with the geochemical groups identified using PCA and CDA.

2.4.5 Principal Components Analysis

Principal components analysis was then performed on the data set for selected major, minor and trace elements (Al, Ca, Na, Sc, Ti and V). We chose these elements as they have been established as ones that allow for differentiation between geochemical groups (Popelka-Filcoff et al., 2008). This analysis shows how variable the samples are, and which variables drive the variance within the data set. Each element included in the test is assigned an eigenvector score that reflects the positive or negative influence each has on the principal components as well as the strength of that influence. The first principal component accounts for 79.1% of the variability in the sample set. Elements that positively drive the variance are Ti and V, likely because they are associated directly with the Fe oxide matrix. The elements Al, Ca, Na and Sc negatively drive the variance within the sample set, and we believe that they could be associated with the outcrop-specific matrix of the ochre, the parent rock from which the deposit was derived, or other mineralogical inclusions. The results of the PCA also show that there are four distinct geochemical groups within the sample set. Figure 2.5 is a bivariate plot of PC1 and PC2 showing those geochemical groups, taking into account the contexts from which the samples came. What is apparent about these results is that each of the geochemical groups corresponds to clusters of sites that are geographically close to each other. Samples from Group 1 come exclusively from Stskiutl, Nut'l, Joashila and ElSx-10. Samples from Group 2 are from Kisameet, ElSx-10, and Sagar Lake. Group 3 includes samples from Namu, Katit, Cockmi, Kisameet, and EjSv-3. Geochemical Group 4 includes samples from Namu, Katit and EjSv-5.

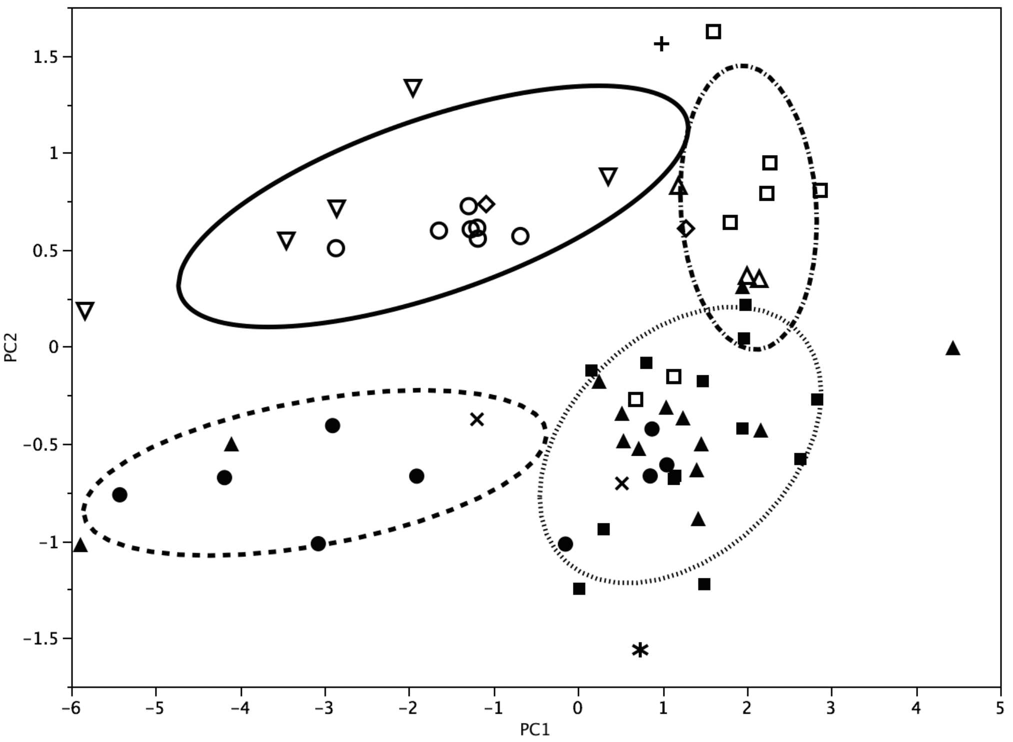

Figure 2.5: Bivariate Plot showing same geochemical groups and including sites. Legend: ◇ = Residential Camp (ElSx-10), ○ = Nut'l (FeSr-7), ✚ = Joashila (FaSu-19), ▽ = Stskiutl (FcSq-8), □ = Kisameet (ElSx-3), ■ = Cockmi (EjSw-1), ▲ = Namu (ElSx-1), ● = Katit (EkSt-1), △ = Sagar Lake, ✱ = Small Camp (EjSv-3), ✕ = Small Camp (EjSv-5). Confidence ellipses at 80%.

2.4.6 Canonical Discriminant Analysis

To further test the validity of the geochemical groupings and variability we performed a canonical discriminant analysis on the statistical set for the Fe-normalized elements Al, As, Ca, Ce, Eu, Na, Nd, Sb, Sc, Sm, Ti and V. In contrast to the PCA, the CDA test takes groups of samples with known differences and determines which variables (elements) contribute to those differences. For this test only forty-two of the sixty-four samples could be included since twenty-two of the samples did not have detectable levels of some of the listed elements. Figure 2.6 shows the results of this test. The CDA produced results similar to PCA, showing four different geochemical groups, and illustrating which elements drive the variance within the set. These results show that the majority of samples fall within the same geochemical group clusters as identified by PCA with some exceptions. Upon performing this statistical test that included a larger number of variables (more minor and REEs compared to the PCA test), the Katit and Namu samples separated from each other on the basis that Eu, Sm, Nd and Ce contribute significantly enough to drive that difference. This result further confirms that considerable variability in REE concentrations exists between sites located in the western and eastern portions of the study area.

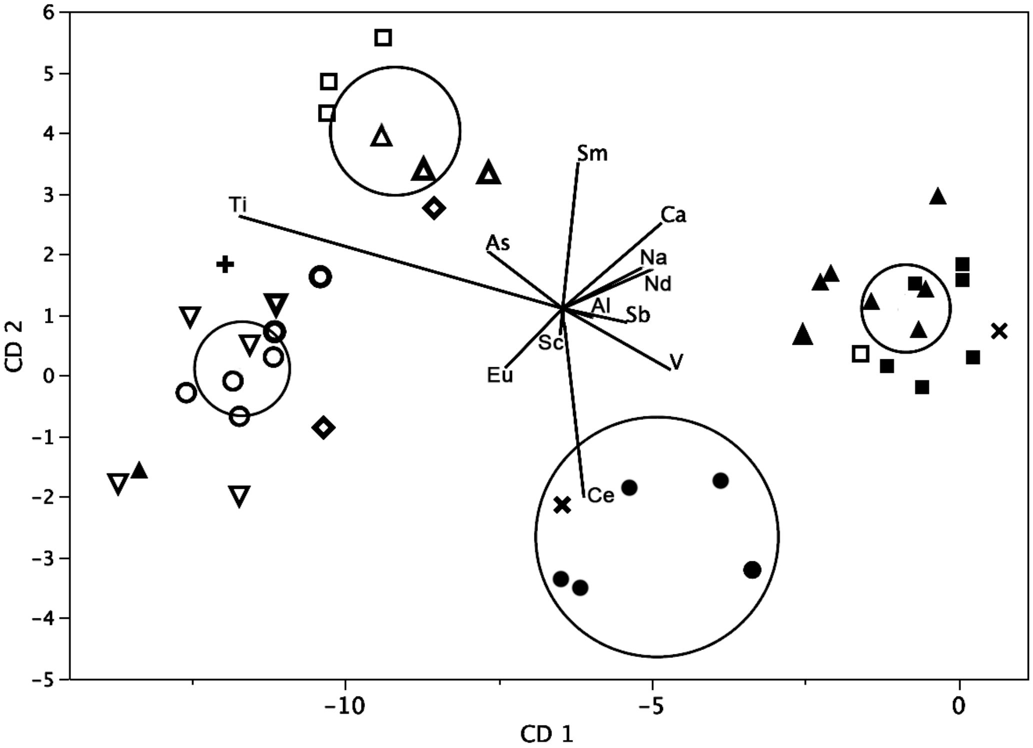

Figure 2.6: Canonical discriminant plot illustrating four different geochemical groups. Legend: ◇ = Residential Camp (ElSx-10), ○ = Nut'l (FeSr-7), ✚ = Joashila (FaSu-19), ▽ = Stskiutl (FcSq-8), □ = Kisameet (ElSx-3), ■ = Cockmi (EjSw-1), ▲ = Namu (ElSx-1), ● = Katit (EkSt-1), △ = Sagar Lake, ✖ = Small Camp (EjSv-5).

2.5 Results and Discussion

2.5.1 Geographic Locations and Scale

As stated, the results for both PCA and CDA show that the identified geochemical groups are in general agreement with their broad geographic location. For each group, the sites that are represented most within that group are geographically close to each other. Figure 2.7 illustrates this pattern.

Samples in Group 1, including Nut'l, Joashila and Stskiutl, are all located in the north-eastern most part of the study area and are all in traditional Nuxalk Territory. One sample in this chemical group was found at ElSx-10, which is a residential campsite located at the entrance to Burke Channel. It potentially served as a residential location for visitors to the outer coast area. It is reasonable for ochre from an outcrop in Nuxalk territory to be present at this site. Ochres from Group 2 come primarily from sites in the north-western portion of the study area and were retrieved from Sagar Lake, Kisameet, ElSx-10 and one from Namu, all in traditional Heiltsuk Territory. The largest group, Group 3, has samples from Namu, Cockmi and EjSv-3 with a small number from Kisameet and Katit. Finally, Group 4 ochres are primarily from Katit with two from Namu and one from EjSv-5. The clusters of sites present in Groups 3 and 4 both overlap Oweekeno and Heiltsuk territories where there is reasonable potential for trade or access to shared outcrops of ochre. That there are two geochemical groups supports the notion that a minimum of two ochre outcrops were being accessed in this area.

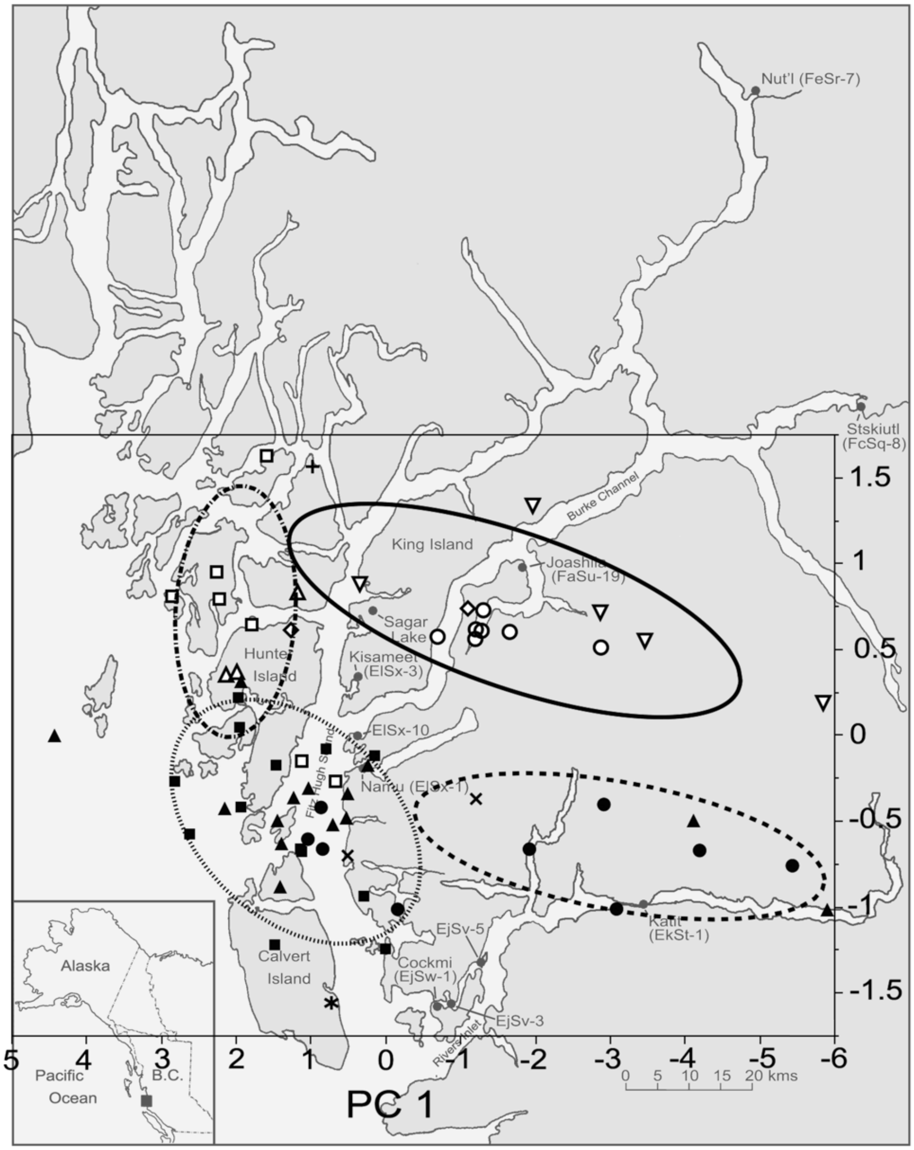

Figure 2.7: Map of study area with PCA plot superimposed. This figure illustrates how closely linked the chemical groups are with their geographic origin. Legend: ◇ = Residential Camp (ElSx-10), ○ = Nut'l (FeSr-7), ✚ = Joashila (FaSu-19), ▽ = Stskiutl (FcSq-8), ☐ = Kisameet (ElSx-3), ■ = Cockmi (EjSw-1), ▲ = Namu (ElSx-1), ● = Katit (EkSt-1), △ = Sagar Lake, ✱ = Small Camp (EjSv-3), ✖ = Small Camp (EjSv-5). Confidence ellipses at 80%.

There exists a broad pattern whereby sites in the western portion of the study area toward the outer coast exhibit greater transition metal substitution and enrichment of rare earth elements, while sites in the eastern portion of the study area exhibit dilution of these traits. Because the local bedrock geology is essentially the same, post-depositional and diagenetic processes would most likely be responsible for highly-localized variability in iron oxide outcrops. Lake sediment and water surveys completed by the British Columbia Geological Survey (Haggart et al., 2007) show a gradual increase from low pH (4.0-5.5, medium-high acid) to mid pH (5.5-7.0, medium to low acid) to high pH (7.0-8.5, neutral to low basic) as one moves from the west, outer portion of the coast toward inland areas. They directly attribute this pattern to increased precipitation and surface weathering of rock in the west as compared to the east (Nelson, pers. comm). At the same geologic scale, these weathering processes could potentially explain REE enrichment at western sites. Rare earth elements mobilize during rock weathering and therefore we would expect to see enrichment in areas subject to more of these processes (Pollard et al., 2007, 213).

2.5.2 Geochemical Groups, Statistics and Issues of Scale

On the basis of bivariate plotting, principal components analysis and canonical discriminant analysis, there are four groups of ochres within this sample set. Those four groups possess sufficient geochemical variability to satisfy the provenance postulate, taking into account that there is some degree of variability and spread within these groups. However, caution must be used in taking these statistical distinctions at face value, specifically with regard to issues of geographic scale and sample size. One limitation associated with discriminant statistical analyses is that a group of samples will only exhibit the degree of statistical difference from each other from within that group of samples. Because the majority of these samples are from unknown origin, we must be careful in how we interpret them as actual 'sources' of ochre. While these tests show four distinct groups, it could be possible that there are multiple outcrops of geochemically-similar ochre being represented in any one group. Increasing the sample size and expanding the geographic range of sampling could very well pull apart or more closely cluster together any one of these groups. As an example of this, Figure 2.8 shows preliminary results of separate, forthcoming work by the same authors.

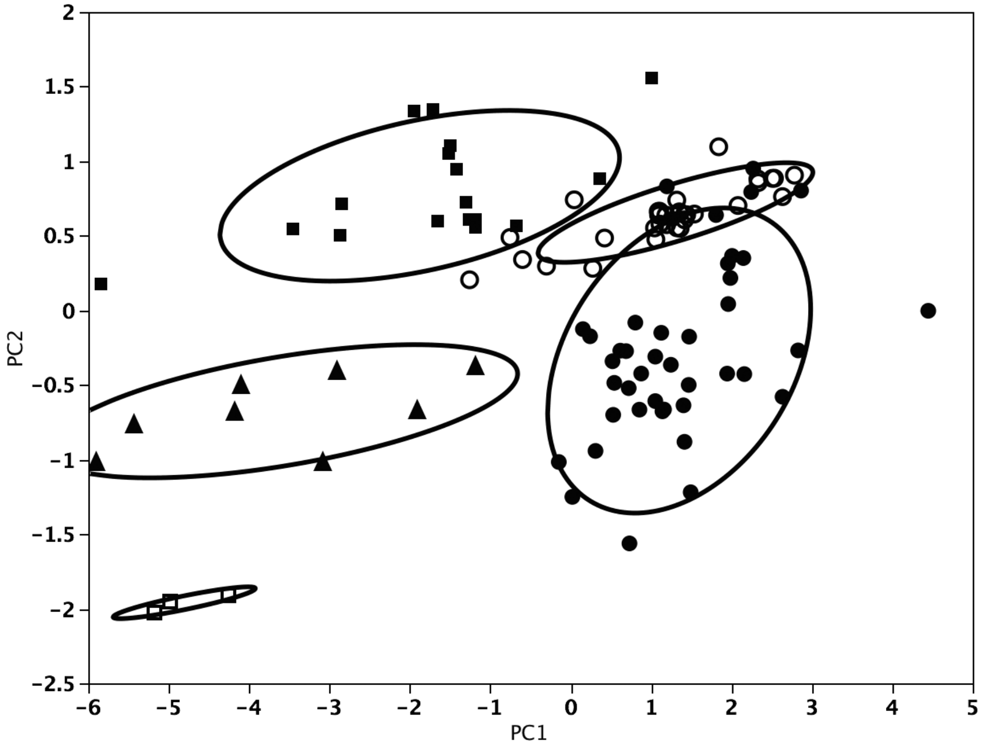

Figure 2.8: Bivariate plot of PC1 and PC2 for ochre samples from the central and south coast of British Columbia. Legend: ■ = Central Coast Eastern sites (A), ▲ = Central Coast Eastern sites (B), ● = Central Coast Western sites, ○ = South Coast Western sites, □ = South Coast Interior sites.

Figure 2.8 is a plot of principal components 1 and 2 for all samples from the central coast region with an additional thirty-seven samples from sites and ochre sources on the south coast of British Columbia. All methods of analysis and statistical treatments of data are identical to the central coast data set already described in this paper. Central Coast Eastern sites (a) include Qwliutlh, Joashila, Nut'l, Stskiutl. Central Coast Eastern sites (B) include Katit and three samples from Namu. Central Coast Western sites include Katit, Kisameet, Cockmi, Sagar Lake, EjSv-3, EjSv-5 and the remainder of the samples from Namu. South Coast Western sites include Sta'mis (DkRs-6), Chichen Stenach (DkRs-14), Paul Ridge Formation and Pilchuck Creek Outcrop, all located in traditional S<u>k</u>wxwú7mesh (Squamish) Territory. The South Coast Interior samples are from the Tulameen ochre bluffs in the Upper Similkameen Valley. All materials from the South Coast groups were collected with and facilitated by Rudy Reimer of Simon Fraser University, British Columbia. Again, the groups identified here continue to correspond roughly with their geographic location, and with the pattern of transition metal and REE enrichment to dilution from west- to eastward direction. However, at this scale the majority of the samples from the Central Coast Western sites begin to look geochemically similar whereas without the South Coast samples included they were more distinctive. From this perspective one could easily interpret the Central Coast Western sites group as one homogenous geochemical group of ochre. However, it is only with careful consideration of scale that we are able to more accurately tease apart the complex geochemistry of ochre outcrops in British Columbia. It is only at the smaller, regional scale that we are able to categorize groups and sub-groups of ochre based on their chemical characteristics. By increasing the sample set to include more sites and sources, and by focusing in on specific regions we will be able to create a detailed geochemical map of ochre sources from which we can then begin to interpret ochre-related behaviours over time and space.

2.6 Discussion and Conclusions

The purpose of this study was to determine if it were possible to differentiate geochemically distinct ochre groups within an archaeological assemblage using elemental data derived from NAA. We tested 64 samples from archaeological and geologic contexts within a relatively restricted geographic context and performed multiple statistical tests to explore the data set. The results illustrated geochemical trends in the ochres, including variable amounts of transition metal substitution and rare earth element enrichment between different geochemical groups. Principal components analysis and canonical discriminant analysis illustrated four discernable geochemical groups and confirmed that elements such as transition metals and rare earth elements were the most significant factors driving variance within the data set. This geochemical trend has been reported by others (Erlandson et al., 1999; Popelka-Filcoff et al., 2008). In combination, the results of these tests offer strong evidence for distinction between geochemical groups of ochre from primarily unknown sources.

Based on what we determined of the trends in ochre geochemistry and differentiating source groups, as well as the proportions of archaeological sites represented in each of those groups we suggest a modest interpretation of highly-localized, long-term model of ochre acquisition practices, with a small degree of movement of ochre to neighbouring geographic locations. The general pattern of acquisition for any given location was limited to one or two sources of ochre, and this persisted for the last ~2000 years of occupation of these sites. Other evidence suggests highly-localized procurement of resources (Cannon et al., 2008, 2011) with the exception of obsidian, which was traded extensively (Carlson, 1994). Trade networks that included obsidian and fish oil existed in this region, however ochre does not appear to be component of this network. What we do see is a pattern of localized acquisition, whereby inhabitants consistently accessed a small number of nearby sources over long periods of time with no dramatic changes in that behaviour. While there may be some shared access to a source, or small-scale trade or gifting of a specific source, it is clear that there was no need or desire to trade this resource.

To expand this project, and to be able to generate a basis for detailed archaeological interpretation, several key areas will need to be considered: temporal resolution, the spatial extent of patterning, and the locations of ochre sources. Testing additional samples from older contexts from these sites will indicate how far back this pattern of ochre acquisition existed. Analyzing ochre from different archaeological contexts will expand our knowledge on the varieties of its use, for example camp sites and pictographs. Sampling from other regions of the British Columbia coastline, and expanding current work on the South Coast will also provide a basis for comparison between different areas of the coast. As well, survey and geochemical study of additional ochre sources in the region would be critical to establish the geographical extent of ochre procurement. This would contribute to a further understanding of how far village inhabitants may have traveled to get ochre.

Understanding ochre geochemistry is a necessary foundation towards interpreting wide scale ochre-related practices such as quarrying, trade and exchange, and use contexts. This project contributes to a growing body of knowledge on trends in ochre geochemistry and demonstrates the potential for characterization studies of ochre, and the utility that these types of study can have to archaeologists. Ochre-based research should be considered as an expansion of what is currently available to archaeologists as indicators of trade and exchange, cultural interaction, raw material economics and social and symbolic practices. Ochre sources in the central British Columbia coast region are geographically close but geochemically distinct from each other. Despite a lack of access to multiple ochre sources in the area it is possible to determine the number and geochemical range of ochre sources present within a given archaeological assemblage. In this regional context, this study provides the foundation for future analysis of ochre from nearby sites and sources as part of a broader study of ochre procurement, trade and exchange. The results of this research verify the need for specific research protocols as attested in current literature, such as the need for data on a wide range of elements, including transition metals and REEs, and the need for rigorous statistical applications and consideration of geographic and geologic scale.

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CHAPTER 3

ELEMENTAL ANALYSIS OF OCHRE OUTCROPS IN SOUTHERN BRITISH COLUMBIA, CANADA

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ABSTRACT

Ochre is a red mineral pigment that was a key element of social and ceremonial practices among cultures of the Pacific Northwest Coast. It is recovered routinely from archaeological excavations, is visible as pigment for pictographs, and is described in the historic record as a trade item and component of ceremonial practices. Despite its ubiquity in the archaeological record, it is difficult to interpret its significance without first understanding the nature of its procurement and distribution. As a step towards identifying procurement practices, trade, and resource use it is necessary to thoroughly characterize ochre outcrops with regard to their intra-source and regional variability. We analyzed ochre from three outcrops using INAA to determine their elemental chemistry. The purpose of this study is threefold: to provide an example of the range of elemental variability

within and between outcrops, to illustrate the effect of scale and geomorphologic processes on elemental compositions and statistical interpretation, and to create a database of known deposits in southern British Columbia. The results demonstrate that ochre deposits may be differentiated on the basis of their chemistry, and that conservative statistical interpretation needs to be employed to assess true elemental variability within and between ochre deposits and regions.

3.1 INTRODUCTION

Mining and usage of ochre has been documented at a global scale and throughout a great deal of human history (Roper 1991). It has been used for a range of purposes, including medicinally (Mahaney et al. 1993, Velo 1984, 1986), as a pigment for face painting, pottery decoration (Capel et al. 2006), and pictographs (Carlson 1993, Dewdney 1970, Rajnovich 1994), and as an element of funerary ritual. In the context of coastal British Columbia, Canada, ochre is yielded routinely from archaeological excavations, is visible as pigment for pictographs (Carlson, 1993; Williams, 2001, 2006), is described at length in the historic record as a trade item (Mitchell and Donald 1988: 237; Williams, 2006), and as a component of ceremonial practice (Bouchard and Kennedy, 1986: 246; Matthews 1955: 47; Olson 1955). However, in this area there have been no systematic surveys or analyses of known red pigment sources. Previous work in British Columbia (MacDonald et al. 2011) has demonstrated that ochre from archaeological sites in this area can be differentiated on the basis of their elemental chemistries. Continuation of that work focuses on location, sampling and characterization of ochre deposits in the region toward assessing the potential range of geologic and chemical variability in iron oxides. The goals of this project were to assess the degree of elemental variability within and between three known deposits across southern British Columbia, and to begin to establish a database of information that would enable future studies of raw material resource use and trade. For the purpose of this paper we use the terms *ochre* and *iron oxides* interchangeably in reference to geologic deposits of iron oxides found in British Columbia. Our use of the term *source* refers to a geographically specific deposit of ochre, regardless of its chemical signature. We use the term *geochemical group* in reference to what we consider to be a statistically determined signature group of iron oxides, irrespective of its geographic extent or location.

3.2 PREVIOUS RESEARCH

Methodological examples of ochre research have focused primarily on elemental, mineralogical and isotopic characterizations. Elemental studies are based on the provenance postulate described first by Weigand et al. (1977:24), that “chemical variability between sources must be greater than the variability within any one given source”. As the range of methods used to characterize materials has broadened to include mineralogical and isotopic, Neff (2000: 108) revised this definition to include “qualitative or quantitative chemical or mineralogical differences between natural sources that exceeds qualitative or quantitative variation within each source”. The success of any elemental, mineralogical or isotopic characterization relies upon adequate sample sizes, sub-sampling of sources, and an acceptable degree of precision and accuracy in data collection. Reviews of previous ochre research exist in the current literature (Erlandson et al., 1999, Popelka-Filcoff et al., 2008, Popelka-Filcoff et al., 2007) and will not be elaborated upon in detail here. However, notable recent examples include Erlandson et al. (1999), Smith et al. (1998), Popelka-Filcoff et al. (2007 and 2008) Giachi et al. (2009), Erdogu and Ulubey (2011), Gialanella et al. (2011), and Eiselt et al. (2011). Exploring elemental trends within and between raw material sources has been done extensively for materials such as obsidians, cherts and some clays. However, with respect to ochre outcrops, systematic exploration of intra-source variability is still relatively new. An important consideration for the characterization of iron oxides is the potential variability within and between outcrops at different geologic and geographic scales, and how it pertains to the potential for linking archaeological ochres to their source of origin.

3.3 REGIONAL CONTEXT AND FIELD COLLECTION

In southern British Columbia ochre is yielded routinely from archaeological excavations, was used as pigment for pictographs, and was quarried from historically-known and traditionally utilized outcrops (ARCAS 1999, Reimer 2012). No systematic chemical analysis of ochre from geologic outcrops currently exists in this area. The nearest examples on the north western Pacific coast of North America include Erlandson et al., (1999), MacDonald et al. (2011), and Mrzlack (2003). The three ochre sources targeted for this study are situated in coastal and interior areas of southern British Columbia (see Figure 3.1). Samples from the coastal area are from two sources, Paul Ridge and Pilchuck Creek, located near Mt. Garibaldi and Squamish Valley, respectively, in Squamish First Nation Traditional Territory. The third source is Tulameen Ochre Bluffs located in Upper Similkameen First Nations Territory in the interior of British Columbia. These sources were selected because they are known ethnohistorically as locations that were frequently visited and utilized for their red pigment, and are also associated with known trade routes (Bouchard and Kennedy 1976, Matthews 1955).

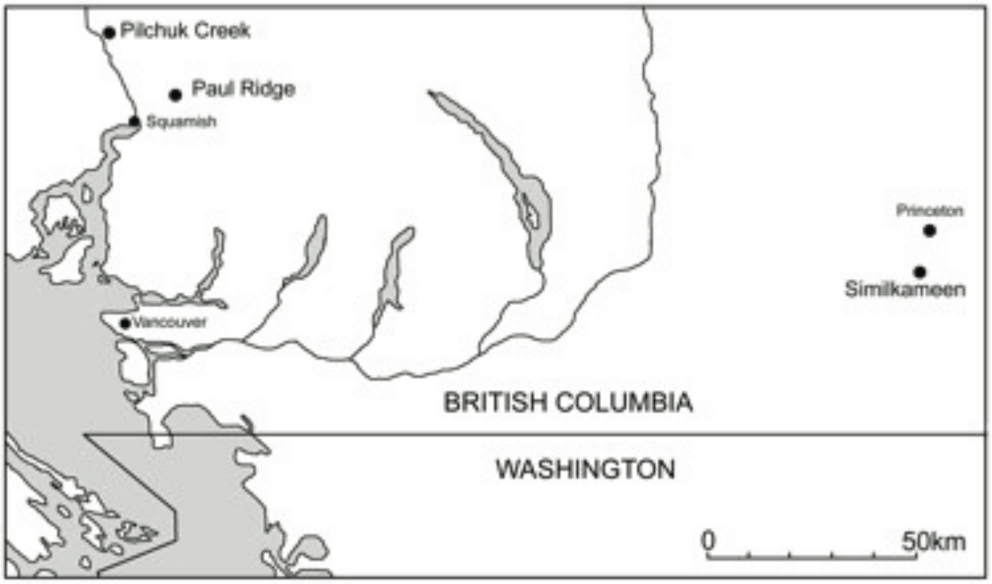

Figure 3.1: Map of ochre outcrop locations in southern British Columbia, Canada.

All field samples were collected by MacDonald and Reimer, (Reimer and MacDonald 2008) with the exception of materials from Tulameen Ochre Bluffs, which were provided by Reimer. The topography of the coastal mountain range is largely a product of the Quaternary-age Mt. Garibaldi volcanic complex (Green et al., 1988; Guffanti and Weaver 1988; Read 1990; Sherrod and Smith 1990; Hickson 1994; Hickson et al 1999: 491), and subsequent alluviation. Paul Ridge ochre deposit is a discontinuous outcrop of oxidized basalt that runs along a mid-elevation ridge approximately 12 km south of the peak of Mt. Garibaldi. This area is characterized by rhyodacite, andesite and basalt deposits (Hickson 1996: 3, Matthews 1958). This source consists of three discrete outcrops along Paul Ridge, each less than 2 km from each other, that were targeted and sub-sampled to assess the range of chemical variability across the deposit as a whole. These sub-sampled groups are referred to as Paul Ridge 1, Paul Ridge 2, Chichen Stenach 1, and Chichen Stenach 2. Chichen Stenach (DkRs-14) is a lithic scatter location situated directly on top of one of the iron oxide deposits and is considered to be part of Paul Ridge. Ochre samples were taken directly from a hearth on the site (Chichen Stenach 1), and ~10 m northeast of the hearth (Chichen Stenach 2) to assess if in-situ, heat-treated ochre from the same outcrop would possess a different chemical signature. Approximately 2kg of ochre was taken from each outcrop.

The second coastal source is Pilchuck Creek located in the alluvial floodplain of Squamish Valley west of Mt. Garibaldi. Roughly 95% of the rocks in this drainage are grandiorites, tonalities and other mixed granitoid and metamorphic rocks (Woodsworth, pers. comm. 2011). The ochre deposit is an iron-rich alluvial silt, grey in colour, with visible, horizontal bands of iron oxides. When heated the colour of this sediment intensifies to a rich orange-yellow hue. Because of restricted access we were unable to cover extensive areas of this deposit, however we were able to sample two locations <5 m from each other. The third source area in this study is Tulameen Ochre Bluffs, located on the British Columbia Interior Plateau near the confluence of Similkameen and Tulameen Rivers, approximately 10 km south of the town of Princeton. Materials from this source were widely used through out the surrounding valley as pigment for surrounding pictographs and for cultural ceremonies (Copp 1975, 2006).

3.4 ANALYTICAL PROTOCOL

Sample selection and methodological protocol

To assess the potential geochemical variability within each source area 2kg samples were taken from multiple points laterally across a source, homogenized, and further sub-sampled in the lab. Paul Ridge source area was divided into four sub-groups, and further sub-sampled: Paul Ridge 1 (n=14), Paul Ridge 2 (n=15), Chichen Stenach 1 (n=11), and Chichen Stenach 2 (n=9), for a total of 49 samples representing this area. Pilchuck Creek source area was smaller in size and could only be sub-sampled into two groups: Pilchuck Creek 1 (n=10) and Pilchuck Creek 2 (n=10). Tulameen Ochre Bluffs samples taken from one location were split into 12 sub-samples. A total of 81 ochre samples were tested using neutron activation analysis (NAA) since it is optimal for measuring elements that are diagnostic for differentiating chemical groups of iron oxides (MacDonald et al. 2011, Popelka-Filcoff et al. 2008). These elements include, but are not limited to, transition metals and rare-earth elements. Detailed descriptions of the theory of NAA have been described elsewhere (Glascock and Neff 2003, Neff 2000, Pollard et al. 2007.), therefore we provide an abbreviated description of our protocol. Large chunks of raw pigment were cleaned with de-ionized water in an ultrasonic bath, dried in a low-temperature oven (80°C), and ground into powder using an agate mortar and pestle. Between samples the mortar and pestle were cleaned with de-ionized water to prevent cross-contamination. The powdered samples were weighed to ~1 g each and sealed into high-purity polyethylene vials.

We performed two neutron irradiations to collect data on elements that produce short-, medium-, and long-lived radioisotopes. As per standard protocol at the McMaster Nuclear Reactor, multiple aliquots of six NIST standard reference materials and in-house control samples were tested concurrently (SRMs 688 Basalt, 278 Obsidian Rock, 1632b Coal and SRM 1633b Fly Ash from NIST). To collect data on elements that produce short-lived isotopes, samples were run through a pneumatic tube system and subjected to a 10-second thermal irradiation at a neutron flux of 3×10^{13} n cm^{-2} s^{-1}. After a 10-minute delay, samples were counted for five minutes each on a HPGe detector (Al, Ca, Cl, Co, Dy, K, Mn, Na, Sr, Ti, and V). After 24 hours, samples were counted again for five minutes (Eu, K, La, Mn, Na, Sm, and Sr). To collect data on elements that produce long-lived isotopes the same samples were irradiated for two hours at a neutron flux of 3×10^{13} n cm^{-2} s^{-1}. After 7-10 days (As, Ba, Fe, La, Na, Nd, Sb, Sc, Sm, and Th), and again after 14-16 days (Ce, Co, Cr, Cs, Eu, Fe, Hf, Lu, Sc, Tb, Th, Yb, and Zn) the samples were counted for 30 minutes each. Spectral data were collected and evaluated with GammaVision (ORTEC) and Aptec (Canberra) peak-fitting software. The data were converted to elemental concentrations using PEAK software.

3.5 STATISTICAL EXPLORATION OF RESULTS

Table 3.1 (*See APPENDIX B for Table 3.1) shows the concentration means and standard deviations of all elements measured for each source group of ochres. The data presented here illustrate prominent differences between coastal and interior groups. The most apparent difference is that of concentrations of major, minor, and trace elements for coastal sources (Pilchuck Creek, Paul Ridge) versus the interior source Tulameen. Based on the chemical compositions, the interior source ochre consists primarily of an admixture of calcium carbonate and iron oxide, while the coastal source ochres are silicate based. Tulameen has considerably higher Ca, Fe, Ba, and Mn, concentrations, and lower Al, Na, V, K, Cr, Sc, Co, and Zn concentrations. Tulameen ochres are also below the detection limits for Ti, As, Sb, Cs, Hf, Ta, and most measured rare earth elements (REEs), in particular the heavy REEs (terbium, dysprosium, ytterbium, and lutetium). Based on these data the Tulameen samples can be differentiated from the coastal sources, which was to be expected given that Tulameen was formed under different depositional conditions and exists within a vastly different geologic region. Differentiation between the coastal sources however, requires advanced, stepwise, statistical analysis. The data show differences between coastal sources such as slightly higher concentrations of Al, Co, and Ti across outcrops along Paul Ridge and Chichen Stenach, higher Fe concentration and almost twice the amount of K and

Ba at Pilchuck Creek, a slight increase in some REEs at Pilchuck Creek, and the only detectable presence of As and Sb across all samples at Pilchuck Creek.

3.5.1 Scatterplots

Scatterplots of elemental concentrations are useful for determining correlations between elements. Elements within the same groups on the periodic table often exhibit similar patterns of behaviour since they possess similar physical and chemical properties. A geochemical trend identifiable through such plotting is elemental substitution, where elements with similarly sized atoms and charges replace each other within a crystal structure as a result of specific geologic conditions (e.g. Na and Cs) (Goldschmidt 1937). Scatter plots of concentration data for element pairs within this set reveals inter-source information, however is moderately useful for illustrating positive correlations between some elements and clustering between sources. Figure 3.2 shows the correlation between V and K for all groups. Concentrations of both elements increase as one moves from the geographic interior (Tulameen), towards the coast (Paul Ridge, Pilchuck Creek, Chichen Stenach). On the basis of V and K content, Tulameen separates from the coastal samples, and Pilchuck Creek separates out from Paul Ridge and Chichen Stenach. On the basis of scatterplots between these and multiple other element pairs, we are able to differentiate all four source areas.

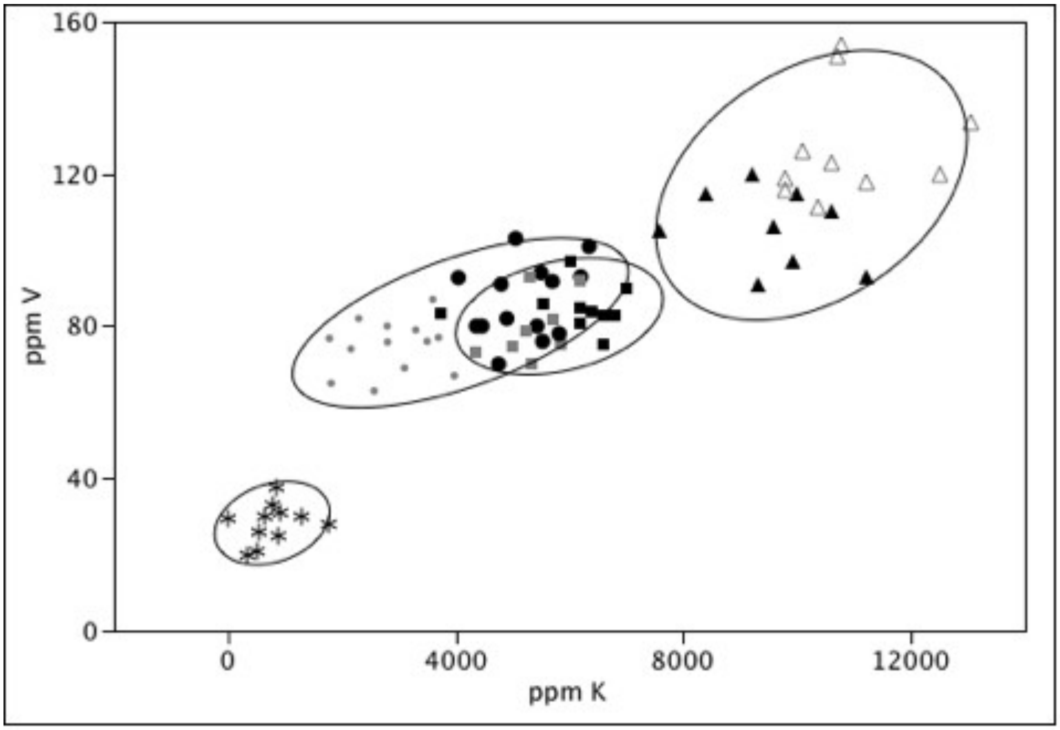

Figure 3.2: Scatterplot of ppm V versus ppm K. Confidence ellipses 90% for each source group. Legend: ✱ = Tulameen, ● = Paul Ridge 1, ● = Paul Ridge 2, ■ =Chichen Stenach 1, ■ = Chichen Stenach 2, ▲ = Pilchuck Creek 1, △ = Pilchuck Creek 2.

3.5.2 Iron normalized and $\log_{10}$ data

The standard process for multivariate statistical analysis of a data set of elemental concentrations of iron oxides first requires converting all element concentrations to a ratio of the Fe content (also referred to as Fe-normalized data) for each sample (Eiselt et al. 2011, MacDonald et al 2011, Popelka-Filcoff et al 2007, 2008). This is performed because the Fe content of each sample can vary significantly, and that variability can amplify or dilute the presence of other potentially diagnostic elements, or where other elements may substitute for Fe. Figure 3.3 is a scatterplot of Fe-normalized K versus Co.

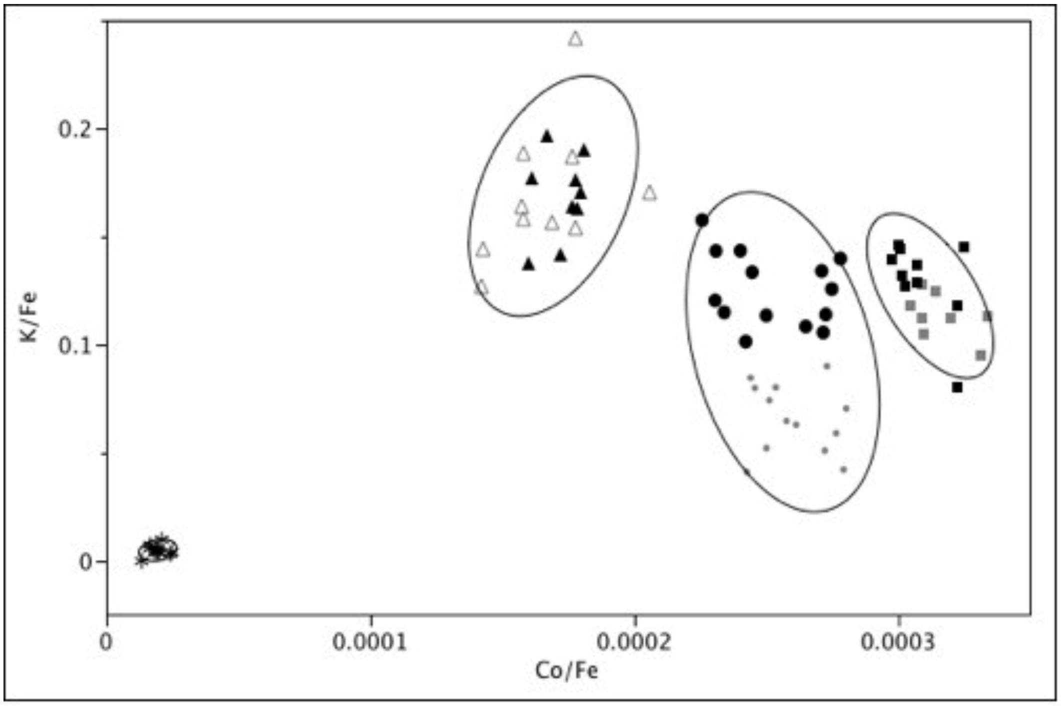

Figure 3.3: Scatterplot of K/Fe versus Co/Fe. Confidence ellipses 90% for each source. Legend: ✱ = Tulameen, ● = Paul Ridge 1, ● = Paul Ridge 2, ■ =Chichen Stenach 1, ■ = Chichen Stenach 2, ▲ = Pilchuck Creek 1, △ = Pilchuck Creek 2.

Before performing principal components analysis (PCA), Fe-normalized values are converted to $\log_{10}$ values as part of standard statistical practice when variability within a set can be across several orders of magnitude (Baxter 2008, p. 974). On the basis of scatterplots we determined that Tulameen ochre geochemistry was significantly different enough from coastal sources that there was the potential for the group to obscure any finer scale variability between coastal samples. Figure 3.4 is a scatterplot illustrating this potential.

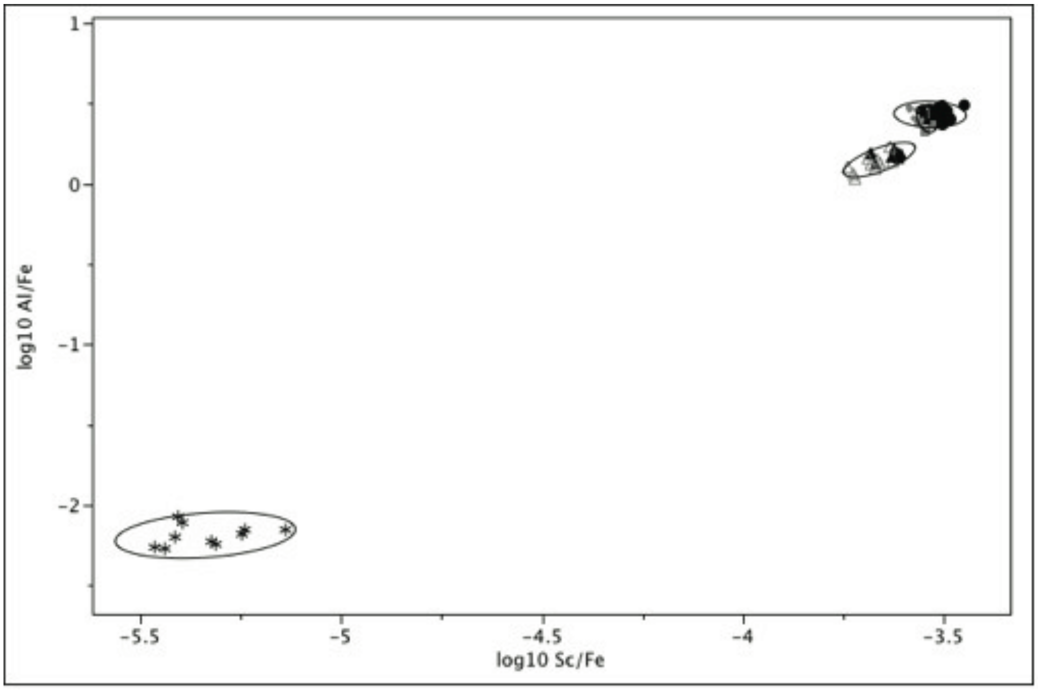

Figure 3.4: Scatterplot of $\log_{10}$ Al/Fe versus $\log_{10}$ Sc/Fe. Confidence ellipses 90%. Legend: ∗ = Tulameen, ● = Paul Ridge 1, ● = Paul Ridge 2, ■ =Chichen Stenach 1, ■ = Chichen Stenach 2, ▲ = Pilchuck Creek 1, △ = Pilchuck Creek 2.

This also demonstrates how vastly different the chemistry of Tulameen ochre is, how the magnitude of that difference could obscure finer scale variability between the remaining sources. Given that our goal was to determine if *all* ochre sources in this study possessed enough geochemical variability that they could be statistically differentiated, and that variability to this degree could influence the results of PCA, we chose to omit Tulameen from further tests and to focus on the differences between coastal sources. Subsequently we plotted elemental data from the remaining samples to determine which correlated positively and negatively with Fe, and which elements would be appropriate to differentiate between groups. On the basis of scatterplots of all element pairs we determined that the

$\log_{10}$ Fe-normalized element concentrations for Ti, V, Al, Cl, Ca, Mn, Na, K, Sc, and Co would be variables included in subsequent PCA.

3.5.3 Principal components analysis

Principal components analysis is a multivariate test that shows how variable samples are within and between groups, and the degree to which each variable drives the variance within the data set. For the data set that consisted of the $\log_{10}$ Fe-normalized concentration values for the coastal sources, the first nine principal components account for 96% of the variability within the set. Figure 3.5a is a scatterplot of PC1 versus PC2 including the elements Ti, V, Al, Cl, Ca, Mn, Na, K, Sc, and Co.

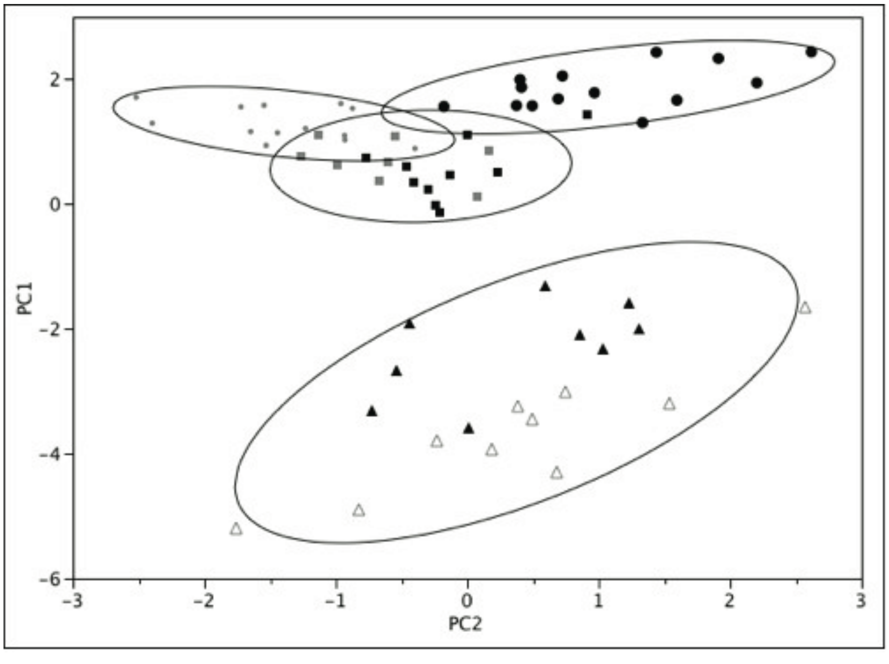

Figure 3.5a: Scatterplot of PC1 versus PC2. Confidence ellipses 90% Legend: ● = Paul Ridge 1, ● = Paul Ridge 2, ■ =Chichen Stenach 1, ■ = Chichen Stenach 2, ▲ = Pilchuck Creek 1, △ = Pilchuck Creek 2.

Elements that positively drive variance for PC1 are Ti, Al, Ca, Na, Sc, and negatively are V, K, Mn. Elements that positively drive the variance for PC2 are V and K, and negatively are Ti, Co and Mn. Data points in Figure 3.5a show a clear separation between Pilchuck Creek and Paul Ridge samples. Differentiation between Paul Ridge samples on the basis of these data shows that elements that positively and negatively drive the variance for PC2 contribute most to the variability between them. Figure 3.5b is a scatterplot of PC1 and PC3 including the elements K, V, Mn, Ti and Co. In contrast to Figure 3.5a, this plot shows that Mn, Ti and Co are the variables that separate Paul Ridge 1, Paul Ridge 2 and Chichen Stenach.

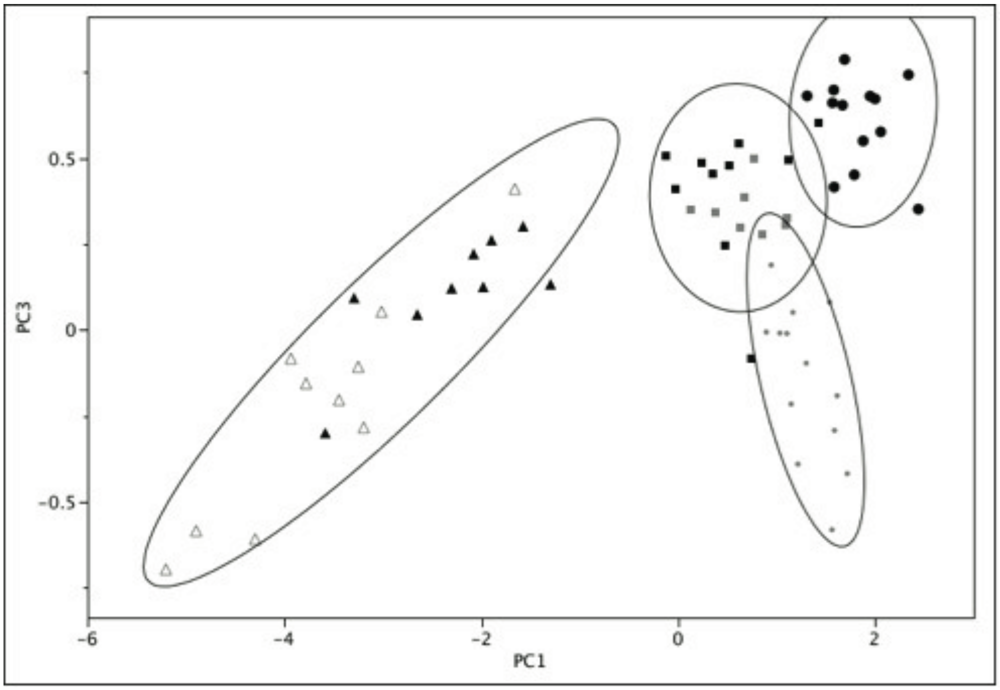

Figure 3.5b: Scatterplot of PC1 vs PC3 including elements K, V, Mn, Ti and Co. Confidence ellipses 90% Legend: ● = Paul Ridge 1, ● = Paul Ridge 2, ■ =Chichen Stenach 1, ■ = Chichen Stenach 2, ▲ = Pilchuck Creek 1, △ = Pilchuck Creek 2.

3.5.4 Canonical discriminant analysis

Canonical discriminant analysis is a multivariate test that takes groups of samples with known differences and determines which variables contribute the most to those differences. To further characterize the variability between the coastal source samples on the basis of a different set of elements we performed CDA on the group of REE concentrations for all coastal sources (La, Ce, Nd, Sm, Eu, Tb, Dy, Yb and Lu.) Rare earth elements have been identified as diagnostic elements for differentiation of ochre sources as a result of their unique chemical behaviours. Figure 3.6 is a biplot of the samples and element vectors illustrating the difference between groups of samples. We excluded Tulameen ochres as they are largely devoid of REEs. There is separation between Pilchuck Creek on the basis of La and Lu content, separation of Paul Ridge 1 samples on the basis of Ce, Nd and Tb, and clustering of Paul Ridge 2, Chichen Stenach 1 and Chichen Stenach 2 on the basis of Yb. The results of this test are similar to that of PCA in that the same geochemical groups cluster together, and that enough variability in REEs exists between sources to differentiate them from each other.

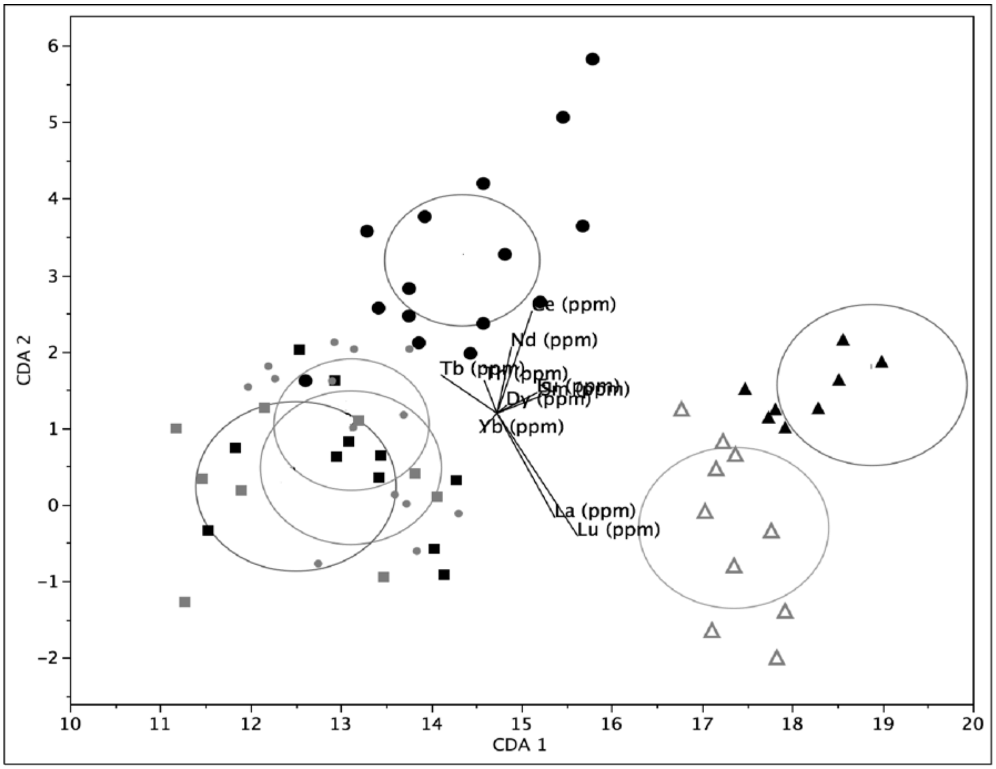

Figure 3.6: Canonical Discriminant Analysis biplot, tested on all outer coast sources using rare earth element concentrations in ppm (La, Ce, Nd, Sm, Eu, Tb, Dy, Yb and Lu). Confidence ellipses 90%. Legend: ● = Paul Ridge 1, ● = Paul Ridge 2, ■ =Chichen Stenach 1, ■ = Chichen Stenach 2, ▲ = Pilchuck Creek 1, △ = Pilchuck Creek 2.

3.6 DISCUSSION

The results of INAA and statistical tests indicate multiple lines of evidence that, when combined, provide the basis for assigning chemical signatures to ochre sources in southern British Columbia. On the basis of elemental concentrations (Table 3.1) it is straightforward to differentiate between coastal and interior sources. Significant differences between major and minor elements demonstrate clear variability between the two regions, and a small degree of variability between sources on the coast primarily on the basis of K and Al. Based on high Fe content Tulameen ochre could be considered more ‘pure’ of a source. Coastal sources are more chemically heterogeneous compared to Tulameen, containing higher concentrations of minor, trace and REEs. The formation (volcanic), diagenetic (alluvial re-deposition), and intensified weathering processes acting on these deposits contributed to their distinctive chemistries. A common pattern observable in archaean-age volcanic deposits, in particular alkaline, plutonic rocks including tonalite and trondjhemite, is the enrichment of light REEs, depletion of heavy REEs, and negative Eu anomalies (Condie 1981: 193). Hickson describes heavy precipitation on ridge tops in these alpine areas, up to 5 m annually, contributing significantly to weathering processes acting on iron oxides (Hickson 1996:2). Rare earth elements mobilize readily during intensive rock weathering (Pollard et al 2007:213), therefore their increased concentrations in coastal source samples is expected and unique to those outcrops.

Further differentiation of coastal sources was demonstrated by PCA and CDA statistical tests. Principal components analysis demonstrated which major and minor elements contributed most to variability within the data set. The CDA test, with a focus on REEs, produced results similar to PCA with respect to group clustering. We argue that the combination of the results of these tests demonstrates sufficient statistical proof to satisfy the provenance postulate, and that each of these outcrops of ochre have distinctive chemical signatures.

3.6.1 On the importance of scale

For this project we have attempted to emphasize the importance of scale for the analysis and interpretation of geochemical studies of this nature with regard to the variability between geographic interior and coastal sources. There are three issues relevant to the discussion of scale in the context of this study: geologic processes, statistical tests, and methodological implications. The scale of geologic processes has implications for the characteristic chemistries of ochre outcrops. These contexts are all regionally specific and possess their own formation and diagenetic histories. For southern British Columbia, variability in geological contexts and processes result in distinct differences between interior and coastal ochre source chemistries. With a narrower regional focus, local-scale formation and diagenetic processes are significant factors to consider for resulting chemical variability. Statistical interpretation is also affected by scales of magnitude. The scale of difference between groups of samples that are broadly chemically distinct (interior versus coastal sources) have the potential to obscure finer-scale variability between sub-groups. These are critical pieces of information that warrant consideration. In southern British Columbia evidence for long-distance exchange of other materials exists (Carlson 1994), therefore there is reason to believe that long-distance movement (>50 km) of ochre likely occurred. However, to be able to assign artifacts or ochre deposits to their geologic origins successfully we need to be able to assign appropriate regional and sub-regional ‘zones’ for statistical interpretation. The data can be easily obscured without careful attention to detail regarding scale. For example, if we were to test an unknown piece of ochre from an archaeological context against this database that included the Tulameen ochre source we would only be capable of determining if it was from an interior or coastal source (or neither of the two). However, narrowing down these statistical tests with respect to local-scale (< ~20 km) geochemistry would allow us to determine specifically where the ochre may have come from. It is these subtle differences that allow us to subsequently generate detailed archaeological interpretations of past ochre acquisition and use practices, and this case study is an example of exactly why detailed databases of elemental concentration data need to exist before archaeological interpretations on resource acquisition, and trade and exchange can be made.

The results of this study illustrate the implications geologic and geographic scales have on methodology. For this project techniques of analysis that are any less sensitive to the elements identified here as diagnostic for characterization of ochre sources may not be suitable for differentiating between coastal sources. A critical consideration for heterogeneous materials such as ochre is that of surface versus bulk analytical techniques. High-resolution techniques such as ICP-MS would be suitable as a comparative level of analysis, however given the current capabilities of some portable XRF systems, (whose popularity has grown exponentially in recent years) with respect to sensitivity to certain elements and limits of detection for specific elements, they may not be able to differentiate between sources at this scale. Instrumentation companies that produce these systems report limits of detection for each element, and the relative degree of accuracy with which those elements could be measured, however there has been little discussion on the challenges of matrix effects for raw materials of different types which is a significant issue for the accuracy of chemical characterization of heterogeneous geologic materials. In the context of this study, portable XRF could, for example, tell the difference between coastal and interior sources, however the level of sensitivity and limits of detection it has for trace and REEs would not be adequate for any finer resolution analysis. However, there are a suite of elements more accurately analyzed by x-ray fluorescence (Sr, Zr, Rb, Pb), that may reveal chemical differences that could complement the results of INAA and satisfy the provenance postulate.

Generating databases of geochemical information on ochre sources is a necessary foundation for future studies that incorporate resource acquisition, ochre quarrying, and trade and exchange. The results of this study contribute a wealth of information on ochre sources in southern British Columbia and have established a baseline of information from which future studies can be derived. As our understanding of ochre source chemistries continues to develop it is apparent that databases that include a range of elemental data, information on geologic histories as well as careful statistical application are a necessary foundation for work of this nature.

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CHAPTER 4

ANALYSIS OF PICTOGRAPHS IN THE SOUTHERN CANADIAN SHIELD: AN EXAMPLE OF THE UTILITY OF PORTABLE X-RAY FLUORESCENCE TECHNOLOGY

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Abstract

Pictographs have long been an area of interest for archaeologists and their analysis has typically focused on their locations within the landscape and the interpretation of their imagery. The Canadian Shield Woodland area boasts rich concentrations of pictographs, and research on these has focused primarily on their aesthetic interpretation and on situating them within a broader context of landscape archaeology (Arsenault 2004a, 2004b; Dewdney 1970; Rajnovich 1994). However, there has been little research on the pigments that were used to create them. By analyzing the ochre used for pictograph paintings we are able to glean further information on the activities surrounding pigment procurement, trade, and use. This paper presents the findings of a survey of pigment sources and pictographs in the southern Canadian Shield region of northern Ontario. We used non-destructive portable x-ray fluorescence (p-XRF) spectroscopy to elementally characterize 62 pictographs and raw materials from two ochre sources in the Greater Temagami, Lake Nipissing, and north shore of Lake Huron areas.

Results indicate that four distinct and identifiable chemical groups of ochres were used across the study area.

Keywords

Pictographs, ochre, pigments, Temagami, Canadian Shield, portable x-ray fluorescence, elemental characterization

4.1 Introduction

The presence of ochre in archaeological contexts is well documented, and is perhaps known most commonly for its use in the creation of pictographs. Despite its ubiquity in the archaeological record, it remains under-examined as a material that existed within frameworks of social practices, resource use, and trade. By determining the geochemical composition of ochre it is possible to trace pigments back to their origin, and by extension, create a record of their procurement, movement, and use. Previous work has shown that the elemental chemistries of geologic sources of ochre satisfy the provenance postulate (Weigand *et al* 1977) and can be differentiated into source groups (Popelka-Filcoff *et al* 2007, 2008; Eiselt *et al* 2011; MacDonald *et al* 2011, 2013; Smith and Pell 1997). Recent advances in the technologies used for elemental characterization, such as portable x-ray fluorescence (p-XRF) instruments, have enabled characterization of pigments *in situ*, a necessity for the non-destructive analysis of pictographs located in remote areas. To date, some successful examples of applications in the field exist (Potts and West 2008, Perardi *et* al 2000; Froment *et al* 2008; Prinsloo *et al* 2008; Williams-Thorpe *et al* 1999). The study of rock art is a diverse field and has garnered interest from a range of disciplines including archaeology, art history, and geochronology (Bednarik 1996, 2006; Whitley 2005). Examples of archaeological research on pictograph pigment characterization and provenance include Perardi *et al* (2000), Froment *et al* (2008), Prinsloo *et al* (2008), and Tournié *et al* (2010). Rodriguez-Gonzalves *et al* (2012) used stereophotogrammetry imaging on Palaeolithic rock art panels in Llonín Cave in Asturias, Spain. Notable distributional and conceptual studies of rock art include Taçon, (2004) Hyder (2004), Bradley (2000), Molyneaux (1987), Fuglestvedt (2011), and Scarre (2004).

4.2 The Southern Canadian Shield Context

The Canadian Shield region has one of the densest concentrations of pictographs in North America, some quoting at least 300 in the northern Ontario Shield Woodland area alone (Dewdney 1970: 3). Human occupation of the Ontario Shield Woodland area by traditional hunter-gatherer societies has been dated to as early as 7,000 BP following the most recent glacial ice retreat at 11,800 BP (Aubert *et* al 2004; Prest, n.d.), and up to and beyond the time of European contact. Gordon (2013) offers an extensive overview of archaeological investigations in the Lake Temagami area. It is generally believed that the majority of the rock paintings there were created within the last 2,000 years (Rajnovich 1994: 34), and this assertion is based on contextual information such as historical accounts, and associations such as depictions of horses with riders, which would not have occurred prior to European contact. However, there exists little chronometric evidence to substantiate any temporal sequences. The only two examples of dated rock art sites in this area include a pictograph at the Nisula Site (2870-2301 and 3163-1861 radiocarbon calibrated years BP, respectively) in Quebec (Aubert *et al* 2004), and Mud Portage petroglyph (7,000 years BP on the basis of artifact associations) in Lake of the Woods, western Ontario (Steinbring *et al* 1987: 8). Aside from these examples there exist no other recent systematic attempts to determine the age of any Canadian Shield rock art. Furthermore, even less is known about the sources from which these pigments came, or when and how those materials were moved around the landscape.

The geographic focus of this study is in northern Ontario, Canada, and includes the areas surrounding Greater Temagami, Mattawa River, French River, Lake Nipissing, and the north shore of Lake Huron (see Figure 4.1). This area comprises a southern section of the Canadian Shield geologic complex, referred to as the Southern Province, a series of Archaean- and Proterozoic-aged metamorphic rocks dating to 3,000-1,000 million years before present (Eyles 2002:5). The surface geology of the area is a patchwork of granite and granitic gneisses, and iron-rich ore deposits (Douglas 1969) exposed most recently by the last glacial retreat. The history of rock art research specific to the southern Canadian Shield is diverse, and includes survey and documentation (Dewdney 1959, 1970; Dewdney and Kidd, 1967; Conway, 1984, 1993, Conway and

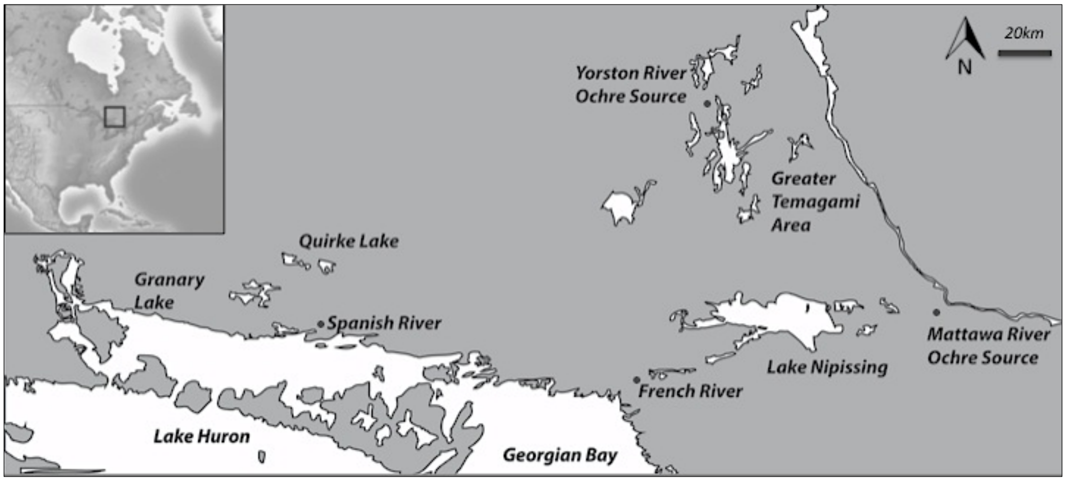

Figure 4.1: Map of northern Ontario ochre sources and pictograph study area.

Conway 1989; Coleman *et al,* 1971, Molyneaux, 1981), recording of oral histories and interpretation of rock art imagery (Rajnovich, 1994; Arsenault 2004a, 2004b; Colson, 2007; Vastokas, 1992; Zawadzka 2009, 2011, 2013), and attempts at dating pictograph sites (Aubert *et al,* 2004, Steinbring *et al* 1987). Arsenault's work in particular has explored pictographs in the context of landscape archaeology and mapping cultural and spiritual places. Characteristically, pictograph art forms in this region typically exist as either individual glyphs or panels of glyphs. They are generally described as abstract imagery, with commonly recurring forms to include tally marks, dots, lines, birds, canoes, turtles, power lines, human figures, lightning bolts, serpents, and other amorphous shapes. Depictions of Thunderbird, a prominent figure in Anishnaabeg mythology, are encountered frequently. These glyphs or panels are almost exclusively located on water or in rockshelters, and are associated with massive, continuous rock outcrops, portage routes, unique mineralogical features, or as waypoint markers. These sites are often associated with culturally significant places and events, such as vision quest sites, human burial sites, soundscapes, or areas where mythological beings and their activities occurred (Conway 1993; Rajnovich 1994; Arsenault 2004a, Zawadzka 2013).

The combined history of work in this area has offered a rationale for a study that involves the geochemical characterization of ochre sources and pictograph sites, and to date no such studies in the southern Canadian Shield area are known to exist. The primary goal of this project was to determine if ochre sources and pictographs in this region could be differentiated on the basis of their elemental characterization via p-XRF, and if any source materials could be matched with individual glyphs. We tested 62 glyphs and two ochre sources located in Temagami First Nation, Serpent River First Nation, and Henvey Inlet First Nation traditional territories, respectively. Table 4.1 below describes the locations and forms of the pictographs and sources tested.

Table 4.1: Summary of Locations and Pictographs Tested in the Study Area.

Location and Number of Pictographs	Description
Lake Temagami (n=11)	-Panels and glyphs located in the Northeast Arm, Portage Bay, and Gibson's Bay -Forms include tally marks, Thunderbird, dots, paw with three digits
Lake Obabika (n=13)	-Pictograph locations include Shining Lake, Devil's Ledge, Grandparent's Rock and Mystery Rock -Depictions include a four-legged being, Thunderbird, tally marks, and dots
Diamond Lake (n=15)	-One large panel with 20+ individual glyphs. Glyphs not tested were either too faded or physically inaccessible. -Glyph forms include tally marks, a bear, a bullseye, downward-facing chevrons, arrows, a canoe with six passengers, a bird, dots, and a depiction of a spirit referred to as 'Rabbit Man'
Anima-Nippissing (n=12)	-Glyphs include tally marks, canoes with riders, and a faux painted handprint
Spanish River (n=4)	-One panel with six discernable glyphs. -Two human figures made with white pigment -Glyph forms include lightning bolt, a key, an arrow, and a serpent
Granary Lake (n=5)	-One long rock outcrop with an unknown number of individual glyphs -Glyphs include tally marks, two canoes with riders, and a turtle
Quirke Lake (n=1)	-One human form riding a serpent
French River (n=1)	-One human form surrounded by faded lines and amorphous shapes
Mattawa River Ochre Source (n=10)	-10 subsamples of material from this source -source located approximately 20 km east of Lake Nippissing
Yorston River Source (n=20)	-tested 19 subsamples of this source -located approximately 100 km south of Lake Temagami
TOTAL = 92	

One of the two ochre sources is a quarry located on the Mattawa River (also referred to as *Porte de L'Enfer* [Hell's Gate]), a historically significant canoe route extending westward connecting the Ottawa River to Lake Nipissing. The other source is located on the Yorston River on a portage route between Seagram and Long Lakes, approximately 40 km west of Lake Temagami. Two other ochre sources, one on Lake Obabika, and another referred to as Gargantua on the north shore of Lake Superior, are known, however to date have not been accessible to us. The results of this study demonstrate three key findings: 1) that the coarse geochemical groups of ochre in Central Ontario satisfy the provenance postulate; 2) that there exists a pattern of variable use of ochre for pictograph pigments; and 3) the capabilities and limitations of p-XRF for *in situ* analysis of pictograph pigments.

4.3 p-XRF Testing and Results: Accuracy and Limitations

The recent increase in the use of p-XRF technologies has triggered rigorous discussion on its utility and accuracy for characterization of different materials relevant to archaeologists (Craig *et al* 2007; Frahm 2013, Frahm and Doonan 2013; Goodale *et al* 2012; Nazaroff *et al* 2010; Potts *et al* 1995; Shackley 2011; Shugar and Mass 2012; Speakman and Shackley 2013; Williams-Thorpe *et al* 1999). These portable units perform under the same principles as benchtop XRF systems, however are designed with micro technologies and generally operate at lower voltages and for shorter analytical durations than their larger counterparts. They use internal algorithms in attempt to eliminate background radiation and to calculate elemental peaks into concentration data in real-time. The publications referred to above all discussed or highlighted varying degrees of success in their applications of these technologies, and offered insight into the challenges and limitations associated with their use. The concerns with using p-XRF systems for the elemental characterization of materials are primarily related to sensitivity, accuracy, precision, peak misidentification, matrix effects, and user error. While these new systems perform generally well under suitable conditions, what is gained in portability and efficiency is lost in sensitivity, which can pose problems for the quantification of some elements. The limits of detection for p-XRF devices are often significantly higher than other techniques (e.g. NAA, ICP-MS), which can limit the ability to differentiate chemical groups on the basis of trace elements below a few hundred ppm. These systems also tend to exhibit high peak-to-background ratios, which can contribute to the mis-identification or inaccurate quantification of some elements along a spectrum. The concentration data that are calculated by internal, proprietary algorithms have shown to be questionable in some circumstances, yet not in others, which may be symptomatic of user error and not necessarily any shortcoming of the manufacturer. Studies that test the performance of these units describe some false-positive errors of peak misidentification and a lack of sensitivity required for the analysis of trace elements of interest (Craig *et al* 2007; Liritzis and Zacharias 2011; Philips and Speakman 2009; Sokaras *et al* 2009). This is why it is necessary to take a cautious approach to using data generated by the proprietary software programs. It is advised to manually review spectral files to determine whether or not spectral interferences could have occurred, and that the data are representative of the sample material being analyzed, and not ‘artifacts’ of the equipment used. Some examples of the performance testing of these devices are reported by Pessanha *et* *al* (2009), Potts *et al* (1995), and in case studies in Shugar and Mass (2012). Furthermore, it has been argued that any use of these technologies for the analysis of archaeological materials should include some combination of cross-referencing, calibration, or normalization using established international standard reference materials (Speakman and Shackley 2012: 1435), which we have incorporated into our evaluation of this technology (described in further detail below).

Despite the challenges and limitations for using p-XRF, these systems remain of great interest to archaeologists as they enable the study of objects of heritage interest *in situ* in a non-invasive and rapid format. In many circumstances, such as the case study presented here, where access, geography, and preservation of archaeological materials present significant limitations for analysis, portable technologies such as p-XRF, although not ideal, are one of few available options for the preliminary, coarse analysis of objects of archaeological interest. Under the correct conditions these systems can and do perform well, and they have seen significant improvement over their albeit short time on the market. While bearing in mind these limitations, our approach to this case study has been that of a preliminary field survey to discern whether enough differences in the coarse pigment chemistries exist to warrant further investigation using complementary, micro-destructive techniques. Therefore, we offer this study as a contribution to the ongoing assessment of these new technologies.

For this application we used an Innov-X Delta Premium model p-XRF unit. The instrument uses a gold (Au) anode as the excitation source, has a SDD-type detector, and operates at 40kVp and 0.1 mA. It is equipped with a series of modes, each applying different voltage, current, and filter combinations customized for different material types. The mode selected for this work was 3-Beam Soil Mode (40 kV, 40 kV, 15 kV), which is calibrated for determining trace element concentrations in low-Z matrices. In this mode, one beam is optimized for heavy elements, one for transition metals, and the third for light elements (Goodale *et al* 2012: 876). We performed a series of trials on the NIST-issued standard reference materials SRM 1633b (Coal Fly Ash), SRM 278 (Obsidian Rock), and SRM 688 (Basalt Rock), as well as on previously characterized materials from six ochre sources, to assess the precision and accuracy of the device and its ability to calculate elemental concentration values of materials of known chemistries. The pressed SRM powders and ochre source materials were tested ten times each for a minimum of 120 s per test. Concentration values calculated and reported by the unit's internal software are listed in Table 4.2 alongside the certificate concentration values. For most elements of interest the reported concentrations align well with the certificate values, with a few exceptions. The elements arsenic (As), barium (Ba), calcium (Ca), copper (Cu), iron (Fe), potassium (K), manganese (Mn), zinc (Zn), rubidium (Rb), and strontium (Sr) are in excellent agreement in most cases.

Table 4.2: Reported p-XRF concentration values of NIST issued standard reference materials. Concentrations reported in ppm unless otherwise stated.

	SRM 1633b (Coal Fly Ash)			**SRM 278 (Obsidian Rock)**			**SRM 688 (Basalt Rock)**		
Element	**Rep. Value**	**Cert. Value**	**Ratio**	**Rep. Value**	**Cert. Value**	**Ratio**	**Rep. Value**	**Cert. Value**	**Ratio**
As	130	135	*0.96*	4.2	4.7	*0.89*	2.3	2.4	*0.96*
Ba	700	710	*0.98*	1020	1140	*0.89*	190	200	*0.95*
Ca (%)	1.9	1.5	*1.3*	.7	.7	*1.0*	11.2	12.1	*0.93*
Cu	130	103	*1.3*	<LOD	6	*n/a*	100	95	*1.1*
Fe (%)	7.8	7.8	*1.0*	1.3	1.4	*0.93*	7.2	7.2	*1.0*
K (%)	2.3	1.9	*1.2*	2.8	2.5	*1.1*	.23	.15	*1.5*
Mn	130	130	*1.0*	350	400	*0.88*	1145	1290	*0.89*
Ti (%)	0.95	0.79	*1.2*	0.12	0.14	*0.86*	0.72	0.70	*1.0*
Zn	220	210	*1.0*	55	55	*1.0*	71	58	*1.2*
Rb	156	140	*1.1*	146	127	*1.1*	2.1	1.9	*1.1*
Sr	1140	1040	*1.1*	72	64	*1.1*	165	169	*0.97*
Zr	335	n/a	*n/a*	420	n/a	*n/a*	70	n/a	*n/a*

To further assess the accuracy and precision of p-XRF reported data, and the potential for cross-comparison of elemental concentration data using different techniques for analysis (e.g. NAA and p-XRF), and for materials with similar matrices, we tested archived materials from six previously characterized geologic ochre sources. Those six sources were characterized via neutron activation analysis and formed the basis for a different study on ochre use in southern British Columbia, Canada (MacDonald *et al* 2013). Ten sub-samples of each of the archived source materials were tested via p-XRF using the same protocol described above. Table 4.3 shows the comparison between NAA and p-XRF results. Elements selected are only those that are measured accurately by both techniques.

Table 4.3: Comparison of NAA and p-XRF characterization of ochre sources in British Columbia, Canada. Concentrations reported in ppm unless otherwise stated.

Element	**Paul Ridge 1 (n=15)**			**Paul Ridge 2 (n=16)**			**Chichen Stanach A (n=15)**		
	NAA	**pXRF**	**Ratio**	**NAA**	**pXRF**	**Ratio**	**NAA**	**pXRF**	**Ratio**
As	<1.6	2.9	*n/a*	<2.0	4.0	*n/a*	<2.8	3.8	*n/a*
Ba	390	665	*0.6*	340	565	*0.6*	340	565	*0.6*
Ca (%)	3.5	3.0	*1.1*	3.3	3.5	*0.9*	3.4	3.2	*1.1*
Cr	30	30	*1.0*	35	35	*1.0*	37	37	*1.0*
Fe (%)	4.2	4.6	*0.9*	3.3	3.5	*0.9*	3.4	3.2	*1.1*
K (%)	0.53	0.64	*0.8*	0.29	0.45	*0.6*	0.64	0.77	*0.8*
Mn	475	700	*0.7*	530	715	*0.7*	675	1200	*0.6*
Ti (%)	0.41	0.49	*0.8*	0.46	0.69	*0.7*	0.46	0.70	*0.7*

Table 4.3:... cont't. Comparison of NAA and p-XRF characterization of ochre sources in British Columbia, Canada. Concentrations reported in ppm unless otherwise stated.

Element	**Chichen Stenach B (n=10)**			**Pilchuck Creek 1 (n=10)**			**Pilchuck Creek 2 (n=11)**		
	NAA	**pXRF**	**Ratio**	**NAA**	**pXRF**	**Ratio**	**NAA**	**pXRF**	**Ratio**
As	<2.8	3.6	*n/a*	2.9	3.8	*0.8*	3.2	4.4	*0.7*
Ba	340	500	*0.7*	615	610	*1.0*	610	645	*0.9*
Ca (%)	3.8	3.5	*1.1*	3.6	4.7	*0.8*	3.6	4.8	*0.8*
Cr	35	40	*0.9*	35	40	*0.9*	30	30	*1.0*
Fe (%)	3.8	3.5	*1.1*	3.6	4.7	*0.8*	3.6	4.8	*0.8*
K (%)	0.53	0.49	*1.1*	0.95	1.3	*0.7*	1.1	1.4	*0.8*
Mn	685	1270	*0.5*	650	790	*0.8*	650	855	*0.8*
Ti (%)	0.46	0.70	*0.7*	0.37	0.39	*0.9*	0.38	0.42	*0.9*

Concentration data for the elements Ca, Cr, and Fe are in good agreement, while the elements As, Ba and K are in reasonable agreement for most source groups. The results for Mn and Ti are slightly inflated, however they are still within an acceptable range of error. Based on these results we argue that for a suite of elements (Ca, Fe, Rb, Sr, Zr, Ba, K, and others), the unit performs very well at quantifying elemental concentrations, and that there is merit to using these systems under the right circumstances. With these considerations in mind, we proceeded to conduct a trial study of p-XRF analysis of ochre sources and pictographs *in situ* in northern Ontario.

4.4 p-XRF Testing of Pictographs and Ochre Sources: Data Collection and Geochemical Trends

Each of the 62 glyphs included in this study was tested individually with multiple readings (minimum of two, maximum of six times depending on the size and suitability for areas of testing on the glyph) and for 90 seconds wherever possible. Measurements were carefully taken in areas where pigment appeared to be densest in consistency and not obstructed by lichen or other visible surface features, and where the rock surface was as optically flat as possible. Control samples were also taken at each site, whereby a reading was taken on a pigment-free spot on the rock face adjacent to the glyph. This was done to compare data to see if there may be any potential contribution of trace elements in the rock to the overall signal detected. In the lab, samples of Mattawa River and Yorston River ochre source materials were tested alongside additional runs of standard reference materials. The spectral results from the tests were manually reviewed for peak overlap or misidentification. Elemental concentrations were calculated using a Compton normalization calibration via the instrument's proprietary software, and the data were compared to those of standard reference materials. Table 4.4 shows the concentration means and standard deviations of all elements measured for four geochemical groups of ochres. These geochemical groups were determined on the basis of bivariate plotting of $\log_{10}$ Fe-normalized described in further detail below (Section 4.5).

Table 4.4: Means and standard deviations of elemental concentrations for four geochemical groups of ochre, including Mattawa River and Yorston River ochre sources.

Elemental Data		***Group 1 (n=19)***	***Group 2 (n=11)***	***Group 3 Mattawa Source (n=40)***	***Group 4 Yorston Source (n=20)***
		Mean ± St.Dev	**Mean ± St.Dev.**	**Mean ± St.Dev.**	**Mean ± St.Dev.**
K	**%**	1.9 ± 0.7	1.5 ± 0.4	1.4 ± 0.8	1.0 ±0.2
Ti	**%**	0.6 ± 0.4	1.0 ± 0.5	0.6 ± 0.4	**11.2 ± 0.6**
Fe	**%**	0.3 ± 0.1	1.7 ± 1.3	**5.1 ± 2.9**	**5.7 ± 3.1**
Ca	**ppm**	1650 ± 1450	**5060 ± 1870**	**7170 ± 2050**	1950± 1300
Cr	**ppm**	31 ± 17	69 ± 28	103 ± 48	62 ± 24
Mn	**ppm**	47 ± 38	240 ± 0	**840 ± 740**	<10
Co	**ppm**	<50	230 ± 110	**620 ± 520**	<50
Ni	**ppm**	<50	<50	<50	<50
Cu	**ppm**	<10	<10	55 ± 75	29 ± 7
Zn	**ppm**	<10	21 ± 12	59 ± 47	<10
As	**ppm**	<10	<10	51 ± 140	49 ± 12
Rb	**ppm**	110 ± 70	110 ± 40	100 ± 40	48 ± 35
Sr	**ppm**	78 ± 40	**104 ± 44**	**180 ± 100**	22 ± 12
Zr	**ppm**	92 ± 68	**180 ± 60**	**510 ± 570**	103 ± 25
Ba	**ppm**	620 ± 250	**1100 ± 430**	**1020 ±410**	280 ± 110
Pb	**ppm**	<10	14 ± 5	**120 ± 430**	<10

The concentration data presented here illustrate coarse differences between the four groups. Group 1 is characterized by low Fe concentration, and generally low diversity of transition metals present above limits of detection. Group 2 shows a higher mean concentration of Ca and Ba, comparable to Group 3. Group 3, which includes raw material from Mattawa River ochre source, has mean values for Mn, Co, Sr, Zr, Pb, significantly higher than other Groups 1 and 4. Group 4, which is exclusively raw material from the Yorston River ochre source, is differentiated from the rest on the basis of high Ti, the lack of transition metals Mn and Co, and low mean concentrations of Ba, Sr, and Rb. The high Ti content could be representative of small amounts of ilmenite ($FeTiO_3$) in the sample matrix, which is a mineral commonly associated with iron oxides. However, further analysis via XRD or a similar technique would be necessary to verify this.

The elemental concentration values were averaged (in the case of multiple readings), and converted to a ratio to iron. This is referred to as Fe-normalization and is common practice in the characterization of iron oxides to account for variability in iron content, and to show which groups of elements correlate positively or negatively with iron, often revealing different chemical groups within a set (Popelka-Filcoff *et al* 2007, 2008; Eiselt *et al* 2011, MacDonald *et al* 2011, 2013). The iron content can vary significantly within and between ochre sources, therefore converting the concentrations of other elements as a ratio to iron accounts for the amplification or dilution of other potentially diagnostic elements, as well as reveals which elements may substitute for iron. Ochre sources are never pure iron oxide and their geochemistry is often a combination of varying amounts of Fe, Ca, and Si, with a series of elemental substitutions. Elemental substitutions occur when elements with similarly-sized atoms and charges replace each other within a crystal structure (Goldschmidt, 1937; MacDonald *et al* 2011: 3625). Cornell and Schewertmann (2003) suggest that some transition metals and rare earth elements may substitute in the Fe-III oxide lattice, leading to signatures in the iron oxide that are characteristic of their diagenesis, despite weathering or other post-depositional processes. It is these elements that contribute to the unique signature of any given ochre source. We found that geochemical patterns in groups including large ion lithophile and large ionic valence elements (such as Sr, Ba, Rb, and Zr) as well as transition metals (including Ti, and Cr) were diagnostic for differentiating clusters of source groups. Bivariate plotting of the Fe-normalized values of these groups of elements showed similar group clustering patterns for most element pairs.

4.5 Pigment Groups

Bivariate plotting of $\log_{10}$ Fe-normalized element pairs including Ba, Rb, Sr, and Zr, showed that there are four primary iron oxide groups with two outliers that are potentially from an additional source. Figure 4.2, a bivariate plot of $\log^{10}$ Fe-normalized Ba by Rb ratios, illustrates the trends of the four groups, and plotting of other element pairs consistently produced similar clustering patterns. It contains data points from all pictographs tested, and from the characterization of the Mattawa River and Yorston River ochre sources. Greater than 95% of the pictograph data points tested fall into three of the four groups at 90% confidence. The cluster in the upper right corner of Figure 4.2 is pigment Group 1 and it contains 19 data points, including pictographs located on Granary Lake (5 of 5) near the north shore of Lake Huron, and Diamond Lake (14 of 15) in the greater Temagami area. Group 1 chemistry shows a trend of high Rb and Ba concentrations relative to Fe. The geologic source for this pigment is not consistent with either of the Yorston River or Mattawa River ochre sources and remains unknown. Group 2 (to the left of Group 1) is a cluster of 11 pictographs that is differentiated by negative geochemical correlations within the large-ion lithophile element (LILE) group (e.g. Rb, Sr, Ba). This chemical group includes pictographs from Grandparent's Rock (4 of 6), Diamond Lake (1 of 15), Mystery Rock (1 of 1), Shady Grove (1 of 1), and 4 of 11 on Anima-Nipissing Lake, all located in the greater Temagami area. Group 2 pictograph pigment chemistries also do not match the Yorston River or Mattawa River ochre sources, and the geologic source is unknown. The largest pigment group in Figure 4.2 represents the Mattawa River ochre source materials. In this cluster there are 30 pictograph associations: Devil's Ledge (1 of 3), Anima-Nipissing Lake (7 of 11), Spanish River (4 of 4), Shining Lake (2 of 2), Lake Obabika (1 of 1), French River (1 of 1), and ten glyphs on Lake Temagami, as well as ten data points representing

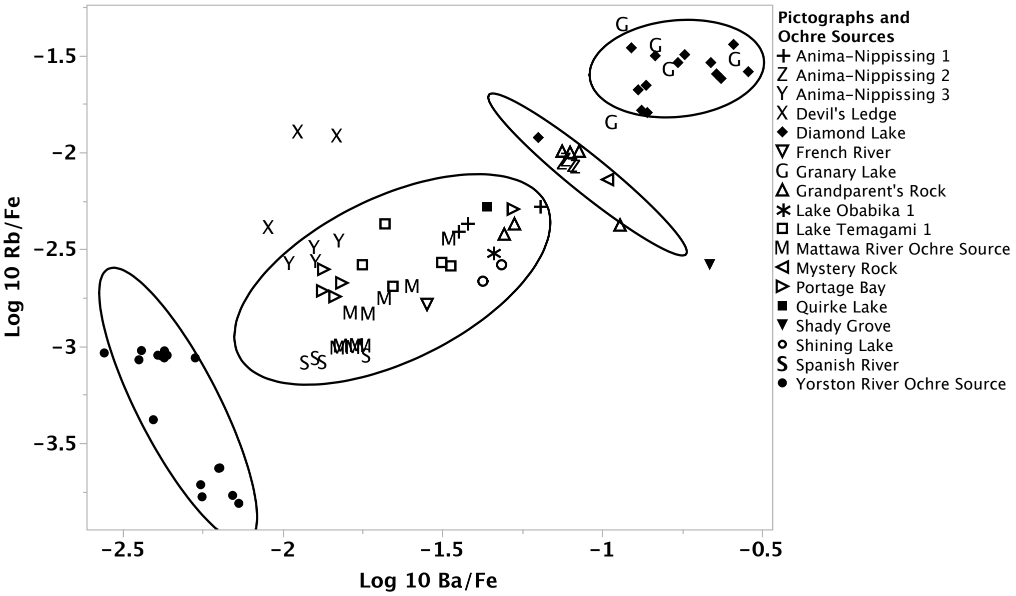

Figure 4.2: Bivariate plot of log$_{10}$ Fe-normalized Ba vs. Rb. Ellipses are at 90% confidence.

repeat tests from the Mattawa River ochre source materials. The group at the bottom left of Figure 4.2 plot consists of 20 data points representing the chemistry of the Yorston River ochre source. This ochre source has characteristically low LILE element group concentrations relative to iron, and the source chemistry does not appear to match any of the pictographs tested in any areas. In addition to the four groups, there are data points for 2 of 3 pictographs on Devil's Ledge that fall outside of the main groups. These two samples were not included in the geochemical groups described in Table 4.4. These are considered outliers that may be related to the Mattawa River source, however, could be mixed with other pigment or could be representative of a different ochre source altogether.

Table 4.5 describes the pigment groups and their corresponding pictographs. In summary, there are four pigment groups within this data set, although only three of them were being used to create the pictographs that were tested. The Mattawa River ochre source, as well as Groups 1 and 2 of unknown origin, were being used variably across the study region, with some occurring well over 100 km apart in distance. In some cases, different pigment groups were

Table 4.5: Summary of four pigment groups including sources and pictographs.

Pigment Group 1 (n=19)	**Granary Lake (n=5):** tally marks (x2), canoe with five riders, a turtle **Diamond Lake (n=14):** various forms including tally marks, chevrons, a bear, a 'bullseye', an arrow, a bird, a canoe, dots, a form that resembles a square-root symbol
Pigment Group 2 (n=11)	**Diamond Lake (n=1):** 'Rabbit Man' depiction **Grandparent's Rock (n=4):** tally marks, 4-legged creature **Mystery Rock (n=1):** Thunderbird **Anima-Nippissing 2 (n=4):** various tally marks **Shady Grove (n=1):** series of four tally marks
Mattawa River Source (n=40)	**Mattawa River Source (n=10)** **Devil's Ledge (n=1):** depiction of shaman **Shining Lake (n=2):** Thunderbird **Anima-Nippissing 1 & 3 (n=7):** stripes, painted handprint, canoe with four passengers (x2), canoe with one passenger, small cluster of amorphous shapes **French River (n=1):** one panel of a human form and other amorphous shapes **Lake Obabika 1 (n=1):** panel of various forms, a canoe form **Temagami 1 (n=6):** paw, chevron, stripes, tally marks **Portage Bay (n=5):** Thunderbird depictions, triangle **Quirke Lake (n=1):** human form riding a serpent **Spanish River (n=4):** lightning bolt, serpent, key **Grandparent's Rock (n=2):** unknown morphs
Yorston River Ochre Source (n=20)	-does not match any tested pictographs -source located on the Yorston River

being used for glyphs within the same panel and also at locations in close proximity to each other. These could have been created at different times by different individuals, or, less likely, by the same individual using two different pigments. The Mattawa River ochre source materials were moving distances greater than 150 km, as far north as Anima-Nipissing Lake and Lake Temagami, as far west as the Spanish River and Quirke Lake, as well as being used along the French River canoe route. Curiously, the Yorston River ochre source materials could not be geochemically associated with any of the pictographs tested despite its proximity to surrounding pictographs. The reasons why this source was not used are unknown, however, it could be due to: 1) lack of access, as it may not have been discovered until recently; 2) the materials being of poor quality for processing into pigment and therefore not ideally suited for this use; 3) some cultural or mythological preference for not using materials from this source (e.g. it was a cursed location, or associated with evil), or; 4) a preference for using 'exotic' materials traded or gifted from farther distances by significant individuals. The pictographs and locations have associated oral histories, place names, and cultural significance to them, and an important element of this work is to recognize these associations within the context of pigment use and movement within the region. Furthermore, the individuals who guided our visits were forthcoming in sharing their unique personal perspectives on these places. The following sections are descriptions of those places as told to us and as experienced by us in the field, and of the pictographs, pigments, and stories associated with them.

4.6 Diamond Lake Pictographs

The Diamond Lake pictographs, located in traditional Temagami First Nation territory, consist of a panel of 30+ individual glyphs painted on a massive quartzite outcrop. Figures 4.3 and 4.4 show the panel and details. The association of clusters of pictographs with quartz veins and outcrops across the Canadian Shield has been described by Conway (1993). Quartz veins are typically associated with Thunderbird power (Conway 1993), which is believed to split and alter the rock when it emits lightning bolts. A quartz outcrop of this size is rare across the Canadian Shield and it is viewed by Temagami First Nation members as a spiritually powerful place. The oral history associated with the Diamond Lake panel describes a renowned and powerful 19th C Wabeno shaman named Wendaben, known in Hudson Bay trade records as Boney Blanc, or White Hat. He always wore white, and white was associated with the rising sun and morning star from which Wabeno shamen derived their power. Wendaben travelled through the area regularly and drew spiritual power from this place. It is believed that his ancestors painted the pictographs, which depict spiritual figures, abstract shapes, and a series of canoes representing the Nodaway or Iroquois, who after defeating the Huron-Wendat travelled north to attack the Anishnaabeg. The pigments used for 14 of the 15 glyphs tested along this panel are of the same unknown source group of ochre that matches the pigments used along a granite outcrop at Granary Lake, approximately 60 km west-southwest in Serpent River traditional territory. The one exception at the Diamond Lake panel was a form described to us as ‘Rabbit Man’, a human figure with rabbit ears. ‘Rabbit Man’ was painted with the Group 2 ochre source of unknown origin, potentially at a different time or by a different individual.

Figure 4.3: Diamond Lake quartzite outcrop and pictograph panel

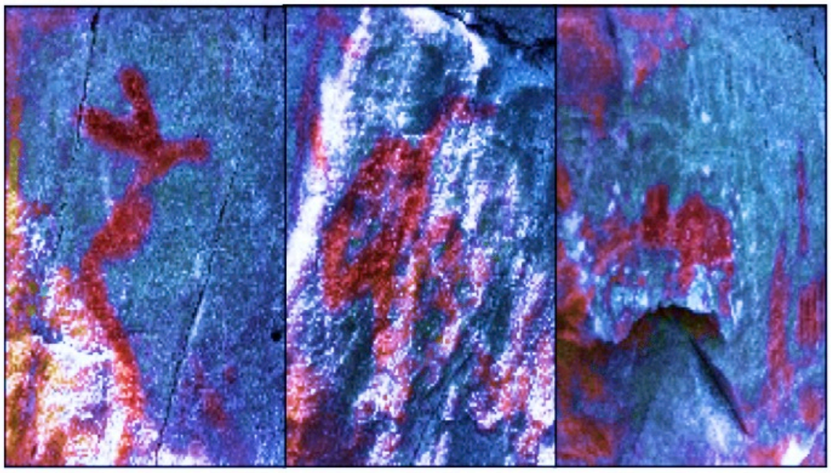

Figure 4.4: Diamond Lake pictograph panel details. Photo enhanced to show greater pigment contrast.

4.7 Lake Obabika Pictographs

Lake Obabika is just west of Lake Temagami, connected by a portage and the narrow inlet in the northwest arm of Lake Temagami. In fall 2011, Temagami Elder Alex Mathais, the only Bear Island band member to still reside on traditional hunting territory, guided MacDonald and Cooper to all of the documented pictograph sites on the lake. We visited Grandparent's Rock (CgHb-11), Grandmother's Rock (CgHa-16), Devil's Ledge (CgHb-4), Shining Rock (CgHb-5), Lake Obabika 1 (CgHb-1), and Mystery Rock (CgHb-3). In addition to the paintings, Mathais described important landscape features such as *Kokomis*

Figure 4.5: Grandmother's Rock (CgHa-16), part of the Grandparent's Rock outcrop, in the background. Six associated pictographs (Grandparent's Rock, CgHb-11) are located on vertical rock faces in the foreground and in the background beyond the rock columns.

and *Mishomis wabikong* (Grandfather and Grandmother Rocks), and *Chee-skon-abikong*, the great rock column resembling a shaking tent, which remains an important place for the Anishnaabeg to fast and dream.

We tested a total of 13 pictographs at five different panels, all of which had been identified and registered during Conway's field surveys in the 1970-1980s. Two different pigment sources (Mattawa River and Group 2) were being used to paint the pictographs on Lake Obabika. The six glyphs associated with Grandparent's Rock (CgHb-11, CgHb-16) consist of tally marks and a four-legged being. They occur at three different points along the outcrop that is associated with fasting and vision quests. Four of the six groups of tally marks and the four-legged being match Group 2 geochemistry, while the remaining two tally marks were made with Mattawa River ochre. Mystery Rock (CgHb-3) is a depiction of a Thunderbird and matches Group 2 pigment chemistry. Shining Rock (CgHb-5) panel consists of a Thunderbird and an unidentified form that were both made with ochre from the Mattawa River source. Lake Obabika 1 (CgHb-1, see Figure 4.6) is a panel of various forms, most of which were too faint for analysis. As a result, only one was tested and it too matched the Mattawa River ochre source chemistry.

Devil's Ledge (CgHb-4) is a panel of three glyphs, consisting of a skeletal human form, six dots, and an infinity symbol (∞). The word 'devil' was used by missionaries to replace the term '*manidoo*', the Anishnaabeg term for spirit. Mathais recalled a story his grandfather told him of this pictograph that commemorates a young girl who drowned at the location many centuries ago. The human figure represents the girl, while the six dots represent her age. Many pictograph sites are associated with stories involving people diving below the surface of the water never to be seen again. These individuals were typically on vision quests, and it is believed that after going below the surface of the water they enter the rock where they continue to live. Two different pigments were used for the Devil's Ledge glyphs. The human form was painted with the Mattawa River ochre source materials, while the infinity symbol and the six dots were

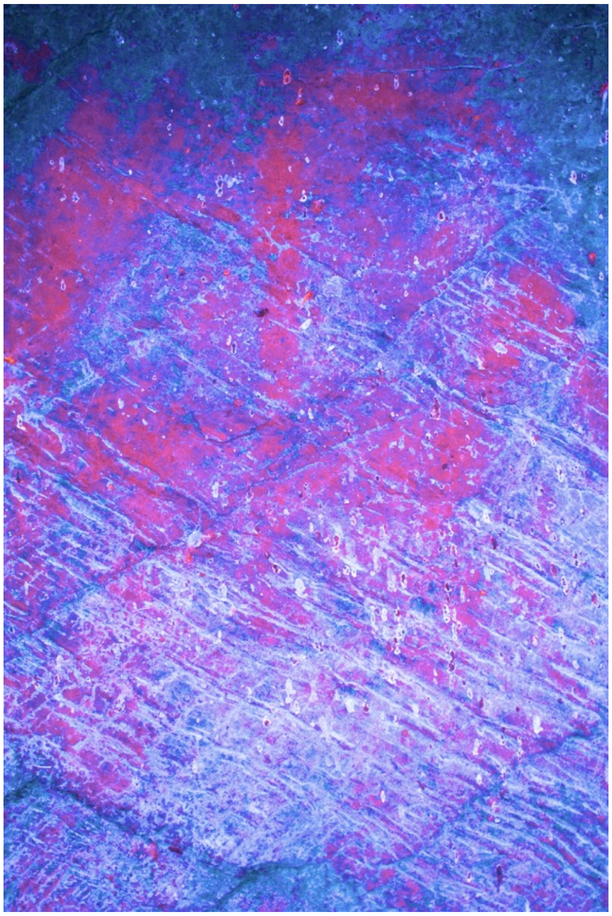

Figure 4.6: Detail of Obabika Lake 1 (CgHb-1) panel, faded Thunderbird depiction. Photo digitally enhanced to show pigment contrast.

Figure 4.7: Devil's Ledge (CgHb-4) pictograph panel. From left to right: six dots, human figure, elongated infinity symbol.

made using a different unknown source, indicating that they may have been painted at different times, by different people, or at the very least by two separate prepared pigments.

4.8 Lake Temagami Pictographs

Lake Temagami is the largest and deepest lake in the area (*Temagami* is Anishnaabeg for 'deep water'). There are greater than thirty documented pictographs located on rock outcrops on the lake, and of those we tested 11. We tested pictograph clusters at Portage Bay (CfHa-7, CfHa-6), and Temagami 1 (CgHa-28, CgHa-20), near Granny Bay. Others that we visited were deemed too faded for XRF testing, or were physically inaccessible by canoe during ice-free summer months. The Portage Bay pictograph group was located in the southern arm of Lake Temagami opposite *Kaw-ishpa-cawg* (High Rock Island). According to Temagami elders, High Rock Island was an important vision quest location. Most glyphs in this cluster were too faded for testing, however one series of tally marks, two Thunderbird depictions, and a triangle form were suitable. The Thunderbird glyphs were painted beside a visually striking quartz vein in the rock. The pigment geochemistry of these pictographs was consistent with that of the Mattawa River ochre source.

Five unnamed pictographs in the west area of Temagami (noted as Lake Temagami 1, CgHa-28, CgHa-20), were documented by Bill Buchan (pers. comm. 2011). These are in association with an area called Granny Bay (*kokomis wabikong*), similar to the one on Lake Obabika. Granny Bay derives its name from a rock effigy, recognized as a dwelling place for spirits, with the pictographs being reflective of this spiritual importance. The five glyphs consist of a three-fingered paw, a series of tally marks, and chevrons in three different locations, and these glyphs were painted with Mattawa River ochre.

4.9 Anima-Nipissing Lake

Anima-Nipissing Lake is located north of Lake Temagami. A total of 12 pictographs on this lake were tested and glyph forms include a series of tally marks, stripes, a painted handprint, a series of amorphous shapes, and three canoes with riders. The tally mark and stripe glyphs were previously documented by Buchan (pers. comm. 2011), while the three canoes with riders and other shapes were a cluster of recorded sites documented by Conway (ChGx-1). We also located a previously undocumented painted handprint (Figure 4.8)

Figure 4.8: Faux painted handprint pictograph on Anima-Nipissing Lake.

Pigment from the Mattawa River ochre source was used to paint the canoes, amorphous shapes, the handprint, and the stripes. A series of stripes, and a group of tally marks near the handprint were painted with the Group 2 unknown ochre source, also used to paint glyphs on Lake Obabika and Diamond Lake.

4.10 Spanish River

We tested an unregistered pictograph panel located on the north shore of Lake Huron at the mouth of the Spanish River in Serpent River and Sagomok First Nations traditional territory. Chief Isaac Murdoch, a cultural heritage specialist for the Serpent River First Nation, guided us to this spiritually significant location. The site is located on an 800 m long granite rock outcrop that has features such as caves, ledges, crevasses, and overhangs that are all considered to be dwelling places for powerful *manidoo* (spirits), in particular, a great horned serpent. The pictograph panel, said to be painted during the early colonial period, consists of paintings of two serpents, a lightening bolt, a ‘key’ shaped figure, and two human forms painted with both white and red pigments, the only circumstance in which we have encountered the use of white pigment. One of the human forms had ‘power lines’ radiating from its head, as well as a red lightning bolt through its arm. The pigments used for this panel are consistent with the geochemistry of the Mattawa River ochre source, while the white pigment appears to be calcium-based. Figure 4.9 shows details of the panel. The cultural significance of this location is that the paintings tell a tale of appropriation of power. Isaac Murdoch described to us that the white figures with lightning bolt arms and ‘power lines’ foretold prophecies of Europeans invading with hostility. A few hundred metres from this location lay the remnants of the Spanish Residential school, a visible relic of that colonial power. The positioning of these two places, both visible within one’s peripheral vision; a culturally and spiritually significant rock outcrop, and a residential school, is a striking juxtaposition depicting power and colonial oppression.

Figure 4.9: Spanish River pictograph panel details. Upper left: white human form with 'power lines' radiating from the head. Right: second human form with red lightning bolt on left arm to symbolize power, and serpent radiating from the figures' right arm. Lower left: view of rock face showing evidence of eagle's nest in upper left corner. That the eagle chose this nest location above the pictograph is viewed as a spiritual validation and communication about the site from Thunderbird.

4.11 Granary Lake

The pictographs on Granary Lake are located north of Blind River in Mississauga First Nation traditional territory. They are located along a 900 m long granite outcrop and consist of a few series of tally marks, and depictions of canoes with riders, and a turtle (see Figure 4.10). All of the glyphs painted along the Granary Lake outcrop were made with pigments from Group 1, the same pigment used for most glyphs on the Diamond Lake panel.

Figure 4.10: Granary Lake pictograph details. Upper left: series of intersecting tally marks. Lower left: canoe with five riders. Right: Depiction of a turtle.

4.12 Quirke Lake Rooster Rock

According to Serpent River First Nation elders, Rooster Rock is a significant spiritual site used for vision quests and fasting until the early 1950s when uranium mining prevented them from visiting the location. The rock formation consists of a granitic outcrop about 200 ft tall (see Figure 4.11). The glyphs at Rooster Rock consist of several panels of abstract figures, most of which were too faded for testing. We were able to test one, a human form riding a serpent. Serpent River First Nation elders recount a story of how the paintings were created. One ledge located close to the water is a place where young boys would go to fast and have visions. A boy was fasting there and after 10 days he still did not have a vision, and he was told by an elder to stay there. When the elder returned the next day the boy who had been dreaming all night dove into the water and was never seen again. It is believed that the paintings on the rock were made from the splash from the water when the boy dove into the lake, and that the boy's spirit now lives inside a cave in Rooster Rock.

Figure 4.11: Quirke Lake pictographs. Upper left: Rooster Rock view. Lower left: granitic gneiss banding. Right: detail of human form riding a serpent and other glyph forms too faded for testing.

4.13 French River Pictograph Panel

This pictograph panel, in Henvey Inlet First Nations Territory, is located on a large granite outcrop on the French River. The panel had a small number of glyph forms, however only one was deemed suitable for testing (see Figure 4.12).

The pigment used for paint was consistent with the Mattawa River ochre source chemistry. This particular location is significant as it is along a heavily-used canoe route during the early European contact era fur trade. It was likely a part of the route via which the Mattawa River ochre source materials traveled westward into the Greater Temagami and Lake Huron north shore areas.

Figure 4.12: French River pictograph panel: granite outcrop (left), and glyphs (right).

4.14 Yorston River and Mattawa River Ochre Sources

The Yorston River ochre source is located approximately 40 km west of Temagami along a portage route between Long Lake and Seagram Lake. The materials were previously collected by Brian Back, and the portage trail is described as 'red with material and more off the trail' (Buchan, pers. comm. 2011). We tested 20 subsamples of this source and its chemical composition was not consistent with any of the pictographs tested.

The Mattawa River to the east is along a canoe route connecting the St. Lawrence valley via the Ottawa River to the Upper Great Lakes via Lake Nipissing in the west. This route was used extensively for movement of goods and people in pre- and post-European contact eras. Materials from this ochre source were provided by Buchan. We tested 10 subsamples of ochre from this source and it matched the pigment chemistries of 48% (30 of 62) of the pictographs tested.

4.15 Discussion

The purpose of this study was to assess the potential for characterization and differentiation of ochre sources and pigments used to create pictographs in the southern Canadian Shield region. To first test the accuracy, precision, and validity of results tested via p-XRF, we analyzed a series of standard reference materials and ochre sources of previously known chemistries. The results of these trials demonstrated the capacity and limitations of the p-XRF unit, and we concluded that they were within an acceptable range of accuracy. Subsequently, we tested 62 pictographs and 30 subsamples from two ochre sources to determine the elemental composition of the pigments to assess whether or not geochemical groupings could be identified, and to determine if any source materials could be matched with pictographs. The results showed coarse differences in four chemically distinct pigment groups, which warrants further chemical analysis using complementary, micro-destructive techniques to verify if these groupings persist. Two of the chemical groups were being used variably throughout the study region to paint pictographs, however their source location remains unknown. The Mattawa River ochre source materials were being used most frequently and traveled geographical distances of greater than 150 km. The Yorston River ochre source was not being used at any of the pictograph locations tested, despite its close proximity to many in the area. There does not appear to be any correlation between the glyph forms and the type of pigment used. However, the results do suggest that pigments were moving significant distances along known trade routes, they were being used in variable amounts at different locations, and there may have existed preference for specific types of ochre over others.

This study could be expanded in four ways: 1) by testing the pictographs using a complementary technique to further validate chemical groupings; 2) by broadening the pictograph survey area to include other known sites; 3) by locating and testing the two remaining known ochre sources, and; 4) by attempting to assess when the pictographs were being created. This preliminary survey represents 62 of a potential >300 pictographs in the northern Ontario vicinity, therefore it could be possible to expand to include additional sites. The two remaining known sources, one near Lake Obabika, and the other, Gargantua, on the north shore of Lake Superior, could be located and analyzed to add to the growing database and compare with other pictograph data to see if further spatial patterns of ochre movement emerge. Dating the glyphs using chronometric techniques will enable a critical layer of temporal contextualization and interpretation on the variability and form of ochre-related activities and how they changed over time. Studies by others (Aubert 2012, Bonneau *et al* 2011, 2012; Morwood *et al,* 2010; Nelson *et al* 1995; Taçon *et al* 2012; Watchman *et al* 1997; Watchman, 2000) have demonstrated the potential for dating rock art sites, with one successful example occurring elsewhere on the Canadian Shield (Aubert *et al* 2004), therefore, a programme of dating pictographs is a key priority. By establishing a temporal resolution for the pictograph making it may be possible to see differences in the use of pigment sources over time, the evolution of glyph form styles over time, or to link pictographs with nearby occupation sites of known time periods. Furthermore, the majority of trade goods that would have moved within the area, including animal skins, textiles, and foodstuffs, were too perishable to persist in the archaeological record (with the exception of native copper, some chert types, precious minerals, and iron oxide pigments). As a result, there is a scant record for documenting trade prior to the arrival of European-made metals and glass goods. Therefore, determining the temporal resolution of ochre procurement, movement, and use will provide a better understanding of both pre- and post-colonial contexts of movement of goods across the southern Canadian Shield area.

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CHAPTER 5

CONCLUSION

5.1 SUMMARY AND SIGNIFICANCE OF RESULTS

5.1.1 Geochemical characterization of ochre from central coastal British Columbia, Canada

This study represents the first published case study of neutron activation analysis of ochre, and the differentiation of ochre source groups using advanced multivariate statistics in a Canadian context. A total of 64 ochre samples recovered from ten archaeological sites and one ochre source located in traditional Heiltsuk, Wuikinuxv, and Nuxalk territories underwent elemental characterization. The challenge for this study was in successfully differentiating ochre artifacts within a relatively restricted geographic context on the basis of their geochemistry. Because ochre is chemically complex, it is necessary to obtain quantitative concentration data on as many elements as possible to determine what trends and patterns may exist (Popelka Filcoff *et al* 2008; MacDonald *et al* 2011). Furthermore, it was deemed necessary to convert elemental concentrations to ratios of iron, and to transform those values to logarithmic scale. Using multivariate statistical tests including principal components and canonical discriminant analyses, it was determined that four different ochre source groups were present and that their chemistries satisfied the provenance postulate. Results showed that the differentiation of ochre sources on the central coast of British Columbia is based primarily on variability in concentrations of diagnostic elements (as a ratio to iron) in the transition metal and rare earth element groups.

Ochre sources on the central coast of British Columbia are in close geographic proximity to each other, yet are geochemically distinct. The patterns identified and described in this study demonstrate that it is possible to determine the number and chemical fingerprint of groups present within an archaeological assemblage prior to a full-scale survey of ochre sources. Focusing heavily or exclusively on archaeological assemblages is sometimes necessary where extensive field survey and access to ochre sources is cost prohibitive or otherwise not possible (Shackley 2008). Based on the geochemical data and source group differentiation, the presence of artifacts from multiple sources at archaeological sites in close proximity suggests a model of highly-localized ochre acquisition, with a small degree of movement of ochre between adjacent archaeological sites. One or two sources were present at any given site, and this pattern persisted for the last ~2000 years of occupation for each site. In this area there is evidence for both long-distance trade in materials such as obsidian and fish oil (Carlson 1994), and highly-localized resource procurement, such as fish, shellfish, and plants (Cannon *et al* 2011). Ochre acquisition patterns appear to be more consistent with models of localized acquisition and not with long distance trade. However, further analysis of additional ochre sources is necessary to verify this. Some evidence for the potential of shared use, exchange, or transport of ochre materials between sites or communities was evident, and there was little variability in that behaviour over time, suggesting that there may have been no need or desire to trade ochre over long distances. Preference for locally-sourced ochre could be a result of its ubiquity within the landscape, or, an indication that each source was considered culturally or symbolically significant, regardless of its quality as pigment. Each source of ochre may have been specific to and preferred by a particular community group.

5.1.2 Significance of Results

The results of this study are significant in two ways. Methodologically, they show that ochre chemistry in the central coast region satisfies the provenance postulate, and that by applying the appropriate analytical techniques, ochre can be studied as a trade good in the same light as other materials common to the Northwest Coast, such as obsidian, copper, amber, and shell (Carlson 1994). Satisfaction of the provenance postulate is a critical first step in establishing the validity of characterization studies of ochre. This provides a foundation for future research in that the technique and protocol necessary (NAA, or another technique with comparable sensitivity for elements of interest), the resolution of data needed (concentrations of major, minor, and trace elements with limits of detection in low parts per million), and the statistical exploration required of those data have been established. Without establishing this methodological framework there would be no basis for expanding and exploring additional detailed ochre-related practices, such as quarrying, long distance trade and exchange, and other use contexts including rock art and mortuary sites. In the context of archaeological practice in British Columbia, these results also complement and reinforce other interpretations of highly-localized use of resources (Cannon *et al* 2008, 2011).

5.2.1 Elemental Analysis of Ochre Outcrops in Southern British Columbia, Canada

This study focused on the elemental characterization of three ochre outcrops (and multiple sub-outcrops) located in southern British Columbia, and is the first published intensive survey and analysis of ochre outcrops in Canada. Ochre has been routinely recovered from archaeological sites in southern British Columbia, has been used as pigment for pictographs, is described as a trade item (Williams 2006), and still remains a significant component of ceremonial practices. The purpose of this project was to create a database of information on ochre source geochemistries, setting a foundation for future study of ochre from archaeological contexts. The primary challenge for characterizing a source of any lithic raw material, especially those that are discontinuous in form across a landscape, is in assessing the chemical variability across the outcrop (Popelka-Filcoff *et al* 2008). This is necessary to adequately determine a unique geochemical signature specific to that outcrop. To do this requires thorough subsampling across a source, and further sub-sampling and repeat testing in the lab to verify if the source chemistry satisfies the provenance postulate. For this study, three sources were targeted: Paul Ridge, Pilchuck Creek, and Tulameen Ochre Bluffs. Wherever possible, sub-zones within these sources were sampled. Paul Ridge is a discontinuous outcrop of oxidized basalt running along a mid-elevation ridge 12 km south of the peak of Mt. Garibaldi, and samples were collected along the ridge at four different locations across ~6 km of distance. Pilchuck Creek is an iron-rich silt deposit located in the alluvial floodplain of Squamish Valley west of Mt. Garibaldi. This outcrop was limited in its accessibility and exposure, however samples were taken in two locations along the cut bank of the creek and analyzed separately. Both Paul Ridge and Pilchuck Creek ochre outcrops are located in Squamish First Nation traditional territory. The third source analyzed in this study is from Tulameen Ochre Bluffs, located on the British Columbia Interior Plateau near the confluence of Similkameen and Tulameen Rivers. Materials from this ochre source were used throughout the surrounding valley as pigment for surrounding concentrations of pictographs and cultural ceremonies (Copp, 1979, 2006).

5.2.2 Significance of Results

The results of this study showed that the three the red ochre sources each have unique chemical signatures that satisfy the provenance postulate. Elemental concentration data, primarily on the basis of quantities of potassium and aluminum, were sufficient in differentiating coastal from interior ochre sources. Coastal ochre sources are more chemically heterogeneous as compared to the interior, containing more diversity and higher concentrations of minor, trace, and rare earth elements. In particular, the enrichment of light rare earth elements, the depletion of heavy rare earth elements, and negative europium anomalies are evident, and are typically characteristic of Archaean-age volcanic deposits such as these (Condie 1981: 193). Statistical differentiation of coastal ochre deposits relied on the use of principal components and canonical discriminant analyses. The methodological significance of this study is that it demonstrates the importance of scale in characterization studies with regard to geographic distances, geologic processes, and the statistical treatment of data. Each of the sources analyzed possesses its own specific diagenetic history resulting in a unique geochemical signature. In this case study, the statistical interpretation of data was greatly affected by scales of magnitude, whereas differentiating between geographically distant and geographically restricted ochre sources required different mathematical approaches. Scales of difference between groups or samples that are widely chemically distinct, such as that of coastal versus interior sources, were shown to have an impact on the ability to determine finer-scale variability in sub-group source chemistry. The archaeological significance of this study is that it has created a database of geochemical information upon which to build further research on ochre acquisition, trade, and use from archaeological contexts.

5.3.1 Analysis of Pictographs in the Southern Canadian Shield: an example of the utility of portable x-ray fluorescence technology

The purposes of this study were twofold: 1) to assess the potential for characterization and coarse differentiation of ochre pigments and geologic sources using p-XRF technology; and, 2) to conduct a field study of pictograph pigment characterization. The current debate amongst archaeological scientists on the accuracy, validity, and suitability of p-XRF systems for characterization of different material classes has become increasingly contentious (Speakman and Shackley 2013, Frahm 2013, Killick 2015, and others). As p-XRF technologies have become an increasingly popular tool used in archaeological sciences, a significant number of case studies evaluating their performance have been published (Craig *et al* 2007, Goodale *et al* 2012, Liritzis and Zacharias 2011, Nazaroff *et al* 2010, Potts and West 2008, case studies in Shugar and Mass 2012). As a contribution to this subject, the first component of this study presented the results of our assessment of the performance of the p-XRF device. To assess the precision and accuracy of the unit we compared concentration values derived from repeated p-XRF and NAA analyses of three NIST standard reference materials and six previously characterized ochre sources from British Columbia, for a total of 90 comparative values. The results of these clearly demonstrated the fidelity between p-XRF and NAA for elements of interest, indicating that field measurements of pictographs *in situ* should be reasonably accurate when applied under suitable conditions. This established a rationale for a pilot field study. The second component of this study presents the results of an application of this technology for the analysis of 62 pictographs and 30 subsamples of two ochre sources in the southern Canadian Shield region of northern Ontario.

The Canadian Shield Woodland area has one of the densest concentrations of pictographs in Canada, however little is known about the pigments used to create them. Pictographs are typically sites of social and cultural significance, and exist at important locations within a landscape. Other research has shown that the pigments used to paint pictographs are imbued with the same cultural significance as the imagery itself. Therefore, the study and mapping of those pigments with regard to their geologic origins and procurement patterns has the potential to reveal archaeological information on social practices and patterns of associated behaviour. Results of this field study indicated that four different ochre sources were being used to paint the pictographs. The geochemical group that appeared most ubiquitously in the region was from the Mattawa River ochre source, located greater than 150 km from some of the pictographs for which it was used. Pigment from the Yorston River ochre source, located within 40 km to nearby clusters of pictographs on Lake Temagami, was not used to create any of the glyphs surveyed in this study. The remaining two geochemical source groups were being used variably for pictographs across the region, though the locations of those source outcrops remain unknown. No correlations between pigment sources or glyph forms could be discerned, but some ochre pigments were indeed moving significant distances along known trade routes and were being used in variable amounts at different locations, suggesting that preference for specific sources over others existed.

5.3.2 Significance of Results

The results of this study contribute to ongoing discussion and evaluation of p-XRF technologies for the analysis of archaeological materials. The study also contributes archaeological information on the variability in ochre use and movement in northern Ontario, not previously addressed in Canadian archaeology. Recent advances in technologies have enabled the characterization of features *in situ*, and for sites such as pictographs and other immovable features (murals, mosaic tiles, floors, fragile or unstable objects), analysis via portable technologies is key. While the precision, accuracy, and validity of results derived from these portable devices has been critically reviewed, studies have indicated they are a reliable methodology, but only when international standard reference materials are used for calibration, and when they are applied prudently in archaeological contexts. Methodologically, this case study offers a contribution to this body of knowledge in two ways. By testing a series of standard reference materials as well as other previously analyzed (via INAA) ochre source materials of known chemistries, the capacity and limitations of p-XRF have been demonstrated. Field-testing of pictographs *in situ* and examination of samples from two known ochre sources have shown patterns of variable use, which has archaeological implications for trade, transport, and preference for specific ochre sources.

This study contributes to Canadian archaeology in its exploration of pictograph sites as places of interest in a way that moves beyond documentation, description, and interpretation of glyph symbology, toward re-framing conceptions of ochre pigments and sources within networks of community interaction. Pictographs have long been an area of interest for archaeologists, but primarily for the purpose of interpreting imagery and cosmology, cultural beliefs, and social practices. However, this paper demonstrates the potential for characterization studies to add a new layer of information that maps out these practices, and preferences for and selection of raw materials over space. The majority of trade goods during the pre- and early European contact era, including pelts, textiles, and foodstuffs, were too perishable to survive the archaeological record, therefore, ochre can and should be considered a new traceable class of trade good alongside copper, chert, glass trade beads and other precious ores and minerals.

5.4 FUTURE WORK

5.4.1 Geochemical characterization of ochre from central coastal British Columbia, Canada

An expansion of the ochre analysis project on the central coast of British Columbia would involve three key elements: expanding the spatial extent to include more sites and sites of different types; expanding the temporal resolution to include older sites and areas within sites that have older components to them; and location and testing of additional geologic outcrops of ochre. Evidence has suggested a highly-localized mode of procurement, and the diversity of ochre sources at any of the ten given sites within a restricted geographic area is low.

Analyzing ochre from additional sites, such as encampments and pictograph locations, will expand this geographic range to determine if and how this pattern persists at a broader scale. Similarly, targeting ochre finds from older sites and older components within sites (for example, from areas of Namu dating pre-2000 BP), will reveal if and how these patterns may have changed over time. There are ochre sources on the central coast that have not yet been visited or analyzed, which is critical to establishing the spatial extent and pathways of ochre acquisition. This combination of spatial, temporal, and geologic source chemical data will provide deeper insight into ochre-related behaviours.

5.4.2 Elemental analysis of ochre outcrops in southern British Columbia, Canada

The results of this study have provided a foundation upon which to expand to include analysis of ochre finds from archaeological sites, including those from previously excavated village sites and pictographs. Linking archaeological finds to geologic sources will add new information to what is currently understood about ochre procurement, transport, and use in southern British Columbia, beyond the basic documentation of its presence at sites. The next steps would include analyzing ochre artifact geochemistries and comparing them to the source chemistry database to see if, when, and where ochre was moving between sites in the region. There is also the potential for linking pictograph pigment chemistry with source materials using portable x-ray fluorescence, as demonstrated in Chapter 4. A project that would include mapping networks of ochre procurement and use over time and space will enable me to integrate interpretations of these behaviours into broader archaeological narratives of resource acquisition and cultural interaction.

5.4.3 Analysis of Pictographs in the Southern Canadian Shield: an example of the utility of portable x-ray fluorescence technology

This paper presented the results of a pilot study on elemental analysis of ochre sources and pictographs from locations in northern Ontario. Its first purpose was to test the efficacy of portable XRF technologies. To do this, we conducted a series of analyses on standard reference materials as well as six ochre sources of previously known chemistries (via NAA). The second component of this study involved the field application of this technology for *in situ* analysis of iron oxides used to paint pictographs, which resulted in the differentiation of four geochemical groupings. The results showed that one group of pictographs could be matched to the Mattawa River ochre source, the Yorston River ochre outcrop could not be linked to any pictographs, and that the two remaining source groups are from unknown origins. Future work on this project would involve the location and testing of additional ochre sources to determine the locations from which the remaining unknown pigments may have originated. Expansion of this project would also include elemental characterization of ochre from occupation sites in the area in attempt to link use contexts of different types (e.g. village to pictograph to source). Village sites, such as Witch Point (CgHa-7) located on the north arm of Lake Temagami yielded ochre during excavation (Gordon 2013: 119), however, to date those physical collections cannot be located. Refining the chronology of ochre use for pictographs using one or more geochronological techniques would enable an important level and scale of interpretation on the nature of ochre-related activities and how those may have changed over pre- and post-European contact eras. Methodological developments in the chronometric dating of individual pictograph sites has demonstrated success (Aubert 2012), and a systematic, regional-scale program of dating Canadian Shield pictographs will help refine and clarify the temporal trajectory of ochre-related activities.

5.5 CONCLUSIONS

Ochre is a culturally significant material that should be considered alongside other classes of evidence that archaeologists currently investigate as indicators of trade and exchange, cultural interaction, resource procurement economics, and symbolic and ceremonial practices. Understanding ochre chemistry, and how to accurately measure and quantify it, is a necessary foundation for subsequent interpretation of ochre-related activities such as quarrying, exchange, and use. The results of this dissertation offer new insights into methodological applications for the study of ochre using techniques in radiation physics in multiple archaeological contexts. This thesis contributes to a growing body of knowledge on ochre geochemistry, and demonstrates the potential for characterization studies of ochre and the utility that they may have for archaeologists. It provides evidence that supports the continued need for and evaluation of suitable techniques for geochemical characterization, such as NAA and portable XRF systems, and, perhaps more importantly, their careful and appropriate application to archaeological materials with consideration to instrumental accuracy, chemical complexity, statistical interpretation of data, and geologic scales. While the full range of ochre-related activities has not yet been addressed, the foundation this thesis has created will allow for further exploration into these patterns. The next intellectual challenges for all of the studies presented here lie in interpreting reasons for variability in ochre-related activities. Factors such as the locations, distance of movement, quality of pigment, and sites of use are important for understanding cultural perceptions of landscapes and the mineral world, however, there are other intangible and archaeologically invisible reasons why pigment sources were valued and used differently. Characterization studies of ochre are otherwise unknown in the context of Canadian archaeology, and the papers presented in this thesis all possess merit and potential for further expansion.

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APPENDIX A

*Table 2.2 Reported Elemental Concentrations of NIST Standard Reference Materials. Italicized values taken from Glascock et al. 2007. *nm = concentrations not measured. Concentrations presented in ppm unless otherwise noted.*

Element	SRM 1632b		SRM 1633b		SRM 688	
	Report. Value	Cert. Value	Report. Value	Cert. Value	Report. Value	Cert. Value
Al (%)	0.87	0.85	15.05	15.05	8.95	9.18
Au	0.024	nm	0.765	nm	0.41	nm
As	3.97	3.72	137	136.2	3.1	2.4
Ba	76.5	67.5	665	709	206	200
Br	17.3	17	2.5	2.9	450	169.2
Ca (%)	0.2	0.2	1.51	1.51	6.2	8.6
Ce	9.5	9.0	209	190	9.6	8.9
Cl	1264	1260	70	<70	27.6	*34*
Co	2.26	2.29	46	50	48.4	49.7
Cr	11.3	11.0	198.2	198.2	330	332
Cs	0.64	0.44	10	11	0.36	*0.26*
Dy	1.125	nm	17.2	17	4.2	*3.3*
Eu	0.18	0.17	4.1	4.1	1.2	1.07
Fe (%)	0.738	0.778	7.2	7.78	6.8	7.2
Hf	0.5	0.43	6.77	6.8	1.2	1.6
K (%)	0.082	0.074	1.75	1.95	0.23	0.15
La	4.5	5.1	94	94	5.1	*5.3*
Lu	0.054	nm	1.1	1.2	0.4	0.34
Mg	330	383	5300	4820	nm	50660
Mn	12.2	12.4	131.8	131.8	1227	1292
Na (%)	0.0409	.0515	0.202	0.201	1.62	1.59
Nd	9.35	nm	87	85	7.9	*8.9*
Sb	0.25	0.24	5.9	6	0.23	*.26*
Sc	1.92	1.90	41	41	36.01	38.1
Sm	0.844	0.87	20.3	20.0	2.42	2.79
Sr	99.8	102	860	1041	190	169.2
Ta	0.243	nm	2.4	1.8	0.34	*0.31*
Tb	0.169	nm	2.8	2.6	0.36	0.448
Th	1.46	1.34	25.7	25.7	0.39	0.33
Ti	548	454	8163	7910	7700	7010
V	14.8	14.0	295.7	295.7	254	250
Yb	0.482	nm	7.37	7.6	2.4	2.09

*Table 2.2 cont'd… Reported Elemental Concentrations of NIST Standard Reference Materials. Italicized values taken from Glascock et al. 2007. *nm = concentrations not measured. Concentrations presented in ppm unless otherwise noted.*

Element	SRM 278		Ohio Red Clay	
	Report. Value	Cert. Value	Report. Value	Cert. Value
Al (%)	7.18	7.48	6.86	*9.45*
Au	0.55	nm	0.43	nm
As	7.3	4.7	15.2	*14.1*
Ba	1250	1140	605	*668*
Br	nm	nm	nm	nm
Ca (%)	0.768	0.702	0.352	*0.45*
Ce	63.4	62.2	116	*110*
Cl	587	*620*	38	*<100*
Co	3.3	1.5	23	*20.2*
Cr	6.5	6.1	82.8	*90.7*
Cs	7.1	5.5	13.7	*10.6*
Dy	6.6	*6.3*	5.7	*7.4*
Eu	0.88	.84	1.6	*1.54*
Fe (%)	1.4	1.42	4.27	*5.33*
Hf	5.3	8.4	7.34	*7.16*
K (%)	3.45	3.45	2.96	*3.55*
La	33.4	*32.0*	49	*50.9*
Lu	0.6	0.73	0.68	*0.64*
Mg	1700	1387	nm	nm
Mn	404	402	252	*253*
Na (%)	3.52	3.59	0.127	*0.140*
Nd	29.4	*30.0*	40.6	*42.3*
Sb	2.4	1.5	1.35	*1.39*
Sc	5.14	5.1	16.4	*19.0*
Sm	6.2	5.7	7.6	*8.0*
Sr	nm	63.5	70	*66*
Ta	1.25	1.2	2.4	*1.65*
Tb	0.6	1.0	1.63	*1.06*
Th	12.6	12.4	14.5	*15.1*
Ti	1630	1468	4700	*5940*
V	8.5	*9.0*	183	*211*
Yb	3.8	4.5	5.13	*4.27*

APPENDIX B

Table 3.1: Means and standard deviations of elemental concentrations for each source group of ochre. Values are expressed in weight percent (%) or ppm where indicated. *This table reflects the removal of outliers and the addition of more samples since the time of print publication of MacDonald et al 2013.

Element	***Paul Ridge 1 (n=14)***	***Paul Ridge 2 (n=15)***	***Chichen Stenach 1 (DkRs-14) (n=11)***	***Chichen Stenach 2 (DkRs-14) (n=9)***
	Mean ± St.Dev.	Mean ± St.Dev.	Mean ± St.Dev.	Mean ± St.Dev.
Al %	11.9 ± 1.9	11.7 ± 1.5	11.6 ± 1.5	11.3 ± 1.2
Ca %	3.5 ± 0.4	3.3 ± 0.2	3.4 ± 0.4	3.7 ± 0.5
Fe %	4.23 ± 0.32	4.40 ± 0.10	4.70 ± 0.13	4.93 ± 0.25
Na %	2.80 ± .18	2.4 ± 0	2.3 ± 0.20	2.42 ± 0.13
Ti ppm	4140 ± 580	4560 ± 460	4580 ± 540	4600 ± 430
V ppm	91 ± 19	77 ± 9	79 ± 11	81 ± 8
Mn ppm	480 ± 70	528 ± 48	676 ± 64	684 ± 46
K ppm	5270 ± 710	2940 ± 890	6400 ± 1230	5270 ± 740
Cl ppm	<190	<190	<100	<100
Cr ppm	31 ± 3	34 ± 2	37 ± 1	36 ± 2
Sc ppm	13 ± 1	11.9 ± 0.8	14.0 ± 0.7	14.0 ± 0.8
Co ppm	11 ± 1	11.2 ± 0.8	14.5 ± 0.8	14.6 ± 1.0
Zn ppm	66 ± 20	70 ± 10	68 ± 14	80 ± 11
As ppm	<1.6	<2.0	<2.8	<2.8
Sb ppm	<0.11	<0.13	<0.13	<0.13
Ba ppm	392 ± 59	342 ± 64	340 ± 70	390 ± 60
Cs ppm	0.34 ± 0.10	0.29 ± 0.10	<0.19	<0.18
Hf ppm	3.0 ± .20	2.5 ± 0.2	2.9 ± 0.2	2.6 ± 0.5
Ta ppm	<.1	<.1	0.15 ± 0.03	0.15 ± 0.03
La ppm	11 ± 1	10.4 ± 0.8	9.9 ± 0.6	9.2 ± 0.9
Ce ppm	25 ± 3	21 ± 2	22 ± 2	19 ± 4
Nd ppm	15 ± 2	13 ± 2	11 ± 1	11 ± 1
Sm ppm	3.5 ± 0.5	3.0 ± 0.4	3.1 ± 0.4	3.1 ± 0.7
Eu ppm	1.0 ± 0.2	0.9 ± 0.1	0.84 ± 0.09	0.8 ± 0.1
Tb ppm	0.38 ± 0.14	0.32 ± 0.08	0.35 ± 0.09	0.3 ± 0.1
Dy ppm	3.2 ± 1.1	2.54 ± 0.83	2.5 ± 0.8	2.3 ± 1.0
Yb ppm	1.1 ± 0.4	0.91 ± 0.30	1.0 ± 0.3	0.9 ± 0.2
Lu ppm	0.18 ± 0.02	0.18 ± 0.02	0.20 ± 0.02	0.20 ± 0.03
Th ppm	<0.05	<0.06	<0.06	<0.06

Table 3.1 cont'd…: Means and standard deviations of elemental concentrations for each source group of ochre. Values are expressed in weight percent (%) or ppm where indicated.

Element	***Pilchuck Creek 1 (n=10)***	***Pilchuck Creek 2 (n=10)***	***Tulameen Ochre Bluffs (n=12)***
	Mean ± St.Dev.	Mean ± St.Dev.	Mean ± St.Dev.
Al %	8.6 ± 0.5	8.6 ± .30	0.10 ± 0.02
Ca %	3.5 ± 0.3	3.5 ± 0.3	21.5 ± 3.1
Fe %	5.69 ± 0.25	6.56 ± 0.64	17.0 ± 2.9
Na %	2.49 ± .13	2.38 ± 0.08	0.074 ± 0.016
Ti ppm	3680 ± 320	3770 ± 490	<500
V ppm	105 ± 10	127 ± 13	29 ± 5
Mn ppm	647 ± 39	648 ± 30	1600 ± 140
K ppm	9500 ± 1040	10890 ± 1090	860 ± 410
Cl ppm	<170	<170	200 ± 60
Cr ppm	34 ± 3	33 ± 4	7.1 ± 1.7
Sc ppm	12.9 ± 0.6	13.6 ± 0.7	0.72 ± 0.09
Co ppm	11.4 ± 2.9	12 ± 3	3.2 ± 0.6
Zn ppm	61 ± 15	73 ± 11	3.8 ± 0.5
As ppm	2.9 ± 1.1	3.2 ± 1.0	<6
Sb ppm	0.30 ± 0.07	0.24 ± 0.07	<0.23
Ba ppm	615 ± 128	610 ± 110	1030 ± 80
Cs ppm	0.71 ± 0.29	0.98 ± 0.24	<0.6
Hf ppm	3.6 ± 0.4	3.3 ± 0.3	<0.3
Ta ppm	<0.1	<0.22	<0.4
La ppm	17.5 ± 4.3	13.7 ± 0.7	1.35 ± 0.27
Ce ppm	35 ± 6	29 ± 1	2.9 ± 0.7
Nd ppm	17 ± 2	16 ± 2	<1
Sm ppm	4.0 ± 0.4	3.6 ± 0.4	0.20 ± 0.04
Eu ppm	1.10 ± 0.04	1.01 ± 0.10	0.16 ± 0.02
Tb ppm	<0.23	<0.25	<0.35
Dy ppm	4.6 ± 0.8	3.9 ± 1.0	<0.16
Yb ppm	2.1 ± 0.6	2.08 ± 0.44	<0.3
Lu ppm	0.22 ± 0.02	0.25 ± 0.04	<0.32
Th ppm	<0.06	<0.06	<0.06

APPENDIX C

Table A: Elemental concentration data presented in Chapter 2, Table 2.3, Group 1 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation.

Sample ID	Borden ID	Site info	Cl (ppm)	Sc (ppm)	Ti (ppm)
NWCO 1-1	EjSw-1	COCHMI	172	11.2	203
NWCO 1-2	EjSw-1	COCHMI	162	26.8	841
NWCO 1-3	EjSw-1	COCHMI	88	49.6	286
NWCO 1-4	EjSw-1	COCHMI	180	3.8	154
NWCO 1-5	ElSx-1	NAMU	361	7.9	361
NWCO 1-6	EjSw-1	COCHMI	154	6.8	437
NWCO 2-1	EjSw-1	COCHMI	225	23.2	330
NWCO 2-2	EjSw-1	COCHMI	369	11.6	285
NWCO 2-3	EjSw-1	COCHMI	97	11.1	300
NWCO 2-4	EjSw-1	COCHMI	nm	33.0	145
NWCO 2-5	ElSx-1	NAMU	115	13.5	612
NWCO 2-7	EjSw-1	COCHMI	304	15.6	241
NWCO 2-8	EkSt-1	KATIT	78	15.1	561
NWCO 2-9	ElSx-3	KISSAMEET	168	12.5	356
NWCO 3-1	EkSt-1	KATIT	34	1.2	25
NWCO 3-2	EkSt-5	CAMP	62	15.0	477
NWCO 3-4	EkSt-1	KATIT	54	12.7	494
NWCO 3-8	EkSt-1	KATIT	426	14.2	416
NWCO 4-5	ElSx-1	NAMU	392	13.8	570
NWCO 4-6	ElSx-1	NAMU	372	17.5	619
NWCO 4-7	ElSx-1	NAMU	222	9.2	393
NWCO 4-8	ElSx-1	NAMU	nm	21.6	591
NWCO 4-9	EjSv-5	CAMP	192	16.4	286
NWCO 4-10	ElSx-3	KISSAMEET	816	53.6	777
NWCO 5-1	ElSx-1	NAMU	190	8.0	517
NWCO 5-2	ElSx-1	NAMU	292	8.4	338
NWCO 5-3	ElSx-1	NAMU	160	5.5	221
NWCO 5-4	ElSx-1	NAMU	254	13.4	395
NWCO 5-5	ElSx-1	NAMU	157	21.1	1230
NWCO 5-6	EjSw-1	COCHMI	584	30.4	187
NWCO 5-7	EjSw-1	COCHMI	906	9.4	380
NWCO 5-8	EjSw-1	COCHMI	150	7.8	269
NWCO 5-10	EjSv-3	CAMP	63	1.5	29

Table A: Elemental concentration data presented in Chapter 2, Table 2.3, Group 1 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation….. cont'd.

Sample ID	**V (ppm)**	**Al (ppm)**	**Ca (ppm)**	**Fe (ppm)**	**Na (ppm)**	**Zn (ppm)**
NWCO 1-1	162	31389	49624	23883	683	4085
NWCO 1-2	347	54374	76541	28997	7697	1142
NWCO 1-3	286	40364	39698	31975	6721	nm
NWCO 1-4	25	81782	55099	39445	18732	6920
NWCO 1-5	82	73488	35019	24123	33921	nm
NWCO 1-6	245	90097	69645	58648	1671	2090
NWCO 2-1	245	74253	74936	52663	39769	nm
NWCO 2-2	166	65538	57253	20142	15023	92
NWCO 2-3	320	58982	54637	17524	2142	268
NWCO 2-4	78	107414	61726	32489	41660	396
NWCO 2-5	172	95129	77355	5314	32462	nm
NWCO 2-7	130	70543	40619	34333	24691	205
NWCO 2-8	126	88847	51503	50362	26491	80
NWCO 2-9	121	65144	13738	39083	24125	499
NWCO 3-1	8	8220	4432	7921	4156	114
NWCO 3-2	87	68551	15111	43312	29400	522
NWCO 3-4	74	97404	50038	40692	41000	335
NWCO 3-8	95	71955	59811	47133	38800	486
NWCO 4-5	116	74173	31990	56273	28687	95
NWCO 4-6	155	84093	44245	44838	50897	115
NWCO 4-7	85	82135	30850	16756	51822	64
NWCO 4-8	195	75471	50484	51758	28968	167
NWCO 4-9	119	57922	110612	51770	7500	120
NWCO 4-10	530	95199	61246	80348	28693	397
NWCO 5-1	127	75944	170590	53578	5710	274
NWCO 5-2	39	105332	69389	25580	35849	61
NWCO 5-3	75	49629	35385	19644	28074	41
NWCO 5-4	116	85691	40451	48057	22500	89
NWCO 5-5	124	80351	42624	92213	41100	735
NWCO 5-6	99	82759	34537	62746	23154	nm
NWCO 5-7	148	105332	73712	16771	64000	326
NWCO 5-8	121	65996	20978	9170	36600	274
NWCO 5-10	26	77310	10278	13333	32851	nm

Table A: Elemental concentration data presented in Chapter 2, Table 2.3, Group 1 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation….. cont'd.

Sample ID	**Co (ppm)**	**As (ppm)**	**Sb (ppm)**	**Ba (ppm)**	**Au (ppm)**	**Cs (ppm)**
NWCO 1-1	3.2	nm	0.38	nm	1.16	4.45
NWCO 1-2	4.3	nm	0.43	660	1.15	5.40
NWCO 1-3	2.5	1.7	0.05	850	0.68	2.88
NWCO 1-4	4.6	1.6	0.32	330	0.86	4.46
NWCO 1-5	6.1	6.5	0.24	1100	0.71	2.25
NWCO 1-6	11.6	26.6	1.87	350	nm	5.29
NWCO 2-1	7.0	2.7	0.41	370	0.69	3.70
NWCO 2-2	2.0	5.1	0.63	460	0.42	5.20
NWCO 2-3	0.0	2.5	0.53	4220	0.42	9.70
NWCO 2-4	5.0	nm	0.29	310	0.5	6.90
NWCO 2-5	49.2	5.3	0.61	211	0.4	2.38
NWCO 2-7	4.6	1.1	0.15	321	nm	2.81
NWCO 2-8	15.9	nm	0.11	890	0.27	1.69
NWCO 2-9	5.9	nm	0.99	510	1.38	2.86
NWCO 3-1	1.6	nm	0.12	56	0.11	0.97
NWCO 3-2	14.0	6.9	1.06	480	4.8	2.53
NWCO 3-4	3.8	nm	nm	180	nm	nm
NWCO 3-8	13.1	nm	nm	980	nm	nm
NWCO 4-5	8.4	1.78	0.28	786	nm	4.68
NWCO 4-6	7.3	4.64	nm	384	nm	4.04
NWCO 4-7	0.5	nm	0.10	9194	0.06	0.77
NWCO 4-8	6.6	nm	nm	2359	0.11	nm
NWCO 4-9	9.2	1.29	0.69	410	0.06	6.06
NWCO 4-10	13.8	2.30	0.11	83	0.04	nm
NWCO 5-1	2.7	0.75	0.31	nm	nm	nm
NWCO 5-2	4.2	0.26	0.19	1631	0.052	nm
NWCO 5-3	3.2	2.21	0.10	nm	0.003	nm
NWCO 5-4	10.8	2.98	0.18	630	0.063	2.07
NWCO 5-5	16.0	nm	nm	660	0.108	0.80
NWCO 5-6	8.5	nm	nm	1356	nm	1.04
NWCO 5-7	0.5	nm	nm	205	nm	0.39
NWCO 5-8	1.0	nm	nm	750	0.02	0.23
NWCO 5-10	1.2	nm	0.040	2268	0.053	0.68

Table A: Elemental concentration data presented in Chapter 2, Table 2.3, Group 1 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation….. cont'd.

Sample ID	**Hf (ppm)**	**Ta (ppm)**	**Ce (ppm)**	**Nd (ppm)**	**Sm (ppm)**	**Eu (ppm)**
NWCO 1-1	1.6	1.59	11.8	6.5	2.65	4.27
NWCO 1-2	4.22	2.3	57.5	28.3	8.36	4.2
NWCO 1-3	2.11	1.3	33.1	23.6	5.88	1.09
NWCO 1-4	1.89	1.1	20.8	11.7	2.68	1.1
NWCO 1-5	2.94	0.78	38.9	18.6	4.65	1.48
NWCO 1-6	1.28	1.17	8	140.6	0.40	0.9
NWCO 2-1	1.76	0.79	12.2	9.5	3.80	1.5
NWCO 2-2	2.28	0.8	16.3	13.4	3.41	1.2
NWCO 2-3	1.76	1.8	8.6	nm	2.03	0.9
NWCO 2-4	4.08	1.53	12.5	9.7	5.42	1.3
NWCO 2-5	1.89	0.26	37.8	24.9	6.71	2.3
NWCO 2-7	0.75	0.54	24.4	15.0	3.74	1.1
NWCO 2-8	1.89	0.89	26	18.4	4.35	1.0
NWCO 2-9	1.77	5	43	13.9	5.51	2.6
NWCO 3-1	0.187	0.107	1.85	nm	0.34	0.2
NWCO 3-2	5.24	0.1	31.64	4.5	2.55	2.2
NWCO 3-4	4.88	nm	45.5	nm	8.73	2.8
NWCO 3-8	2.62	nm	12.2	19.6	5.49	1.5
NWCO 4-5	3.94	nm	28.9	32.2	3.67	1.3
NWCO 4-6	2.94	1.99	18.3	5.5	3.91	1.4
NWCO 4-7	2.35	nm	40.2	52.5	8.80	1.1
NWCO 4-8	3.38	nm	40.2	nm	6.31	1.0
NWCO 4-9	1.81	nm	18.4	16.2	2.25	0.7
NWCO 4-10	1.30	nm	27.2	23.4	4.40	1.0
NWCO 5-1	5.74	0.56	17.1	10.0	4.07	2.0
NWCO 5-2	6.73	nm	38.8	14.0	5.34	1.3
NWCO 5-3	1.44	nm	28.1	17.0	2.28	0.9
NWCO 5-4	3.06	nm	29.1	26.1	3.57	0.7
NWCO 5-5	8.28	2.6	70.7	26.2	9.3	3.2
NWCO 5-6	2.00	0.62	24.3	5.1	4.39	1.8
NWCO 5-7	3.02	0.08	20.4	4.7	1.25	0.6
NWCO 5-8	3.18	0.49	13.5	2.4	1.06	0.7
NWCO 5-10	1.84	0.09	5.6	1.69	1.24	2.9

Table A: Elemental concentration data presented in Chapter 2, Table 2.3, Group 1 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation….. cont'd.

Sample ID	**Tb (ppm)**	**Yb (ppm)**	**Lu (ppm)**	**Th (ppm)**
NWCO 1-1	0.36	0.55	0.16	1.30
NWCO 1-2	0.65	1.67	0.24	2.28
NWCO 1-3	0.87	1.29	0.40	1.97
NWCO 1-4	nm	0.7	nm	2.39
NWCO 1-5	0.94	1.09	0.09	4.35
NWCO 1-6	nm	nm	0.85	0.18
NWCO 2-1	0.32	nm	0.16	1.43
NWCO 2-2	0.35	0.47	0.11	3.33
NWCO 2-3	nm	0	0.24	1.51
NWCO 2-4	1.06	0.85	0.10	1.10
NWCO 2-5	0.67	0.71	0.04	3.46
NWCO 2-7	nm	0.62	0.84	7.04
NWCO 2-8	0.31	0.53	0.17	3.55
NWCO 2-9	nm	1.1	0.23	6.16
NWCO 3-1	nm	nm	nm	0.25
NWCO 3-2	0.56	nm	4.54	5.27
NWCO 3-4	0.57	nm	0.04	10.78
NWCO 3-8	nm	nm	0.09	3.68
NWCO 4-5	nm	nm	0.15	3.07
NWCO 4-6	nm	2.48	nm	2.23
NWCO 4-7	0.465	1.15	nm	4.88
NWCO 4-8	nm	0	0.46	3.26
NWCO 4-9	nm	0	1.14	1.77
NWCO 4-10	nm	0	0.07	1.20
NWCO 5-1	0.51	0.43	0.03	10.00
NWCO 5-2	0.26	0	0.05	3.16
NWCO 5-3	nm	0	nm	2.97
NWCO 5-4	nm	0	0.21	2.73
NWCO 5-5	0.741	0.14	7.17	0.57
NWCO 5-6	nm	0.56	0.26	4.10
NWCO 5-7	0.033	0.01	2.61	nm
NWCO 5-8	0.006	0.093	2.75	0.47
NWCO 5-10	nm	0.079	0.01	11.60

Table B: Elemental concentration data presented in Chapter 2, Table 2.3, Group 2 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation.

Sample ID	Site ID	Ti (ppm)	V (ppm)	Al (ppm)	Cl (ppm)	Ca (ppm)
NWCO 4-4	ElSx-10	1338	208	34705	361	3209
NWCO 12-1	FcSm-6	647	123	16554	nm	2276
NWCO 12-2	FcSm-6	570	146	16446	32	1923
NWCO 12-3	FcSm-6	431	103	10117	35	2821
NWCO 12-4	FcSm-6	1370	168	17601	nm	2516
NWCO 12-5	FaSu-19	15399	371	60994	nm	50646
NWCO 12-8	FeSr-7	2479	126	34924	38	10450
NWCO 12-9	FeSr-7	4681	204	75577	74	24522
NWCO 12-10	FeSr-7	4373	208	75423	nm	29170
NWCO 12-11	FeSr-7	4666	211	73621	nm	27567
NWCO 12-12	FeSr-7	4666	239	100708	nm	30612
NWCO 12-13	FeSr-7	2833	172	40160	219	19393
NWCO 12-14	FeSr-7	6683	183	80689	nm	29811
NWCO 12-15	FcSq-8	2017	252	38928	72	6876
NWCO 12-16	FcSq-8	6206	186	106713	nm	24041
NWCO 12-17	FcSq-8	1309	235	29242	80	8494
NWCO 12-18	FcSq-8	108	156	5179	97	2084
NWCO 12-19	FcSq-8	1755	58	18432	129	930

Sample ID	Fe (ppm)	Mn (ppm)	Na (ppm)	K (ppm)	Cr (ppm)	Sc (ppm)
NWCO 4-4	109292	nm	13418	nm	2.0	9.2
NWCO 12-1	62823	144	360	722.0	0	9.7
NWCO 12-2	59464	147	272	616	6.3	10.0
NWCO 12-3	45048	82	263	566	6.1	6.3
NWCO 12-4	93621	248	415	653	23	12.3
NWCO 12-5	79258	1000	5614	13920	263	27.3
NWCO 12-8	388910	1592	8772	5829	40	7.6
NWCO 12-9	244882	744	18817	12006	63	13.4
NWCO 12-10	243603	808	17839	12441	67	12.4
NWCO 12-11	258564	568	16445	11919	73	13.3
NWCO 12-12	203019	1048	22663	12702	70	14.3
NWCO 12-13	216834	496	8722	7656	40	9.1
NWCO 12-14	274460	672	15118	12702	38	13.6
NWCO 12-15	374278	728	4441	3236	23	6.81
NWCO 12-16	95429	1040	18207	10962	62	15.3
NWCO 12-17	442836	488	2301	2723	17	5.03
NWCO 12-18	523588	416	88	<290	5.7	3.46
NWCO 12-19	63794	168	2234	3758	10	1.4

Table B: Elemental concentration data presented in Chapter 2, Table 2.3, Group 2 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation…. cont'd.

Sample ID	**Zn (ppm)**	**Co (ppm)**	**As (ppm)**	**Sb (ppm)**	**Ba (ppm)**	**Au (ppm)**
NWCO 4-4	66	1.6	18.82	0.26	819	nm
NWCO 12-1	16.4	6.6	7.54	nm	nm	nm
NWCO 12-2	7.5	4.0	4.17	0.21	nm	nm
NWCO 12-3	11.6	2.2	3.89	0.23	nm	nm
NWCO 12-4	24.4	7.9	6.23	0.70	785	nm
NWCO 12-5	68.4	30.5	1.97	0.32	907	nm
NWCO 12-8	21.5	7.7	3.08	0.57	1622	nm
NWCO 12-9	62.6	19.8	3.06	0.24	nm	nm
NWCO 12-10	63.3	18.2	10.45	0.62	nm	nm
NWCO 12-11	53.6	19.6	3.39	0.36	nm	nm
NWCO 12-12	94.7	20.7	3.56	nm	nm	0.023
NWCO 12-13	136.0	15.2	8.63	0.62	558	nm
NWCO 12-14	128.0	23.7	8.44	6.05	nm	nm
NWCO 12-15	97.33	16.3	121.3	1.70	nm	nm
NWCO 12-16	100.5	29.9	10.21	0.89	506	nm
NWCO 12-17	49.92	10.6	104.3	2.06	541	nm
NWCO 12-18	118.16	11.2	127.4	1.78	192	nm
NWCO 12-19	168.6	6.2	9.88	3.29	nm	nm

Sample ID	**Cs (ppm)**	**Hf (ppm)**	**Ta (ppm)**	**Ce (ppm)**	**Nd (ppm)**	**Sm (ppm)**
NWCO 4-4	1.98	11.12	2.99	20.7	9.3	2.24
NWCO 12-1	0.595	12.42	nm	16.8	8.9	3.00
NWCO 12-2	nm	14.25	nm	15.7	10.9	1.95
NWCO 12-3	0.1085	9.05	nm	14.3	10.5	2.15
NWCO 12-4	nm	16.60	nm	22.4	26.9	2.85
NWCO 12-5	0.63	7.46	nm	52.6	24.4	5.60
NWCO 12-8	0.665	2.13	nm	13.0	5.4	2.97
NWCO 12-9	1.19	3.96	nm	27.9	16.0	3.80
NWCO 12-10	0.245	3.09	nm	27.2	31.2	3.98
NWCO 12-11	nm	3.26	nm	27.3	18.3	3.52
NWCO 12-12	0.35	2.72	nm	31.3	14.8	4.16
NWCO 12-13	nm	1.59	nm	19.2	12.3	1.90
NWCO 12-14	9.345	2.20	nm	31.9	22.3	3.81
NWCO 12-15	2.08	1.82	nm	10.6	7.2	2.61
NWCO 12-16	0.875	4.31	nm	52.5	13.1	4.35
NWCO 12-17	1.35	1.48	nm	12.3	6.4	3.32
NWCO 12-18	1.46	nm	nm	1.9	0.2	1.84
NWCO 12-19	6.09	5.39	nm	17.9	8.4	1.33

Table B: Elemental concentration data presented in Chapter 2, Table 2.3, Group 2 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation…. cont'd.

Sample ID	**Eu (ppm)**	**Tb (ppm)**	**Dy (ppm)**	**Yb (ppm)**	**Lu (ppm)**	**Th (ppm)**
NWCO 4-4	1.0	nm	nm	0.52	0.00	9.58
NWCO 12-1	5.166	nm	nm	nm	0.187	nm
NWCO 12-2	0.666	0.35	1.27	0.11	0.149	nm
NWCO 12-3	0.603	0.20	0.96	0.11	0.128	nm
NWCO 12-4	5.740	1.10	nm	1.20	0.243	nm
NWCO 12-5	1.157	1.05	7.21	0.89	0.695	nm
NWCO 12-8	2.813	0.14	nm	nm	0.203	nm
NWCO 12-9	1.923	1.46	4.01	0.95	0.267	nm
NWCO 12-10	1.972	nm	3.69	2.09	0.264	nm
NWCO 12-11	2.915	0.23	3.85	1.20	0.324	nm
NWCO 12-12	3.059	1.60	9.62	nm	0.325	nm
NWCO 12-13	3.936	0.59	nm	0.82	0.114	nm
NWCO 12-14	7.257	1.28	nm	1.77	0.277	nm
NWCO 12-15	1.313	0.52	4.81	0.85	0.163	nm
NWCO 12-16	1.316	0.91	3.85	1.05	0.372	0.149
NWCO 12-17	1.548	0.34	4.49	0.41	0.244	nm
NWCO 12-18	1.458	nm	2.10	0.19	0.186	nm
NWCO 12-19	1.251	0.68	1.36	0.64	0.158	nm

Table C: Elemental concentration data presented in Chapter 2, Table 2.3, Group 3 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation.

Sample ID	**Site ID**	**Ti (ppm)**	**V (ppm)**	**Al (ppm)**	**Cl (ppm)**	**Ca (ppm)**
NWCO 2-6	NAMU	81	61	18170	564	10254
NWCO 3-3	KATIT	388	130	36719	69	17868
NWCO 3-5	KATIT	304	83	48722	726	36345
NWCO 3-6	KATIT	155	108	39949	835	18587
NWCO 3-7	KATIT	203	79	25742	343	18369
NWCO 4-1	NAMU	210	3	9009	97	5896
NWCO 4-2	CAMP	585	174	73017	742	29251
NWCO 5-9	KATIT	123	39	8599	283	8735

Sample ID	**Fe (ppm)**	**Na (ppm)**	**Cr (ppm)**	**Sc (ppm)**	**Zn (ppm)**	**Co (ppm)**
NWCO 2-6	615119	1444	32.4	0.3	nm	17.7
NWCO 3-3	303131	6300	4.6	5.0	165	17.0
NWCO 3-5	180040	4960	25.6	10.9	nm	5.4
NWCO 3-6	374526	9439	83.0	14.1	309	13.5
NWCO 3-7	476749	1547	39.5	5.6	39	4.8
NWCO 4-1	126521	544	0.0	3.2	nm	8.0
NWCO 4-2	181111	15436	0.0	15.4	nm	10.7
NWCO 5-9	492251	1689	6.1	1.3	8	11.0

Sample ID	**As (ppm)**	**Sb (ppm)**	**Ba (ppm)**	**Au (ppm)**	**Cs (ppm)**	**Hf (ppm)**
NWCO 2-6	1.5	0.35	370	2.5	13.10	0.82
NWCO 3-3	3.2	0.50	380	0.5	3.48	1.03
NWCO 3-5	7.5	2.43	2400	4.7	27	5.00
NWCO 3-6	22.9	2.79	400	5.6	79	5.30
NWCO 3-7	12.2	0.90	1100	3	30	0.00
NWCO 4-1	3.09	0.17	104	0.139	1.60	0.29
NWCO 4-2	5.00	0.32	779	nm	nm	1.27
NWCO 5-9	43.5	5.2	95	0.053	1.92	nm

Table C: Elemental concentration data presented in Chapter 2, Table 2.3, Group 3 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation… cont'd.

Sample ID	**Ta (ppm)**	**Ce (ppm)**	**Nd (ppm)**	**Sm (ppm)**	**Eu (ppm)**	**Tb (ppm)**
NWCO 2-6	1.18	3.7	nm	nm	0.7	1.3
NWCO 3-3	nm	7.57	nm	0.87	0.9	0.10
NWCO 3-5	9.2	54.7	54.65	3.01	8.0	nm
NWCO 3-6	nm	20	nm	4.07	5.7	nm
NWCO 3-7	nm	nm	nm	1.47	3.2	nm
NWCO 4-1	nm	14.3	2.7	1.02	1.79	0.482
NWCO 4-2	0.49	13.9	3.6	1.20	2.43	nm
NWCO 5-9	nm	nm	nm	0.29	0.2	nm

Sample ID	**Yb (ppm)**	**Lu (ppm)**	**Th (ppm)**
NWCO 2-6	0.73	nm	1.01
NWCO 3-3	nm	0.89	0.14
NWCO 3-5	nm	0.26	nm
NWCO 3-6	6.1	0.53	2.36
NWCO 3-7	nm	0.26	1.64
NWCO 4-1	0.2	0.02	0.74
NWCO 4-2	0.23	0.45	20.10
NWCO 5-9	nm	0.17	nm

Table D: Elemental concentration data presented in Chapter 2, Table 2.3, Group 4 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation.

Sample ID	**Site ID**	**Ti (ppm)**	**V (ppm)**	**Al (ppm)**	**Cl (ppm)**	**Ca (ppm)**
NWCO 4-3	NAMU	720	141	88180	213	21674
Sagar-1	SAGAR	1786	63	115182	nm	23881
Sagar-2	SAGAR	1940	41	1655	nm	31253
Sagar-3	SAGAR	2217	41	108407	nm	29811
ElSx-10-2	ElSx-10	6021	180	140898	801	83021
NWCO 10-1	KISSAMEET	7601	662	64621	240	7946
NWCO 10-2	KISSAMEET	7278	314	127253	805	56452
NWCO 10-3	KISSAMEET	8451	106	118224	2	97442
NWCO 10-4	KISSAMEET	11336	136	173018	1005	103295
NWCO 10-5	KISSAMEET	11403	128	277912	984	87112

Sample ID	**Fe (ppm)**	**Na (ppm)**	**Cr (ppm)**	**Sc (ppm)**	**Zn (ppm)**	**Co (ppm)**
NWCO 4-3	15553	7441	nm	4.8	nm	4.2
Sagar-1	16904	26133	4.8	3.5	26.1	3.4
Sagar-2	12150	34729	4.8	2.2	18.4	2.1
Sagar-3	14786	31196	3.8	3.1	24.9	2.9
ElSx-10-2	69702	19681	7.1	21.1	88.2	39.3
NWCO 10-1	39664	29446	10.4	8.0	nm	17.2
NWCO 10-2	41634	28838	10.7	27.0	nm	35.0
NWCO 10-3	50173	37976	10.0	24.0	nm	25.9
NWCO 10-4	44044	38152	8.7	23.0	nm	35.2
NWCO 10-5	31589	44864	11.3	25.0	nm	22.3

Sample ID	**As (ppm)**	**Sb (ppm)**	**Ba (ppm)**	**Au (ppm)**	**Cs (ppm)**	**Hf (ppm)**
NWCO 4-3	nm	0.00	nm	nm	0.13	0.84
Sagar-1	2.25	0.24	942	nm	0.119	1.96
Sagar-2	1.54	0.10	1186	nm	0.1015	1.20
Sagar-3	1.75	0.12	1169	nm	0.175	1.55
ElSx-10-2	1.14	0.48	174	nm	0.035	2.22
NWCO 10-1	85	3.8	1371	0.77	1.53	2.1
NWCO 10-2	nm	0.435	354	nm	2.43	1.3
NWCO 10-3	3	0.343	134	nm	nm	1.2
NWCO 10-4	2.3	0.3432	1341	nm	nm	1.2
NWCO 10-5	nm	0.4224	1163	nm	nm	1.1

Table D: Elemental concentration data presented in Chapter 2, Table 2.3, Group 4 (MacDonald et al, 2011). Data set contains outliers that were removed during logarithmic transformation… cont'd.

Sample ID	**Ta (ppm)**	**Ce (ppm)**	**Nd (ppm)**	**Sm (ppm)**	**Eu (ppm)**	**Tb (ppm)**
NWCO 4-3	0.05	4.2	0.6	4.33	1.22	nm
Sagar-1	nm	13.6	6.5	1.69	0.585	1.30
Sagar-2	nm	19.9	8.7	1.60	0.681	0.23
Sagar-3	nm	18.8	7.2	1.50	0.603	0.16
ElSx-10-2	nm	31.2	19.7	5.97	1.989	1.55
NWCO 10-1	nm	23.0	35.3	13.14	0.68	nm
NWCO 10-2	0.455	35.0	22	6	1.19	1.24
NWCO 10-3	nm	35.0	14	4.8	1.079	nm
NWCO 10-4	nm	30.0	17	5	1.05	nm
NWCO 10-5	nm	33.0	15	4.5	1.2	0.52

Sample ID	**Dy (ppm)**	**Yb (ppm)**	**Lu (ppm)**	**Th (ppm)**
NWCO 4-3	nm	0.02	0.48	2.63
Sagar-1	2.00	0.55	0.064	nm
Sagar-2	0.64	0.18	0.073	nm
Sagar-3	1.28	0.16	0.076	nm
ElSx-10-2	9.46	0.95	0.523	6.3
NWCO 10-1	1.02	3.3	0.239	13.92
NWCO 10-2	3.20	3.3	0.228	3
NWCO 10-3	7.79	3.3	0.217	2.2
NWCO 10-4	7.79	2.6	0.192	2.5
NWCO 10-5	4.82	2.4	0.181	2.5

APPENDIX D

Table A: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Paul Ridge 1 (n=15)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Cl (ppm)	Mn (ppm)
NWCO 6-5	5772	151	176600	17.66	337	nm
NWCO 6-6	3510	103	105900	10.59	143	665
NWCO 8-1	4333	92	113240	11.30	194	480
NWCO 8-2	4060	101	124032	12.40	nm	510
NWCO 8-3	4522	93	108756	10.80	nm	410
NWCO 14-26	3767	80	104670	10.47	<190	433
NWCO 14-27	4776	80	108810	10.88	<190	453
NWCO 14-28	3828	80	105300	10.53	<190	464
NWCO 14-29	3920	93	128184	12.82	bdl	490
NWCO 14-30	4508	91	126222	12.62	bdl	448
NWCO 14-31	3698	76	105300	10.53	<190	474
NWCO 14-32	3828	78	106920	10.69	<190	433
NWCO 14-33	3506	70	97290	9.73	<190	494
NWCO 14-34	3979	94	126222	12.62	bdl	504
NWCO 14-35	4087	82	123933	12.39	bdl	385

Sample ID	Ca (ppm)	Ca (%)	Fe (ppm)	Fe (%)	Na (ppm)	Na (%)
NWCO 6-5	46530	4.65	53136	5.31	27100	2.71
NWCO 6-6	37882	3.78	42034	4.20	29005	2.90
NWCO 8-1	35905	3.90	39813	3.98	26312	2.63
NWCO 8-2	34402	3.44	40295	4.02	27117	2.71
NWCO 8-3	35320	3.53	40020	4.00	26579	2.66
NWCO 14-26	33100	3.31	40358	4.03	29349	2.93
NWCO 14-27	33300	3.33	43273	4.32	30644	3.06
NWCO 14-28	34500	3.45	42319	4.23	29804	2.98
NWCO 14-29	31900	3.19	43275	4.32	27394	2.73
NWCO 14-30	31700	3.17	42376	4.23	26139	2.61
NWCO 14-31	34900	3.49	41300	4.13	29685	2.96
NWCO 14-32	32600	3.26	41688	4.16	30314	3.03
NWCO 14-33	34100	3.41	41798	4.17	31268	3.12
NWCO 14-34	31300	3.13	41253	4.12	26037	2.60
NWCO 14-35	34600	3.46	42694	4.26	26682	2.66

Table A: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions… cont'd.

Paul Ridge 1 (n=15)

Sample ID	K (ppm)	Cr (ppm)	Sc (ppm)	Zn (ppm)	Co (ppm)	As (ppm)
NWCO 6-5	6174	35.9	16.9	nm	11.1	2.9
NWCO 6-6	5054	25.1	13.7	86	9.7	1.2
NWCO 8-1	5700	29.9	12.8	40	9.2	0.38
NWCO 8-2	6344	30.1	14.3	37	9.1	1.56
NWCO 8-3	4050	29.0	12.4	49	9.7	0.23
NWCO 14-26	4365	30.5	13.1	83	10.7	bdl
NWCO 14-27	5432	30.6	14.2	89	11.9	bdl
NWCO 14-28	4462	30.0	13.8	87	11.5	3.952
NWCO 14-29	6200	34.7	13.2	50	10.4	1.536
NWCO 14-30	4800	31.9	13.1	56	10.6	bdl
NWCO 14-31	5529	30.9	12.2	84	11.2	1.04
NWCO 14-32	5820	32.3	13.5	85	11.6	bdl
NWCO 14-33	4753	30.1	13.1	83	11.4	3.22
NWCO 14-34	5500	30.4	12.9	49	10.1	bdl
NWCO 14-35	4900	32.9	12.4	47	10	bdl

Sample ID	Sb (ppm)	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)
NWCO 6-5	0.234	462	nm	2.40	0.17	11.2
NWCO 6-6	0.136	365	nm	2.00	0.11	11.1
NWCO 8-1	0.031	450	0.288	2.65	0.13	11.1
NWCO 8-2	bdl	373	0.464	2.55	0.10	13.9
NWCO 8-3	0.047	407	0.304	2.58	bdl	11.1
NWCO 14-26	bdl	303	0.306	2.47	0.12	10.4
NWCO 14-27	bdl	472	0.374	2.62	bdl	10.5
NWCO 14-28	0.107	250	0.544	2.34	bdl	10.2
NWCO 14-29	0.186	431	bdl	2.6	bdl	11.9
NWCO 14-30	0.180	371	0.308	2.8	0.123	11.1
NWCO 14-31	bdl	423	0.34	2.47	bdl	10.2
NWCO 14-32	0.1788	385	0.306	2.39	0.156	10.0
NWCO 14-33	bdl	384	bdl	2.56	0.17	9.9
NWCO 14-34	bdl	369	bdl	2.9	0.164	11
NWCO 14-35	bdl	442	0.209	2.8	bdl	11.6

Table A: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Paul Ridge 1 (n=15)

Sample ID	**Ce (ppm)**	**Nd (ppm)**	**Sm (ppm)**	**Eu (ppm)**	**Tb (ppm)**	**Dy (ppm)**
NWCO 6-5	32.0	15.0	2.35	1.3	0.519	4.1
NWCO 6-6	22.1	10.0	3.1	0.96	0.451	3.2
NWCO 8-1	25.6	15.2	4.57	1.21	0.246	2.35
NWCO 8-2	30.4	19.2	4.00	1.23	0.720	4.25
NWCO 8-3	23.9	15.8	3.41	1.08	0.435	3.78
NWCO 14-26	23.7	16.9	3.92	1.07	0.177	1.8
NWCO 14-27	24.4	16.3	3.64	1.1	0.390	4.08
NWCO 14-28	23.5	16.2	3.18	1.1	0.210	2.65
NWCO 14-29	26	14.0	3.4	0.89	0.4635	3.8
NWCO 14-30	26.4	13.9	3.41	0.92	0.2266	bdl
NWCO 14-31	23.1	16.1	3.21	1.0	0.240	1.9
NWCO 14-32	22.4	16.0	3.03	1.03	0.362	1.9
NWCO 14-33	21.8	16.0	3.59	1.25	0.341	5.03
NWCO 14-34	25.9	13.3	3.68	0.79	0.4635	bdl
NWCO 14-35	24.7	13.4	3.42	0.78	nm	bdl

Sample ID	**Yb (ppm)**	**Lu (ppm)**	**Th (ppm)**
NWCO 6-5	1.39	0.248	bdl
NWCO 6-6	1.02	0.172	bdl
NWCO 8-1	0.616	0.170	bdl
NWCO 8-2	1.44	0.181	bdl
NWCO 8-3	0.98	0.168	bdl
NWCO 14-26	1.01	0.163	bdl
NWCO 14-27	0.96	0.211	bdl
NWCO 14-28	1.38	0.197	bdl
NWCO 14-29	1.188	0.174	bdl
NWCO 14-30	1.386	0.192	bdl
NWCO 14-31	1.93	0.158	bdl
NWCO 14-32	1.13	0.192	bdl
NWCO 14-33	0.66	0.187	bdl
NWCO 14-34	1.122	0.180	bdl
NWCO 14-35	0.561	0.155	bdl

Table B: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Paul Ridge 2 (n=15)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Cl (ppm)	Mn (ppm)
NWCO 6-8	4315	96	79800	7.98	269	nm
NWCO 8-10	4291	76	128820	12.88	bdl	470
NWCO 8-11	4641	77	105640	10.56	292	470
NWCO 8-12	5796	91	138852	13.88	208	nm
NWCO 14-36	5116	77	130582	13.06	bdl	546
NWCO 14-37	4698	74	108900	10.89	260	577
NWCO 14-38	5155	80	125350	12.54	263	476
NWCO 14-39	4224	87	133089	13.31	bdl	574
NWCO 14-40	4385	67	108270	10.83	bdl	525
NWCO 14-41	4263	82	132435	13.24	200	476
NWCO 14-42	4254	69	110430	11.04	bdl	556
NWCO 14-43	4518	76	110526	11.05	273	511
NWCO 14-44	4463	63	107280	10.73	bdl	567
NWCO 14-45	4220	65	107820	10.78	210	494
NWCO 14-46	4126	79	131563	13.16	500	616

Sample ID	Ca (ppm)	Ca (%)	Fe (ppm)	Fe (%)	Na (ppm)	Na (%)
NWCO 6-8	36754	3.67	43614	4.36	24250	2.43
NWCO 8-10	33650	3.36	44742	4.47	24000	2.40
NWCO 8-11	32647	3.26	43666	4.36	23827	2.38
NWCO 8-12	36573	3.65	43199	4.31	23923	2.39
NWCO 14-36	34700	3.47	43816	4.38	24415	2.44
NWCO 14-37	31200	3.12	42591	4.25	25574	2.55
NWCO 14-38	32100	3.21	43438	4.34	23561	2.35
NWCO 14-39	32600	3.26	45152	4.51	24170	2.41
NWCO 14-40	33000	3.3	44294	4.42	25591	2.55
NWCO 14-41	31500	3.15	44359	4.43	23816	2.38
NWCO 14-42	31800	3.18	44214	4.42	26893	2.68
NWCO 14-43	32700	3.27	43740	4.37	23909	2.39
NWCO 14-44	32000	3.2	43735	4.37	25985	2.59
NWCO 14-45	35200	3.52	43297	4.32	25702	2.57
NWCO 14-46	35300	3.53	44557	4.45	23271	2.32

Table B: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Paul Ridge 2 (n=15)

Sample ID	K (ppm)	Cr (ppm)	Sc (ppm)	Zn (ppm)	Co (ppm)	As (ppm)
NWCO 6-8	4901	27.0	12.80	79	9.5	0.63
NWCO 8-10	2806	35.1	11.60	67	11.7	bdl
NWCO 8-11	1785	38.3	12.00	63	10.6	bdl
NWCO 8-12	1605	34.5	11.60	65	11.2	bdl
NWCO 14-36	3700	34.1	11.30	37	10.7	bdl
NWCO 14-37	2163	34.8	11.30	72	11.6	bdl
NWCO 14-38	2800	33.9	11.70	72	11.2	3.84
NWCO 14-39	3600	36.8	11.70	71	11.1	1.79
NWCO 14-40	3977	35.1	12.10	76	12.1	bdl
NWCO 14-41	2300	34.7	11.50	64	11.1	bdl
NWCO 14-42	3104	35.1	12.30	78	12.4	bdl
NWCO 14-43	3500	33.8	11.70	bdl	11.1	bdl
NWCO 14-44	2571	34.3	12.00	76	12.1	bdl
NWCO 14-45	1814	34.6	11.70	74	12.1	bdl
NWCO 14-46	3300	35.0	11.6	68.6	11.2	8.19

Sample ID	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)	Ce (ppm)
NWCO 6-8	392	nm	2.00	0.10	10.7	19.0
NWCO 8-10	392	0.432	2.68	bdl	11.4	22.0
NWCO 8-11	339	0.176	2.87	0.20	11.7	20.6
NWCO 8-12	388	0.208	2.43	0.17	11.5	23.0
NWCO 14-36	330	bdl	2.50	bdl	10.4	20.6
NWCO 14-37	208	bdl	2.39	bdl	9.4	19.8
NWCO 14-38	276	bdl	2.60	bdl	10.4	23.2
NWCO 14-39	353	bdl	2.50	bdl	11.2	23.7
NWCO 14-40	251	0.335	2.51	0.21	9.8	21.4
NWCO 14-41	362	bdl	2.70	0.33	11	22.6
NWCO 14-42	452	bdl	2.69	bdl	10.1	21.7
NWCO 14-43	320	bdl	2.40	bdl	10.3	21.1
NWCO 14-44	276	0.289	2.67	bdl	9.6	21.3
NWCO 14-45	408	bdl	2.58	bdl	9.3	21.3
NWCO 14-46	333	bdl	2.6	0.166	10.8	22.4

Table B: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Paul Ridge 2 (n=15)

Sample ID	Sb (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Dy (ppm)
NWCO 6-8	0.112	15.0	2.35	1.3	0.519	4.1
NWCO 8-10	0.145	10.0	3.1	0.96	0.451	3.2
NWCO 8-11	bdl	15.2	4.57	1.21	0.246	2.35
NWCO 8-12	bdl	19.2	4.00	1.23	0.720	4.25
NWCO 14-36	bdl	15.8	3.41	1.08	0.435	3.78
NWCO 14-37	0.1204	16.9	3.92	1.07	0.177	1.8
NWCO 14-38	0.0654	16.3	3.64	1.1	0.390	4.08
NWCO 14-39	0.1980	16.2	3.18	1.1	0.210	2.65
NWCO 14-40	bdl	14.0	3.4	0.89	0.4635	3.8
NWCO 14-41	0.1380	13.9	3.41	0.92	0.2266	bdl
NWCO 14-42	bdl	16.1	3.21	1.0	0.240	1.9
NWCO 14-43	bdl	16.0	3.03	1.03	0.362	1.9
NWCO 14-44	0.1364	16.0	3.59	1.25	0.341	5.03
NWCO 14-45	0.0963	13.3	3.68	0.79	0.4635	bdl
NWCO 14-46	bdl	13.4	3.42	0.78	nm	bdl

Sample ID	Yb (ppm)	Lu (ppm)	Th (ppm)
NWCO 6-8	1.08	0.204	bdl
NWCO 8-10	1.20	0.148	bdl
NWCO 8-11	0.53	0.157	bdl
NWCO 8-12	0.08	0.178	bdl
NWCO 14-36	0.96	0.188	bdl
NWCO 14-37	0.81	0.175	bdl
NWCO 14-38	0.92	0.212	bdl
NWCO 14-39	0.76	0.175	bdl
NWCO 14-40	1.00	0.190	bdl
NWCO 14-41	0.92	0.198	bdl
NWCO 14-42	1.38	0.178	bdl
NWCO 14-43	0.79	0.142	bdl
NWCO 14-44	1.19	0.185	bdl
NWCO 14-45	1.21	0.180	bdl
NWCO 14-46	0.924	0.206	bdl

Table C: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Chichen Stenach 1 (DkRs-14, n=15)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Ca (ppm)	Ca (%)
NWCO 6-1	4798	97	110300	11.03	42676	4.26
NWCO 6-2	4701	83	90600	9.06	36284	3.62
NWCO 8-7	4865	75	113848	11.30	35487	3.54
NWCO 8-8	4732	83	115368	11.50	35237	3.52
NWCO 8-9	4522	86	119548	11.90	36406	3.64
NWCO 14-47	4237	83	126549	12.65	29500	2.95
NWCO 14-48	3597	55	nm	nm	27900	2.79
NWCO 14-49	5464	67	105660	10.57	32300	3.23
NWCO 14-50	4067	85	127203	12.72	31900	3.19
NWCO 14-51	5537	84	130800	13.08	36800	3.68
NWCO 14-52	4498	81	131672	13.17	32200	3.22
NWCO 14-53	4390	83	130364	13.04	32700	3.27
NWCO 14-54	4489	66	106200	10.60	35500	3.55
NWCO 14-55	3802	66	86130	8.61	35800	3.58
NWCO 14-56	5027	90	133634	13.36	33800	3.38

Sample ID	Cl (ppm)	Fe (ppm)	Fe (%)	Mn (ppm)	Na (ppm)	K (ppm)
NWCO 6-1	127	47531	4.75	993	26712	6020
NWCO 6-2	bdl	49896	5.03	1058	24955	6552
NWCO 8-7	nm	45547	4.55	720	21284	6588
NWCO 8-8	151	46500	4.65	590	20114	3735
NWCO 8-9	177	47160	4.71	580	19190	5550
NWCO 14-47	bdl	47220	4.72	686	22691	6800
NWCO 14-48	bdl	46042	4.60	655	22635	9200
NWCO 14-49	nm	46154	4.61	773	25379	nm
NWCO 14-50	263	48114	4.81	658	22573	6200
NWCO 14-51	192	46064	4.60	707	22105	6400
NWCO 14-52	bdl	47063	4.70	651	22417	6200
NWCO 14-53	bdl	48162	4.81	630	23139	6600
NWCO 14-54	bdl	46125	4.61	742	24552	nm
NWCO 14-55	bdl	45240	4.52	773	25052	nm
NWCO 14-56	bdl	47941	4.79	630	22316	7000

Table C: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Chichen Stenach 1 (DkRs-14, n=15)

Sample ID	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)	Ce (ppm)
NWCO 6-1	300	nm	2.65	0.13	10.9	20.8
NWCO 6-2	262	nm	2.76	0.15	10.7	20.3
NWCO 8-7	382	bdl	2.94	0.16	9.10	21.5
NWCO 8-8	345	0.432	2.89	0.16	9.50	20.3
NWCO 8-9	213	0.224	2.84	0.20	9.30	21.1
NWCO 14-47	358	bdl	3.30	0.18	10.40	23.1
NWCO 14-48	389	bdl	3.00	bdl	9.8	21.9
NWCO 14-49	301	0.255	2.92	bdl	9.40	20.8
NWCO 14-50	324	0.165	3.10	bdl	10	24.6
NWCO 14-51	326	0.275	2.90	0.134	10	21.5
NWCO 14-52	401	bdl	3.30	0.139	10.3	23.7
NWCO 14-53	365	bdl	3.30	bdl	10.1	23.9
NWCO 14-54	281	0.204	2.99	0.141	9.5	21.1
NWCO 14-55	515	0.646	2.86	0.193	9	20.5
NWCO 14-56	341	bdl	3.2	0.11	10.2	24.0

Sample ID	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Dy (ppm)	Yb (ppm)
NWCO 6-1	12.6	3.70	0.76	0.438	1.9	1.18
NWCO 6-2	11.4	3.90	0.81	0.309	3.7	1.20
NWCO 8-7	9.9	3.44	0.96	0.189	bdl	0.42
NWCO 8-8	9.4	2.64	0.66	0.365	bdl	0.63
NWCO 8-9	10.7	2.64	0.76	0.288	bdl	0.80
NWCO 14-47	10.9	3.51	0.75	0.361	2.1	1.02
NWCO 14-48	9.9	3.20	0.89	bdl	2.12	0.73
NWCO 14-49	13.2	2.57	1.00	0.480	1.14	1.21
NWCO 14-50	11.7	2.97	0.89	0.247	3.07	0.69
NWCO 14-51	10.9	3.32	0.90	0.494	2.4	1.09
NWCO 14-52	11.9	3.32	0.83	0.453	bdl	1.49
NWCO 14-53	12.0	3.25	0.78	0.391	bdl	1.06
NWCO 14-54	12.8	2.50	0.9	0.324	bdl	1.40
NWCO 14-55	13.7	2.94	0.91	0.237	3.23	1.68
NWCO 14-56	11.4	2.95	0.86	0.330	bdl	1.12

Table C: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Chichen Stenach 1 (DkRs-14, n=15)

Sample ID	**Cr (ppm)**	**Sc (ppm)**	**Zn (ppm)**	**Co (ppm)**	**As (ppm)**	**Sb (ppm)**
NWCO 6-1	38.2	14.3	nm	14.4	0.65	0.106
NWCO 6-2	32.8	15.9	nm	12.8	1.01	bdl
NWCO 8-7	36.8	13.00	51	14.8	bdl	bdl
NWCO 8-8	38.1	13.30	59	15.0	bdl	bdl
NWCO 8-9	36.6	14.20	45	15.2	bdl	0.146
NWCO 14-47	37.5	13.20	67	14.2	0.96	bdl
NWCO 14-48	36.2	13.20	47	14.0	bdl	bdl
NWCO 14-49	36.0	13.90	88	15.8	bdl	bdl
NWCO 14-50	37.9	13.70	71	14.8	2.43	0.108
NWCO 14-51	37.5	12.80	66	13.7	bdl	0.102
NWCO 14-52	36.3	13.30	68	14.2	bdl	bdl
NWCO 14-53	37.2	13.90	67	14.8	bdl	bdl
NWCO 14-54	35.4	13.60	85	15.4	bdl	bdl
NWCO 14-55	34.5	13.50	85	15.3	bdl	0.1548
NWCO 14-56	36.8	13.70	79	14.4	bdl	bdl

Sample ID	**Lu (ppm)**	**Th (ppm)**
NWCO 6-1	0.179	bdl
NWCO 6-2	0.192	bdl
NWCO 8-7	0.161	bdl
NWCO 8-8	0.180	bdl
NWCO 8-9	0.172	bdl
NWCO 14-47	0.184	bdl
NWCO 14-48	0.196	bdl
NWCO 14-49	0.182	bdl
NWCO 14-50	0.218	bdl
NWCO 14-51	0.192	bdl
NWCO 14-52	0.241	bdl
NWCO 14-53	0.235	bdl
NWCO 14-54	0.204	bdl
NWCO 14-55	0.187	bdl
NWCO 14-56	0.204	bdl

Table D: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Chichen Stenach 2 (DkRs-14, n=10)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Cl (ppm)	Mn (ppm)
NWCO 6-3	4275	86	105100	10.51	307	bdl
NWCO 6-4	4371	bdl	105900	10.59	237	1084
NWCO 8-4	4298	75	98648	9.86	183	620
NWCO 8-5	5236	79	101308	10.10	bdl	680
NWCO 8-6	3843	75	116432	11.60	300	700
NWCO 14-57	4446	70	110880	11.09	bdl	711
NWCO 14-58	5135	93	131890	13.19	182	693
NWCO 14-59	4969	82	128402	12.84	bdl	679
NWCO 14-60	4776	73	106920	10.69	bdl	762
NWCO 14-61	4606	92	131454	13.15	bdl	623

Sample ID	Ca (ppm)	Ca (%)	Fe (ppm)	Fe (%)	Na (ppm)	Na (%)
NWCO 6-3	39292	3.92	47515	4.75	26312	2.63
NWCO 6-4	45026	4.50	51624	5.22	25195	2.52
NWCO 8-4	42334	4.23	47103	5.22	23785	2.38
NWCO 8-5	40581	4.05	46893	5.19	23669	2.37
NWCO 8-6	43336	4.33	47723	5.22	23245	2.32
NWCO 14-57	35400	3.54	47257	4.72	25886	2.59
NWCO 14-58	34200	3.42	47220	4.72	22509	2.25
NWCO 14-59	31700	3.17	48221	4.82	23074	2.31
NWCO 14-60	35800	3.58	46113	4.61	25010	2.50
NWCO 14-61	30500	3.05	48538	4.85	23182	2.32

Table D: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions… cont'd.

Chichen Stenach 2 (DkRs-14, n=10)

Sample ID	K (ppm)	Cr (ppm)	Sc (ppm)	Zn (ppm)	Co (ppm)	As (ppm)
NWCO 6-3	5922	34.3	15.5	97	12.2	1.81
NWCO 6-4	3794	33.7	15.2	96	13.4	0.9
NWCO 8-4	5856	35.8	13.3	73	14.8	bdl
NWCO 8-5	5246	38.4	13.4	71	15.0	bdl
NWCO 8-6	5002	38.6	13.0	73	14.8	bdl
NWCO 14-57	5335	36.8	14.1	90	15.8	bdl
NWCO 14-58	5300	38.2	13.3	69	14.6	2.62
NWCO 14-59	5700	37.0	13.6	70	14.7	3.26
NWCO 14-60	4365	33.8	13.6	86	15.3	bdl
NWCO 14-61	6200	36.8	13.7	75	15.0	bdl

Sample ID	Sb (ppm)	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)
NWCO 6-3	0.198	363	nm	1.98	0.15	9.2
NWCO 6-4	0.156	259	nm	1.70	0.1	7.2
NWCO 8-4	bdl	406	bdl	2.70	0.12	9.0
NWCO 8-5	bdl	362	0.128	2.67	bdl	8.9
NWCO 8-6	bdl	274	bdl	2.41	0.10	8.9
NWCO 14-57	bdl	322	0.272	2.82	bdl	9.3
NWCO 14-58	bdl	387	bdl	3.00	0.18	9.7
NWCO 14-59	bdl	411	bdl	3.20	0.19	10.3
NWCO 14-60	0.1462	257	bdl	2.90	bdl	9.1
NWCO 14-61	0.1740	337	0.253	3.30	0.18	10.1

Table D: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions… cont'd.

Chichen Stenach 2 (DkRs-14, n=10)

Sample ID	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Dy (ppm)
NWCO 6-3	17.0	10.4	2.90	0.77	0.309	2.2
NWCO 6-4	12.4	10.1	4.80	0.74	0.235	2.5
NWCO 8-4	18.0	10.3	2.95	0.79	0.360	1.01
NWCO 8-5	18.0	10.2	2.24	0.61	0.158	bdl
NWCO 8-6	18.0	9.1	3.51	0.79	0.324	bdl
NWCO 14-57	21.5	12.7	2.59	1.00	0.234	2.09
NWCO 14-58	21.9	10.7	2.94	0.85	0.402	bdl
NWCO 14-59	24.0	10.1	3.15	0.74	0.412	bdl
NWCO 14-60	20.0	13.8	2.80	0.88	0.144	3.89
NWCO 14-61	24.1	12.0	3.17	0.78	0.402	bdl

Sample ID	Yb (ppm)	Lu (ppm)	Th (ppm)
NWCO 6-3	0.85	0.164	bdl
NWCO 6-4	0.86	0.156	bdl
NWCO 8-4	1.02	0.166	bdl
NWCO 8-5	0.99	0.183	bdl
NWCO 8-6	0.57	0.166	bdl
NWCO 14-57	bdl	0.221	bdl
NWCO 14-58	0.89	0.171	bdl
NWCO 14-59	1.22	0.224	bdl
NWCO 14-60	bdl	0.209	bdl
NWCO 14-61	0.66	0.198	bdl

Table E: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Pilchuck Creek 1 (n=10)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Cl (ppm)	Mn (ppm)
NWCO 9-1	3634	97	94770	9.47	288	576
NWCO 9-2	3665	93	92950	9.29	nm	632
NWCO 9-3	4373	97	89440	8.94	169	664
NWCO 14-1	3776	105	88380	8.84	190	659
NWCO 14-2	3617	91	86862	8.68	bdl	682
NWCO 14-3	4030	110	84072	8.40	bdl	627
NWCO 14-4	3555	115	83514	8.35	bdl	605
NWCO 14-5	3238	115	81654	8.16	bdl	649
NWCO 14-6	3414	106	78306	7.83	200	660
NWCO 14-7	3529	120	82770	8.27	bdl	715

Sample ID	Ca (ppm)	Ca (%)	Fe (ppm)	Fe (%)	Na (ppm)	Na (%)
NWCO 9-1	31560	3.15	58976	5.90	25583	2.56
NWCO 9-2	32520	3.25	59161	5.91	23399	2.34
NWCO 9-3	32280	3.22	58349	5.83	26276	2.63
NWCO 14-1	36900	3.69	53435	5.34	26982	2.70
NWCO 14-2	39380	3.93	57197	5.72	25939	2.59
NWCO 14-3	38060	3.80	53955	5.40	24516	2.45
NWCO 14-4	36190	3.61	56506	5.65	25025	2.50
NWCO 14-5	33770	3.37	61231	6.12	22863	2.29
NWCO 14-6	36630	3.66	54440	5.44	24598	2.46
NWCO 14-7	38720	3.87	56117	5.61	24173	2.42

Table E: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions… cont'd.

Pilchuck Creek 1 (n=10)

Sample ID	K (ppm)	Cr (ppm)	Sc (ppm)	Zn (ppm)	Co (ppm)	As (ppm)
NWCO 9-1	9222	30.4	12.32	43.7	10.9	2.99
NWCO 9-2	11223	31.4	12.33	28.8	10.7	2.18
NWCO 9-3	9918	32.5	12.07	52.7	10.5	1.92
NWCO 14-1	7566	28.5	12.70	81.0	9.2	4.06
NWCO 14-2	9300	36.0	14.11	71.8	10.2	2.60
NWCO 14-3	10600	35.8	13.17	66.4	9.0	1.90
NWCO 14-4	10000	38.0	13.18	67.2	9.1	3.75
NWCO 14-5	8400	36.8	13.04	65.8	9.8	5.42
NWCO 14-6	9600	36.7	13.27	67.2	9.7	2.52
NWCO 14-7	9200	32.8	13.70	69.8	9.9	1.62

Sample ID	Sb (ppm)	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)
NWCO 9-1	0.278	942	0.403	3.96	bdl	17.4
NWCO 9-2	0.303	453	0.384	3.61	bdl	15.9
NWCO 9-3	0.278	523	0.365	3.81	bdl	12.9
NWCO 14-1	0.275	614	0.663	3.31	bdl	15.8
NWCO 14-2	0.16	566	0.73	4.20	bdl	16.9
NWCO 14-3	0.362	580	0.793	3.77	bdl	28.2
NWCO 14-4	0.285	622	0.762	3.43	bdl	14.5
NWCO 14-5	0.131	599	1.03	2.94	bdl	20.8
NWCO 14-6	0.308	601	1.28	4.00	bdl	17.3
NWCO 14-7	0.154	651	0.680	3.57	bdl	15.2

Table E: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions… cont'd.

Pilchuck Creek 1 (n=10)

Sample ID	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Dy (ppm)
NWCO 9-1	39.2	15.0	4.02	1.103	0.83	bdl
NWCO 9-2	35.0	15.6	4.06	1.095	bdl	bdl
NWCO 9-3	28.2	16.4	4.37	1.041	0.40	3.53
NWCO 14-1	33.0	18.6	3.16	1.020	0.39	3.32
NWCO 14-2	35.6	16.3	3.79	1.12	bdl	bdl
NWCO 14-3	45.6	19.4	5.10	1.033	bdl	5.28
NWCO 14-4	28.8	14.6	3.87	1.15	bdl	5.28
NWCO 14-5	42.1	18.0	3.85	1.110	bdl	4.07
NWCO 14-6	31.4	16.6	3.97	1.10	bdl	5.39
NWCO 14-7	31.5	14.9	3.82	1.140	bdl	4.84

Sample ID	Yb (ppm)	Lu (ppm)	Th (ppm)
NWCO 9-1	bdl	0.263	bdl
NWCO 9-2	bdl	0.238	bdl
NWCO 9-3	bdl	0.258	bdl
NWCO 14-1	1.56	0.245	bdl
NWCO 14-2	2.02	0.213	bdl
NWCO 14-3	3.11	0.204	bdl
NWCO 14-4	bdl	0.207	bdl
NWCO 14-5	bdl	0.207	bdl
NWCO 14-6	1.55	0.197	bdl
NWCO 14-7	2.02	0.213	bdl

Table F: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Pilchuck Creek 2 (n=11)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Cl (ppm)	Mn (ppm)
NWCO 9-4	4527	151	89830	8.98	162	616
NWCO 9-5	4573	154	89310	8.93	139	624
NWCO 9-6	4111	134	91930	9.19	169	664
NWCO 14-8	3634	120	83421	8.34	bdl	715
NWCO 14-9	3819	118	83607	8.36	bdl	671
NWCO 14-10	3538	123	85002	8.50	246	627
NWCO 14-11	3471	111	84600	8.46	bdl	649
NWCO 14-12	3326	126	86769	8.67	164	638
NWCO 14-13	3358	119	87390	8.73	340	659
NWCO 14-15	4028	116	83700	8.37	100	618
NWCO 14-16	3115	124	86211	8.62	bdl	648

Sample ID	Ca (ppm)	Ca (%)	Fe (ppm)	Fe (%)	Na (ppm)	Na (%)
NWCO 9-4	33360	3.33	62956	6.29	23911	2.39
NWCO 9-5	34200	3.42	70254	7.03	23206	2.32
NWCO 9-6	37280	3.72	53960	5.39	24864	2.49
NWCO 14-8	36630	3.66	66315	6.63	23555	2.36
NWCO 14-9	34430	3.44	60027	6.00	22522	2.25
NWCO 14-10	38280	3.82	73587	7.36	22610	2.26
NWCO 14-11	33500	3.35	63418	6.34	24301	2.43
NWCO 14-12	38830	3.88	64610	6.46	23600	2.36
NWCO 14-13	35900	3.59	62108	6.21	25054	2.50
NWCO 14-15	33200	3.32	77267	7.72	24487	2.45
NWCO 14-16	39270	3.92	66941	6.69	23497	2.35

Table F: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Pilchuck Creek 2 (n=11)

Sample ID	K (ppm)	Cr (ppm)	Sc (ppm)	Zn (ppm)	Co (ppm)	As (ppm)
NWCO 9-4	10701	34.9	12.83	65.7	13.0	2.25
NWCO 9-5	10788	31.5	12.78	62.3	12.5	3.22
NWCO 9-6	13050	28.0	12.54	52.2	9.6	2.73
NWCO 14-8	12500	35.5	14.11	71.0	10.5	4.86
NWCO 14-9	11200	32.3	14.11	71.5	10.6	3.97
NWCO 14-10	10600	35.7	13.80	69.2	10.5	3.63
NWCO 14-11	10379	28.9	13.20	84.8	10.0	2.29
NWCO 14-12	10100	41.3	14.10	74.8	10.9	4.58
NWCO 14-13	9797	30.8	13.40	85.3	9.8	1.87
NWCO 14-15	9797	29.7	14.60	92.6	11.0	2.08
NWCO 14-16	nm	nm	14.20	72.0	10.6	3.52

Sample ID	Sb (ppm)	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)
NWCO 9-4	0.227	715	0.595	3.35	0.24	13.0
NWCO 9-5	0.312	401	0.672	3.70	0.35	13.5
NWCO 9-6	0.273	750	nm	3.26	bdl	13.0
NWCO 14-8	0.193	667	1.236	3.12	bdl	14.7
NWCO 14-9	0.177	640	1.009	3.54	bdl	14.0
NWCO 14-10	0.223	577	0.824	3.05	bdl	13.3
NWCO 14-11	0.4042	581	1.02	2.92	bdl	13.2
NWCO 14-12	0.1694	719	1.19	3.55	bdl	15.0
NWCO 14-13	0.1806	503	1.17	2.90	0.263	13.5
NWCO 14-15	bdl	523	0.867	3.12	bdl	13.0
NWCO 14-16	0.2156	626	1.26	3.75	bdl	14.4

Table F: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Pilchuck Creek 2 (n=11)

Sample ID	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Dy (ppm)
NWCO 9-4	28.3	15.0	3.62	1.058	0.571	bdl
NWCO 9-5	26.9	13.7	3.04	1.078	0.361	2.88
NWCO 9-6	28.8	14.1	4.63	0.84	0.356	3.85
NWCO 14-8	28.4	15.9	3.87	1.07	bdl	5.83
NWCO 14-9	30.3	13.8	3.43	1.16	bdl	4.84
NWCO 14-10	29.4	15.0	3.47	1.09	bdl	2.53
NWCO 14-11	28.0	17.8	3.27	0.9	0.465	4.56
NWCO 14-12	30.1	15.7	3.82	0.941	bdl	nm
NWCO 14-13	29.3	17.4	3.47	0.96	0.540	4.08
NWCO 14-15	28.9	19.0	3.64	0.96	0.300	3.32
NWCO 14-16	29.2	12.7	3.63	1.02	bdl	3.3

Sample ID	Yb (ppm)	Lu (ppm)	Th (ppm)
NWCO 9-4	bdl	0.290	bdl
NWCO 9-5	bdl	0.273	bdl
NWCO 9-6	bdl	0.270	bdl
NWCO 14-8	2.436	0.205	bdl
NWCO 14-9	2.562	0.198	bdl
NWCO 14-10	1.932	0.229	bdl
NWCO 14-11	1.26	0.322	bdl
NWCO 14-12	2.562	0.254	bdl
NWCO 14-13	1.86	0.281	bdl
NWCO 14-15	1.86	0.269	bdl
NWCO 14-16	2.184	0.191	bdl

Table G: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions.

Tulameen Ochre Bluffs (n=12)

Sample ID	Ti (ppm)	V (ppm)	Al (ppm)	Al (%)	Cl (ppm)	Mn (ppm)
NWCO 9-9	<500	38	1303	0.13	320	1512
NWCO 3-9	<500	27	873	0.09	222	1597
NWCO 3-10	<500	29	813	0.08	187	1309
NWCO 14-17	<700	28	1479	0.14	200	1529
NWCO 14-18	<500	33	1190	0.11	201	1683
NWCO 14-19	<500	30	1011	0.10	293	1595
NWCO 14-20	<500	31	1055	0.10	252	1782
NWCO 14-21	<500	20	780	0.08	175	1650
NWCO 14-22	<500	26	930	0.09	<120	1749
NWCO 14-23	<500	21	997	0.10	133	1562
NWCO 14-24	<700	25	925	0.09	120	1496
NWCO 14-25	<500	30	981	0.10	163	1705

Sample ID	Ca (ppm)	Ca (%)	Fe (ppm)	Fe (%)	Na (ppm)	Na (%)
NWCO 9-9	242172	24.22	154207	15.42	789	0.08
NWCO 3-9	193652	19.37	191687	19.17	523	0.05
NWCO 3-10	178879	17.89	213549	21.35	364	0.04
NWCO 14-17	187000	18.70	188752	18.87	983	0.10
NWCO 14-18	195800	19.50	188515	18.85	791	0.08
NWCO 14-19	196900	19.60	189541	18.95	751	0.08
NWCO 14-20	184800	18.40	194580	19.45	828	0.08
NWCO 14-21	271700	27.10	111361	11.13	857	0.09
NWCO 14-22	244200	24.42	139606	13.96	727	0.07
NWCO 14-23	245300	24.53	141942	14.19	770	0.08
NWCO 14-24	235400	23.54	154964	15.49	688	0.07
NWCO 14-25	213400	21.34	172131	17.21	756	0.08

Table G: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Tulameen Ochre Bluffs (n=12)

Sample ID	K (ppm)	Cr (ppm)	Sc (ppm)	Zn (ppm)	Co (ppm)	As (ppm)
NWCO 9-9	861	7.9	0.61	2.9	2.6	<6
NWCO 3-9	nm	4.6	0.55	nm	2.9	<6
NWCO 3-10	nm	6.2	bdl	nm	2.8	<6
NWCO 14-17	1760	10.5	0.76	3.6	4.0	<6
NWCO 14-18	770	7.2	0.73	3.9	3.5	<6
NWCO 14-19	1300	8.5	0.69	3.5	3.2	<6
NWCO 14-20	930	8.5	0.67	3.5	3.7	<6
NWCO 14-21	330	5.8	0.81	4.5	2.7	<9
NWCO 14-22	560	5.2	0.79	4.1	2.8	<9
NWCO 14-23	520	5.5	0.82	4.2	2.8	<9
NWCO 14-24	890	7.8	0.74	4.2	3.1	<6
NWCO 14-25	660	7.5	0.84	4.0	4.3	<6

Sample ID	Sb (ppm)	Ba (ppm)	Cs (ppm)	Hf (ppm)	Ta (ppm)	La (ppm)
NWCO 9-9	0.080	994	0.028	0.30	bdl	1.40
NWCO 3-9	0.01	nm	0	<.3	<.35	1.10
NWCO 3-10	bdl	830	0.42	0.27	<.35	1.00
NWCO 14-17	<.23	1148	<.6	0.52	<.35	1.73
NWCO 14-18	<.2	1116	<.5	<.3	<.3	1.42
NWCO 14-19	<.23	1055	<.5	0.49	<.3	1.74
NWCO 14-20	<.23	1046	<.5	0.80	<.3	1.67
NWCO 14-21	0.2926	1042	<.15	<.24	<.29	1.10
NWCO 14-22	<.27	1028	<.5	0.35	<.32	1.23
NWCO 14-23	<.25	1055	<.5	<.26	<.25	1.09
NWCO 14-24	<.26	986	<.5	0.32	<.14	1.22
NWCO 14-25	0.5082	1017	<.7	<.36	<.34	1.55

Table G: Elemental concentration data groupings for ochre outcrops as described in Table 3.1 (Appendix B). Since the time of publication, additional samples have been added to the database. Therefore, the number of samples here reflects those additions…. cont'd.

Tulameen Ochre Bluffs (n=12)

Sample ID	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Dy (ppm)
NWCO 9-9	bdl	bdl	0.25	<.15	<.35	<2.8
NWCO 3-9	bdl	bdl	0.14	<.15	<.35	<2.8
NWCO 3-10	bdl	bdl	0.13	<.15	<.3	<2.8
NWCO 14-17	3.10	bdl	0.23	0.18	<.35	<2.8
NWCO 14-18	4.33	bdl	0.21	0.16	<.3	<1.8
NWCO 14-19	2.56	bdl	0.19	0.14	<.36	<1.6
NWCO 14-20	2.36	bdl	0.21	0.173	<.36	<1.8
NWCO 14-21	<1.6	bdl	0.19	0.154	<.3	<1.9
NWCO 14-22	<1.6	bdl	0.20	0.125	<.32	<1.6
NWCO 14-23	2.52	bdl	0.20	<.15	<.3	<1.7
NWCO 14-24	2.36	bdl	0.14	<.15	<.34	<2.7
NWCO 14-25	2.95	bdl	0.25	<.15	<.4	<1.9

Sample ID	Yb (ppm)	Lu (ppm)	Th (ppm)
NWCO 9-9	<.35	<.33	bdl
NWCO 3-9	<.33	<.32	bdl
NWCO 3-10	<.33	<.33	bdl
NWCO 14-17	<.35	<.33	bdl
NWCO 14-18	<.35	<.35	bdl
NWCO 14-19	<.25	<.03	bdl
NWCO 14-20	<.35	<.03	bdl
NWCO 14-21	<.3	<.03	bdl
NWCO 14-22	<.3	<.03	bdl
NWCO 14-23	<.32	<.03	bdl
NWCO 14-24	<.3	<.03	bdl
NWCO 14-25	<.5	<.05	bdl

APPENDIX E

Table 1: List of isotopes and gamma ray energies used to determine elements and calculate concentrations of elements for neutron activation analysis data presented in Chapters 2 and 3.
*List includes all isotopes examined in preliminary analysis yet not all are presented in the final data set as they may have been deemed inconclusive, unreliable due to spectral interferences, or not present in detectable quantities.

Short-lived Radio-isotope	**Energy (keV)**
Count Day 1 (10 min)	
Co-60m	58.6
Dy-165	94.7
Ba-139	165.9
Ti-51	320.1
Sn-125m	332.1
Br-80	617
Mg-27	1014
Cu-66	1039
Na-24	1368
V-52	1434
K-42	1524
Al-28	1778
Mn-56	1810
Cl-38	2167
Ca-49	3084
Count Day 2 (24 h)	
Sm-153	103
Eu-152	122
La-140	487
Cu-64	511
Mn-56	847
Na-34	1368
K-42	1525

Long-lived Radio-isotope	**Energy (keV)**
Count Day 7-10	
Nd-147	91.1
Sm-153	103
Lu-177m	208
Cr-51	320
Th-233	459
La-140	487
Ba-131	496
As-76	559
Sb-122	564
Br-82	776
Fe-59	1099
Fe-59	1291
Na-24	1368
La-140	1596
Count Day 14-16	
Nd-147	91.1
Ce-141	145
Lu-177m	208
Yb-169	307
Hf-181	482
Cs-134	604
Tb-160	879
Sc-46	889
Fe-49	1099
Co-60	1173
Ta-182	1221
Fe-59	1291
Co-60	1332
Eu-152	1408

APPENDIX E

Table 2: List of x-rays used to calculate concentrations for elements of interest using x-ray fluorescence analysis as presented in Chapter 4.
*List includes all x-ray energies examined in preliminary analysis yet not all are presented in the final data set as they may have been deemed inconclusive, unreliable due to spectral interferences, or not present in detectable quantities.

Element and X-ray	Intensity per 100 k-shell vacancies	Energy (keV)
K K_{a1}	8.5	3.314
Ba L_{a1}	4.1	4.466
Ti K_{a1}	12.8	4.511
Ti K_{a2}	6.4	4.505
Ca K_{a1}	9.8	3.692
Ca K_{a2}	4.93	3.688
Cr K_{a1}	16.4	5.415
Cr K_{a2}	8.4	5.405
Mn K_{a1}	18.3	5.899
Mn K_{a2}	9.3	5.888
Fe K_{a1}	20.2	6.404
Fe K_{a2}	10.2	6.391
Co K_{a1}	22.1	6.930
Co K_{a2}	11.2	6.915
Ni K_{a1}	24.0	7.478
Ni K_{a2}	12.2	7.461
Cu K_{a1}	26.0	8.048
Cu K_{a2}	13.3	8.028
Zn K_{a1}	28.0	8.639
Zn K_{a2}	14.3	8.616
As K_{a1}	32.7	10.544
As K_{a2}	17.6	10.508
Rb K_{a1}	38.0	13.395
Rb K_{a2}	19.7	13.395
Sr K_{a1}	39.1	14.165
Sr K_{a2}	20.3	14.098
Zr K_{a1}	41.0	15.775
Zr K_{a2}	21.4	15.691
Pb $L1_{a1}$	12.8	10.551

APPENDIX F

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