A COMBINED VISUAL-GEOCHEMICAL APPROACH TO ESTABLISHING PROVENANCE FOR PEGMATITE QUARTZ ARTIFACTS AND APPLICATION WITHIN THE CHURCHILL RIVER BASIN OF MANITOBA AND SASKATCHEWAN

by

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Abstract

This dissertation aims to provide insight into the relationships between environmental factors and the organization of quartz technology in northern Manitoba by evaluating the contribution of large pegmatite quarries to quartz economies around Granville and Southern Indian Lakes. Secondary ion mass spectrometry (SIMS) quantification of trace element (Ti, Ge, U, Th) concentrations and Pb isotope ratios was used to characterize large sources of pegmatite quartz exploited by toolmakers in the Granville Lake and Lac La Ronge regions of northern Manitoba and Saskatchewan, respectively. The same technique was applied to a sample of formal quartz tools from the Churchill River Diversion Archaeological Project (CRDAP) study area in northern Manitoba. Quarry and artifact results were compared. The results of this analysis indicate: 1) characterized pegmatite quartz sources in the Granville Lake district likely played a significant role in quartz economies in the Churchill River basin of northern Manitoba, 2) toolmakers in the study area had large lithic procurement ranges, and 3) lithic resource stress contributed to the selection of technological strategies in the Churchill River basin.

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For Mum.

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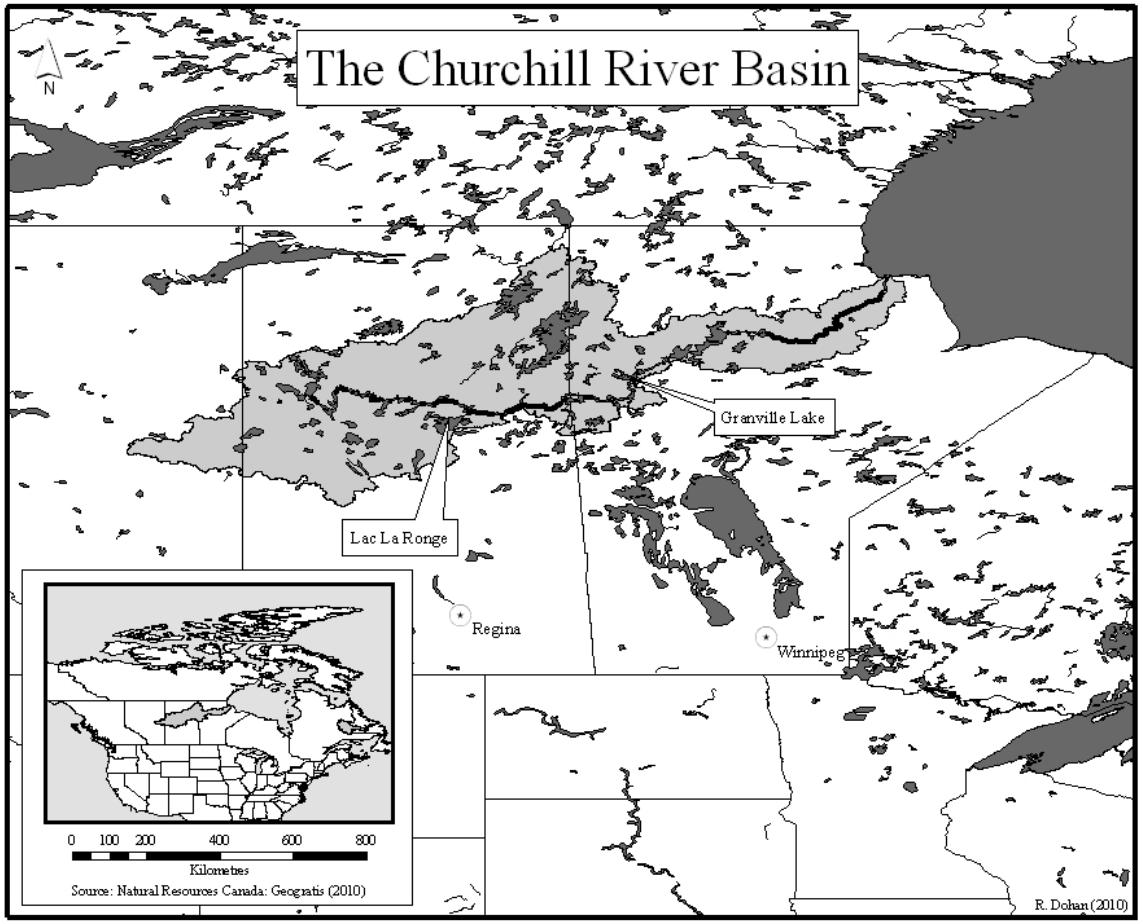
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1.0 Introduction

1.1 Research questions and objectives

My doctoral research consists of a raw material provenance study of pegmatite quartz from the Churchill River basin of northern Manitoba and Saskatchewan (see Map 1.1). This research consisted of two main parts: the development of a characterization technique capable of discriminating between pegmatite quartz from different identified quarries in the study area, and the application of this technique to a suite of quartz artifacts recovered from archaeological sites in the study area. The first part of this research relied on the identification of physical and/or geochemical parameters that could be used to distinguish between material from different archaeologically exploited sources of pegmatite quartz. The second part focused on clarifying the contribution of quartz from analyzed quarries to lithic toolkits in the study area, the relationship between environmental and social variables, and the selection of technological strategies in the Churchill River basin.

The archaeometric study of lithic raw materials constitutes something of a 'boom industry' within archaeology (Shackley 2008:197-196). Analysis of lithic raw materials to assign source provenance constitutes one of the flourishing subfields of this rapidly expanding area of research. In their simplest form, lithic raw material studies consist of the identification of physical and/or chemical variables that vary detectably between archaeologically exploited material sources. Using samples from identified material sources, a database of source signatures is built. Analysis of these variables is then applied to a sample of artifacts made from the same raw material in order to assign source provenance. Early raw material provenance studies relied upon identification of



Map 1.1 The Churchill River basin depicted in grey with Lac La Ronge and Granville Lake locales indicated

macroscopic, microscopic, or visual characteristics of lithic material for source characterization (e.g. Frankfort, 1927; Castiglioni *et al.,* 1963). These approaches are only appropriate for characterizing a few materials, however, and lithic provenance studies could only be applied in the limited contexts where these materials were present until the early 1960s, when improvements to instrumentation made characterization of a broad range of materials based on geochemical parameters possible (Tykot, 2004:408). Continued advancements in instrumentation have resulted in development of more reliable provenance techniques for an impressive list of archaeological raw materials, including different types of toolstone.

However, a reliable technique for accurately establishing source provenance for quartz artifacts has not been previously developed. This is likely a result of material properties that make establishing quartz provenance difficult. As with most other lithic materials, macroscopic analysis is not a viable provenance indicator for quartz. Some macroscopically observable variability exists between different color categories of quartz, including amethyst, citrine, and smoky, rose, colorless, and white quartz (Lehmann and Bambauer, 2003). Grain size and the presence/absence of other mineral inclusions can also vary between samples of quartz (Meighan *et al.,* 2003; Ballin, 2008:43-44). However, visual heterogeneity within quarried sources of quartz, as well as homogeneity *between* sources precludes use of visual characterization as a stand-alone provenance indicator for quartz in most contexts, including the study area of this dissertation (ten Bruggencate *et al.,* 2013). Macroscopic visual analysis is primarily useful as a tool for sorting quartz into broad geological and colour categories, which could aid in the interpretation of other forms of provenance data.

Petrographic analysis is also a useful tool for characterizing quartz samples and detecting microscale anomalies, including mineral and fluid inclusions and secondary crystal formation that might impact geochemical data (e.g. Dong et al, 1995; ten Bruggencate and Fayek, 2013). However, on its own, petrographic analysis is not a suitable technique for establishing quartz raw material provenance in most contexts. In some cases, quartz may be free of mineral inclusions and samples may appear microscopically identical (Götze *et al.*, 2005). In other cases, the relationship between parameters of quartz formation and petrographic appearance is not exact enough to allow it to act as a reliable provenance indicator, as a range of conditions can produce microscopically similar samples (Dong *et al.*, 2005), meaning that provenance information supplied by this type of analysis would likely not be fine-scaled enough to be relevant to developing resource procurement models.

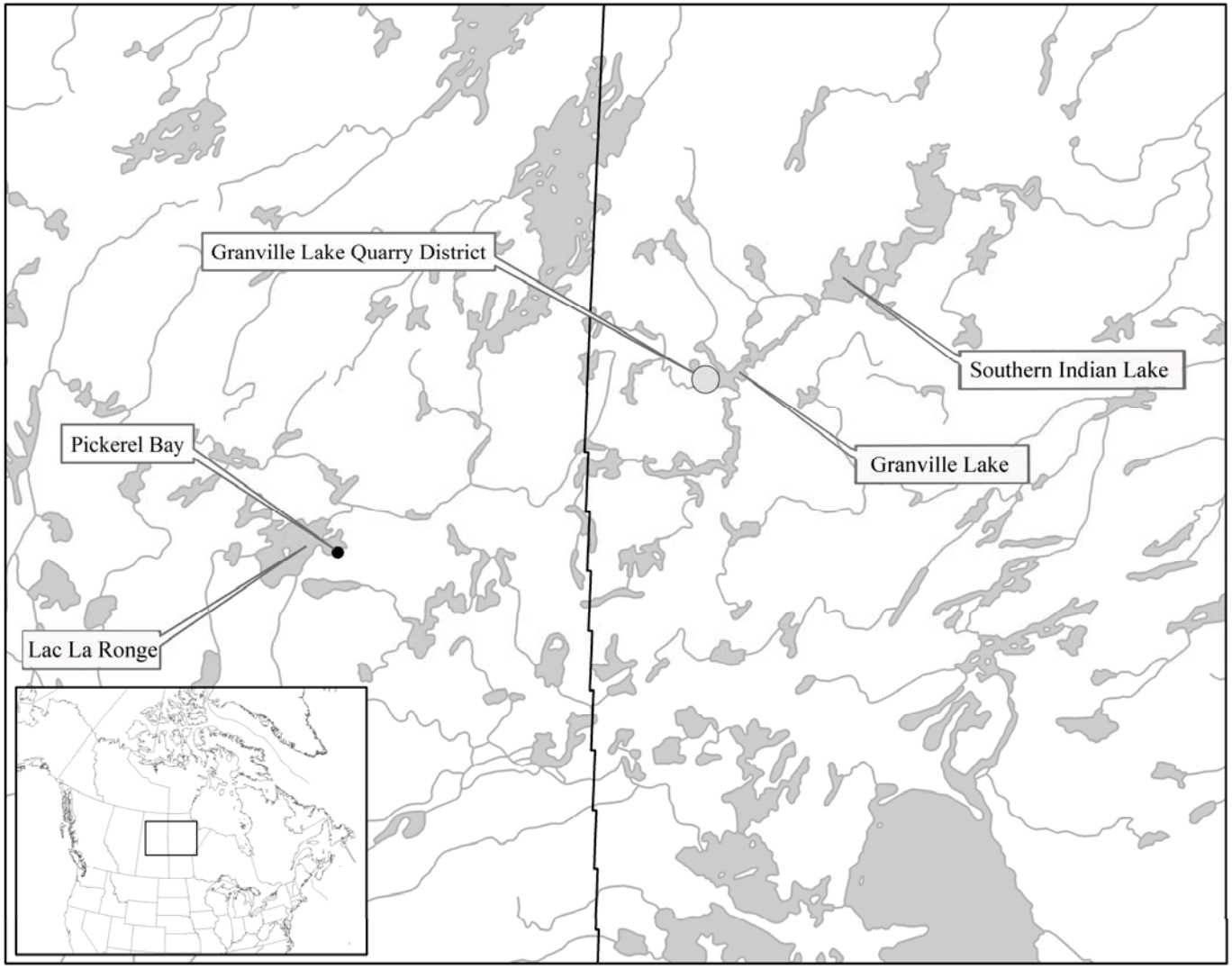
Geochemical characterization of archaeologically exploited quartz sources is also difficult, owing to its chemical structure. Composed of interlocked helices of silicon-oxygen tetrahedra, quartz admits very few trace element impurities (Müller *et al.*, 2003; Götze, 2009) – which are integral to source characterization of other lithic materials. Trace elements that are present in quartz tend to be concentrated at levels difficult to accurately measure with all but the most sensitive equipment. However, geochemical studies have successfully reconstructed quartz provenance on a fine scale (e.g. Larsen *et al.*, 2004), and results of other studies indicate that concentrations of some trace elements in quartz may be sensitive to formation parameters in a way that would result in detectable intersource variability (e.g. Wark and Watson, 2006). This research demonstrates that quantification of some trace element constituents of quartz may be

useful for reconstructing material provenance on a fine enough scale to be of use to archaeologists trying to distinguish between exploited sources in a region. This dissertation takes its inspiration from this literature, as well as geological Pb-isotope provenance studies of quartz (e.g. Hemming *et al.*, 1994) to formulate a characterization technique for pegmatite quartz quarries in the Churchill River basin of northern Manitoba and Saskatchewan.

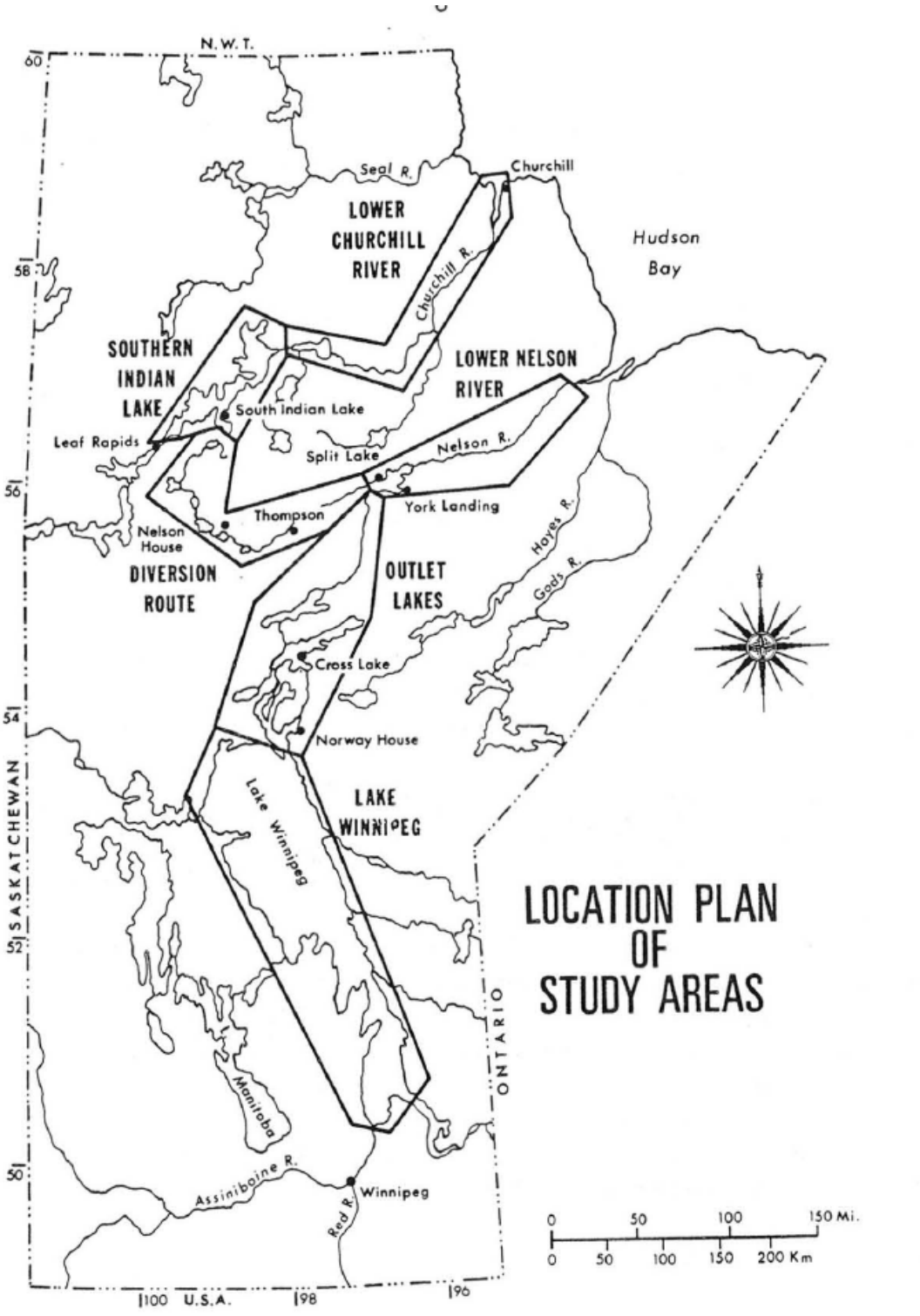
The application phase of this research consists of geochemical provenance analysis of a selection of quartz artifacts, primarily recovered from shoreline sites around Southern Indian Lake. The quarry database to which artifact results are compared was formed through technique development using quartz samples from quarries in the Granville Lake and Pickerel Bay regions of the Churchill River basin. Very little is understood about the organization of lithic technology in the Churchill River basin, including the effects of environmental and social factors, like raw material availability and group mobility, on the selection of technological strategies during raw material procurement and tool manufacture, use, and discard. Quarry samples used during the technique development phase of my research were obtained as part of the Granville Lake quarries project, which was aimed, in part, at clarifying the role of large quartz quarries made known to archaeologists by community members in 2006. Characterization of quarries in the Granville Lake quarry district was a stated goal of the project, as it would demonstrate their contribution to local lithic industries. The collaboration of Dr. Margaret Hanna of the Royal Saskatchewan Museum on the project led to the inclusion of samples from quartz quarries in the Pickerel Bay vicinity of Lac La Ronge, SK in the

quarry sample set, to serve as an indicator of the utility of tested techniques for characterization of sources separated by long distances (see Map 1.2).

Few habitation sites have been surveyed or excavated in the vicinity of the Granville Lake quarries, meaning that a quartz assemblage for comparison to the Granville Lake quarries material had to be obtained elsewhere. Quartz tools collected in the Southern Indian Lake region of the Churchill River basin through the Churchill River Diversion Archaeological Project (CRDAP) were ultimately selected (see Map 1.2), as this constitutes the largest and best documented collection of quartz artifacts from the Churchill River basin. Several interesting hypotheses can be tested through a provenance analysis of these artifacts, especially in light of the distance between the sites from which they were recovered and the quarry areas making up the source database. Identification of artifacts with chemical signatures matching material procured at the Granville Lake or Pickerel Bay quarries, hundreds of kilometers away from their source would imply a high degree of mobility or large intergroup exchange networks in an area where mobility and/or exchange patterns remain poorly understood. Furthermore, by restricting provenance analysis to certain types of artifacts (in this case, formal tool classes), untested hypotheses related to the impact of material availability on technological strategy selection in the Churchill River basin can be evaluated. For example, archaeologists classify quartz as a difficult to reduce raw material with moderate qualities for tool manufacture (Reher and Frison, 1991; Rankama *et al*., 2006) This type of material would likely only be incorporated into formal toolkits curated over large distances in situations of lithic resource stress, where sources of higher quality raw material were unavailable. Determining the extent to which the sampled quarries



Map 1.2: Map of the study area for this dissertation showing locations discussed in the text



Map 1.3: Study areas of the CRDAP. All sites providing artifacts for this study are located in the Southern Indian Lake study area of the CRDAP (reproduced with permission from Kroker, 1990:8).

contributed to the CRDAP quartz assemblage will allow me to approach questions regarding resource availability and raw material selection strategies in the study area.

1.2 The organization of the dissertation.

This dissertation begins with a review of three major areas of scholarship that form the background to my research (Chapters 2-4). The first of these consists of the geographic and archaeological context of the study area – the Churchill River basin of northern Saskatchewan and Manitoba. An introduction of the study area consists of a brief summary of the geography and ecology of the Churchill River basin, followed by a review of the history of archaeological research carried out in the region. Following this, the cultural chronology of the Churchill River basin of Manitoba and Saskatchewan as it is currently understood is described from recoveries made through the course of archaeological investigations in the area and the challenges faced by archaeologists attempting to go beyond culture history in analysis of assemblages in the region.

Raw material provenance analysis is reviewed in Chapter 3. Physical techniques – including macroscopic and microscopic visual analysis – applied to establish lithic raw material provenance are briefly described and illustrated by examples. Geochemical characterization techniques – including trace element and O and Pb stable isotope analysis – are discussed next, again, with examples from current literature to serve as illustration of these techniques' strengths and limitations. The dissertation will then move to a discussion of the geochemistry of quartz, and how this bears on the feasibility of different trace element and isotope systems for characterization of different types of

quartz sources. This is followed by a brief discussion of the exploitation of different quartz sources by toolmakers in the Churchill River basin.

The final component of this review will consist of a discussion of the organization of technology approach to interpretation of geochemical provenance data (Chapter 4). First, I will discuss the relationship between material availability – which subsumes both raw material quality and abundance - and technological strategy selection during different stages of tool use lives, from procurement to discard. Then, I briefly describe the role of provenance studies in reconstructing other facets of social organization related to material procurement, including mobility and exchange. This is followed by a discussion of the qualities of quartz as a raw material for tool manufacture, and archaeologists' current understanding of the organization of quartz technology in the study area.

Chapter 5 summarizes the materials and methods utilized in the course of my dissertation research. First, I discuss the quarries sampled to develop a characterization technique for pegmatite quartz, which also make up the source database to which artifacts were compared. The different sources selected for this study, and how they were sampled over the course of the 2007 and 2009 field seasons are presented at the beginning of Chapter 5. This is followed by a discussion of archaeological sites providing artifact samples for my research. Each site is briefly described, using information obtained from published site reports and unpublished records forms filed at the Manitoba Museum. In Chapter 6, I move into a discussion of the different sampling techniques I employed to obtain my quarry and artifact samples. This is followed by a discussion of the techniques used to obtain quantitative and qualitative chemical data from quartz samples. This chapter provides the reader with basic theory underlying the

function of these instruments, as well as the strengths and limitations that govern their proper use for material characterization.

Chapter 7 includes the interpretive ramifications of different potential outcomes of provenance analysis carried out through my dissertation research, given the relationship between provenance data, mobility and/or exchange, and adopted technological strategies.

The results of geochemical assays carried out using this instrumentation is discussed in Chapter 8. The results of analyses with negative outcomes – i.e. analyses that did not result in development of a reliable characterization technique for pegmatite quartz – are discussed first. This is followed by a discussion of the results of successful quarry characterization through quantification of Ti, Ge, Th, U and Pb isotope ratios. Trace element and Pb isotope results for artifacts, and their relationship to quarry results are presented.

In Chapter 8 non-productive methods are discussed in terms of the potential theoretical or practical causes of their failure. This is followed by a discussion, explaining the efficacy of the trace element and Pb-isotope quantification underlying the successful characterization technique. The next section of this chapter consists of a discussion of the implication of artifact results, relative to quarry results for archaeological interpretation of patterns of technological and social organization in the Churchill River basin. First, the implications of both negative and positive provenance assignments at different sites for reconstruction of mobility and/or exchange within the basin are discussed. The probable relationships between provenance results and environmental factors, including the quality and abundance, follows thereafter.

The final chapter (Chapter 9) presents my conclusions and a brief description of future goals for my research. Detailed data sets are presented as appendices at the end of the dissertation.

2.0 The Churchill River basin

2.1 Environment

The Churchill River basin comprises 281,300km^2 of land drained by the Churchill River (Cree: *Missinipi*. Literally: "big water"). The Churchill River rises from headwaters in the Lac La Biche area of east-central Alberta and flows in a roughly east-west direction across north-central Saskatchewan and northern Manitoba before draining into Hudson Bay (Edye-Rowntree, 2007:1). The Churchill River's headwaters are located among the dense boreal forest and thick soils of the Boreal Plains ecozone, while its drainage lies in the costal tundra of the northern Hudson Plains. For the majority of its course, however, the Churchill River flows through the Boreal Shield, where boreal forest flora overlies the Precambrian metasedimentary rock and granites of the Canadian Shield. Much of the Churchill River basin, including the Pickerel Bay and Granville Lake quarries, and most of the archaeological sites that make up the study area of this dissertation, is subsumed within this ecozone.

The climate of the Churchill River basin today can be broadly classified as cool to cold continental (Beke *et al.*, 1973; Kroker, 1990). Winters in all portions of the basin are long and cold, with January mean temperatures ranging from -25°C to -30°C (Rowe, 1972; Kroker, 1990:27; Rosenberg *et al.*, 2005:857). Summers are short and cool to warm, with July mean temperatures ranging from 15°C to 25°C (Kroker, 1990; Rosenberg *et al.*, 2005:857). The climate of the Churchill River basin is moist sub-humid, with annual rainfall in the driest districts averaging around 400mm, of which, about one quarter to one third falls as snow (Beke *et al.*, 1973; Kroker, 1990: 27; Rosenberg *et al*, 2005).

Overall, boreal forest flora is dominant within the Churchill River basin. Areas of the basin surrounding the uppermost portions of the Churchill River fall within the upper Churchill Section of the boreal forest, which lies between the Mixed Woods Section to the south and the Northern Coniferous Section to the north (Rowe, 1972; Harms, 1995:5). The forests of the upper Churchill are dominated by jack pine stands on upland plains and low ridges. White spruce, aspen, and balsam poplar are more sparsely distributed and characteristic of less exposed, thick-soiled areas (Harms, 1995:5). Poorly drained, lowland portions of the upper Churchill Section of the boreal forest host stands of black spruce or form open muskeg bogs (Harms, 1995:5).

As the Churchill bends northward into the Northern Coniferous boreal forest, closed stands of black spruce begin to dominate the arboreal vegetation of the basin, while in well-drained areas along river banks, lake shores and on islands, stands of white birch, white spruce, trembling aspen and balsam fir are more common (Harms, 1995:5: Kroker, 1990:28). Northern portions of the Churchill River basin surrounding the lower Churchill River are situated within the Northern Transitional Section of the boreal forest (Rowe, 1972; Kroker, 1990: 28). In this area, discontinuous permafrost and lower mean temperatures have shaped the forest into a much more open, parkland environment, dominated by stands of the same tree species making up the Northern Coniferous Section (Kroker, 1990:28). Finally, the Hudson Bay lowlands surrounding the terminal Churchill River are largely characterized by treeless tundra.

Non-arboreal plant species abound within the Churchill River basin. Many of these species were – and continue to be – utilized by populations in the area alongside arboreal by-products for medicine, construction and subsistence (Leighton, 1995). These

include a number of berry-producing species, mosses, lichens, fungi, ferns, shrubs and grasses (Hanna, 1975: 65-67; Kroker, 1990: 28-29; Leighton, 1995).

The different forest zones within which the Churchill River basin lies are host to a variety of mammal and bird species. Among the former, moose, mule deer, woodland caribou, bear, wolf, beaver, wolverine, hare and a number of other small furbearers are common throughout the different microenvironments of the Churchill River basin, while the winter migration of the Kaminuriak barren-ground caribou herd sometimes places them within the northern portions of the Churchill River basin, although this is becoming increasingly rare (Kroker, 1990: 29-30). A wide variety of bird species are present within the Churchill River basin, including raptors, waterfowl, and songbirds (Kroker, 1990: 31-33: Bortolli *et al.,* 1995). Both migratory and resident bird species occur within the Churchill River basin.

Fish are plentiful throughout the lakes of the Churchill River basin and are especially abundant within the lower portion of river itself after Frog Portage, SK, at which point the Churchill River expands to form a chain of large, deep lakes including High Rock, Granville, Opachaunau and Southern Indian lakes. Within these lakes, common large species of fish include lake whitefish, northern pike/jackfish, walleye/pickerel, sucker, burbot, sauger, and goldeye (Kroker, 1990:34; Maher, 1995:49). Smaller fish present in the Churchill River basin include several species of minnow, sculpin, darter, and stickleback (Kroker, 1990: 34; Maher, 1995: 49).

Biotic resources are not distributed evenly within the Churchill River basin, and the availability of subsistence resources in the region can fluctuate drastically in annual or longer-term cycles. For some species, these cycles are predictable, for others they are

influenced by so many variables as to be almost random (Waisberg, 1975). In spite of this periodicity, which can lead to periods of resource scarcity (Brightman,1983:246), as well as the climate of the Churchill River basin, which scholars characterize as harsh or marginal, some areas of the basin have been home to human populations for approximately 8000 years (Meyer, 1995; Malaskiuk, 2001: 110, 138). Since this initial occupation, humans have resided either seasonally or year-round in the basin until the present day (Kroker, 1990:149; Meyer, 1995; Linklater, 1997:6; Pentney, 2002:122)

2.2. History of archaeological exploration

Prior to the late 1960s, archaeological exploration in the Churchill River basin was extremely limited. In the Manitoba portion of the Churchill River basin, the earliest recorded archaeological recoveries were made by members of the Geological Survey of Canada (Bell, 1879; Kroker, 1990:35). American schoolteacher, author and adventurer P.G. Downes also surveyed areas of the Churchill River basin within Manitoba and surface-collected ceramics from the Reindeer Lake area of the basin (Downes, 1938). During the late 1940s and 1950s, Walter Hlady (1971), assisted by a team of amateur archaeologists carried out intensive surveys throughout northern Manitoba, including some areas within the Churchill River basin (Kroker, 1990: 36). Recoveries made through these excavations reversed the prevailing notion that the Churchill River basin had only been sparsely and intermittently populated prior to contact between Europeans and First Nations (Hlady, 1971:3).

In the upper Churchill River basin of Saskatchewan, early archaeological research was even more limited. Artifact recoveries were made at Frog Portage, a historically

important portage route linking the Churchill River system to the Saskatchewan River, by Harry Moody, an amateur archaeologist from the Flin Flon area (Meyer, 1995: 52). These recoveries were improperly documented, however, and made only a vague contribution to the reconstruction of culture history in the area (Meyer, 1995:52).

During the 1960s, archaeological interest in the Churchill River basin intensified dramatically. Notable archaeologists William Mayer-Oakes, Ronald Nash (1969; 1975) and J.V. Wright (1971) conducted surveys in the Cedar Lake, Tailrace Bay, Southern Indian Lake, and Churchill River regions of northern Manitoba (Hlady, 1971; Kroker, 1990:36-37). This work resulted in some of the first culture historical classifications of archaeological material in the Canadian subarctic (Wright, 1971; 1972a). However, the bulk of archaeological data supporting currently projected culture sequences and land-use models in the Churchill River basin was not produced by academic investigation.

During the late 1960s, energy corporations set plans in motion to harness the previously untapped hydroelectric potential of Canada's northern river systems, particularly those of the Churchill and Nelson. Projects were designed to divert and dam rivers throughout northern Manitoba and Saskatchewan to generate electricity for growing southern markets. Under the heritage legislation of both provinces, archaeological mitigation of the huge tracts of land to be inundated or otherwise affected by these hydroelectric projects had to occur before construction could take place (Kroker, 1990:14; Linklater, 1994:48).

In 1966, Manitoba Hydro obtained permission from the province of Manitoba to enhance the hydroelectric potential of the Nelson River by diverting flow from the Churchill River through the Rat-Burntwood River system in what came to be known as

the Churchill River Diversion Project (Kroker, 1990:7-13). The massive impact that water level fluctuations resulting from this project would have on shoreline archaeological resources on the lower Churchill, Rat and Burntwood Rivers was acknowledged by Manitoba Hydro and the Province of Manitoba (Kroker, 1990:14). A six-year archaeological project aimed at mitigating these effects through survey and excavation in the area of the Rat-Burntwood system, South Indian Lake and Opachaunau Lake was carried out from 1969-1975. The Churchill River Diversion Archaeological Project (CRDAP) was renewed in 1990 when burials began to erode out of the disturbed shoreline of South Indian Lake (Riddle, 2000; Speidel and Syms, 2000; Malasiuk, 2001). The project continues today, though with fewer staff and less emphasis on excavation than the research carried out in the 1970s. Materials recovered through the CRDAP form the bulk of archaeological materials recovered from any portion of the Churchill River basin and are the foundation upon which archaeological understanding of culture chronologies and land use in the lower Churchill River basin are based.

The proposed construction of the Wintego Rapids hydroelectric installation resulted in the largest archaeological survey of the Churchill River in Saskatchewan (Meyer, 1995:53). During the summers of 1973 and 1974, survey was carried out along areas of the Churchill River that would be affected by the proposed installation – which did not proceed due to public opposition. Three hundred and thirty-three sites were identified and one site, the Trade Lake site, was intensively excavated (Meyer and Smailes, 1975; Pentney, 2002: 24) during this two-year project. Further archaeological research in the Churchill River basin of Saskatchewan was directed during the 1980s by Meyer at Snake Rapids and Frog Portage (Meyer *et al.*, 1981), by Brumbach in the

Patuanak region (Brumbach *et al.*, 1982), and by Wilson and Light (1980) around Lac La Ronge. This later research was carried out under the auspices of academic institutions or Saskatchewan's Ministry of Tourism, Parks, Culture and Sport (Meyer, 1995: 53; Pentney, 2002: 23-24).

By the early 1990s, archaeologists began to synthesize archaeological data collected from sites in the Churchill River basin with ethnographic information collected during the early Fur Trade and first half of the twentieth century to form cultural chronologies and models of land use in the area (Kroker, 1990: 145-163; Meyer, 1995: 55-57). Assemblages recovered from the Churchill River basin through the course of more recent projects, such as the renewed CRDAP, are generally categorized and interpreted using chronologies and land-use models developed at this time (Linklater, 1997; Speidel and Syms, 2000; Malasiuk, 2001; Pentney, 2002).

While these chronologies and land use models are sometimes advanced as factual and complete, it is important to remember that they are based on a relatively small sample of materials, considering the size of the area and temporal depth of occupation they represent. The Churchill River basin has by no means been completely surveyed. Significant portions of it have yet to be archaeologically investigated, while most identified sites have not been subjected to subsurface excavation (Meyer, 1995:53-54). Further, most archaeological work in the basin has been carried out to mitigate the effects of hydroelectric development (e.g. Meyer and Smailes, 1975; Dickson, 1975; 1980; 1983; Hanna, 1975; Kroker, 1990; Malasiuk, 2001). Because these effects are most profound along the shorelines of rivers and lakes, inland survey in the Churchill River basin has been extremely limited. Aspects of land use that may take place away from large bodies

of water, such as winter hunting and trapping, may be underrepresented in these archaeological samples.

The formulation of cultural chronologies from assemblages recovered in the Churchill River basin is further hampered by the lack of stratigraphy of most sites in the region. Thousands of years of material culture is preserved within only a few centimetres of soil at many sites, making the task of assigning material culture types to different temporal phases based on stratification difficult, and in some cases, impossible (Meyer, 1995:54). Because of this, the organization of cultural chronologies for the Churchill River basin borrow much from those proposed for nearby portions of the plains, parkland and subarctic.

Reconstruction of cultural chronologies, and diachronic shifts in past social and economic behaviour is also stymied by the acidity of boreal forest soils, which can dissolve organic remains within mere decades (Meyer, 1995:54). Faunal remains, which are crucial to reconstructing subsistence, and bone tools which may have been used for resource procurement activities such as fishing, clothing manufacture and plant procurement are absent from most sites of any antiquity in the Churchill River basin, although exceptions occur (see: Dickson, 1975:69). Where radiocarbon dating has been carried out in the Churchill River basin, however, collapsed stratigraphy often prevents researchers from associating dated features with cultural material in other parts of the site.

Contrary to Wright's (1968) suggestion that the boreal forest constitutes a relatively homogenous culture area, review of archaeological data from different parts of the Churchill River basin suggests a degree of east-west cultural variability throughout

human occupation of this part of the boreal forest. This variability seems to be related to differences in climate and ecology between the upper and lower Churchill River basin, and was heightened by the influence of different neighbouring culture groups. Generally, assemblages from the upper Churchill tend to exhibit stronger ties to materials produced by parkland, plains and barrenland-adapted groups (Meyer, 1995). Assemblages recovered from the lower Churchill tend to share similarities with material culture produced by other boreal forest groups, although some interaction with plains and northern groups also occurred in this region, especially during the early Archaic period (Kroker, 1990:147; Malasiuk, 2001:66, 138).

2.3 Culture History

2.3.1 The Palaeo period (8000-7000BP)

After deglaciation 10,000 years ago, the upper Churchill River basin was exposed as dry land, and quickly colonized by spruce forest (Ritchie, 1976:1805). At this time, the lower Churchill River basin was submerged beneath Lake Agassiz. There is no evidence for human occupation of any portion of the Churchill River basin until 8000-7500 before present (BP). At this point, the spruce forest of the upper Churchill had changed into mixed boreal forest with stands of deciduous parkland (Meyer, 1995: 54; Ritchie, 1976:1811), while the lower Churchill was slowly emerging from beneath Lake Agassiz. The open parklands of the upper Churchill would have been ideal winter habitat for the plains bison known to have been present to the south of the basin, and this is what Meyer (1995: 54-55) hypothesizes attracted Palaeo groups to the area during this period. Evidence for Palaeo occupation of the upper Churchill River basin was recovered at

Buffalo Narrows and Besnard Lake, SK in the form of two characteristic lanceolate spear points (Meyer, 1995: 55).

Material remains indicative of occupation during this early period are also present, though more sparsely distributed in the lower Churchill River region. One lanceolate projectile point attributed to the Northern Plano Agate Basin tradition, produced by nomadic caribou hunters who lived in the barren lands and northern forests of the Northwest Territories, Nunavut, Saskatchewan and Manitoba between 8000 and 7000 years ago, was recovered from the Wapisu Lake area of the lower Churchill River basin (Malasiuk, 2001: 110). It is hypothesized that this artefact may represent a very early, transient incursion by mobile big game hunters attracted into the area by caribou herds skirting the retreating edge of glacial Lake Agassiz (Malasiuk, 2001:138). The scanty distribution of Palaeo materials in the Churchill River basin is either an artifact of poor preservation of these older materials, or indicates that people did not make intensive or long-term use of the area at this time (Kroker, 1990: 150; Meyer, 1995: Malasiuk, 2001:137).

2.3.2 The Archaic Period (7000-2000BP)

More permanent occupation of the upper Churchill River basin appears to have commenced sometime between 7000-5500 years ago (Meyer, 1995: 55). At this point, the population of the upper Churchill seems to have consisted of Plains Archaic groups – or groups heavily influenced by Plains Archaic culture – represented in the archaeological record by Early Side-Notched, Oxbow, and McKean projectile points and associated assemblages of other lithic tools (Meyer, 1995: 57; Pentney, 2002: 21). These

materials are more densely distributed within the upper Churchill than those associated with earlier Palaeo peoples, leading archaeologists to hypothesize that Plains Archaic occupation of the area was more stable, though these groups are still characterized as highly mobile, and likely were not year-round residents of the boreal forest (Kroker, 1990: 151). Plains and parkland Archaic material culture has also been recovered from the South Indian-Opachaunau Lakes region of the lower Churchill River basin, however, this material is more sparsely distributed, and is largely absent by 3000BP (Hanna, 1975; Kroker, 1990: 150-151).

By about 3200 years ago, vegetation in both the upper and lower Churchill River basin was similar to that of the present day (Ritchie, 1976: 1803; Kroker, 1990: 28; Meyer, 1995:55), and Plains influences on material culture assemblages in both areas begins to diminish (Meyer, 1983:159). In the upper Churchill River basin, Plains and Parkland Archaic groups are still represented by scattered finds of Hanna and Pelican Lake projectile points (Meyer, 1995: 55). However, by about 3000 years ago, assemblages in the area are dominated by material remains attributed to the Taltheilei, a culture group identified as the ancestors of the *Denesuliné*, who continue to live in northern and western portions of the basin today. Material culture recognized as diagnostic of Taltheilei occupation includes distinctive stemmed, diamond-shaped or lanceolate projectile points (Meyer, 1995:36; Malasiuk, 2001:20). Those recovered in the Churchill River basin are often manufactured from what is assumed to be local quartz, although chert and shale were also exploited by these groups (Meyer and Smailes, 1975:59; Dickson, 1980: 93; Pentney, 2002:70, 72).

The *Denesuliné* were historically identified as migratory barrenground caribou hunters, to the point that other Dene groups refer to them as *Et-en-eldili-dene* (literally: caribou-eater Dene) (Janes, 1973: 41). It is likely that similar subsistence strategies were pursued by the early ancestors of the *Denesuliné*; geographic distributions of material culture associated with Taltheilei occupations closely follow projected subarctic distributions of barrenground caribou (Malasiuk, 2001: 20-22; Pentney, 2002:69). It is probable that pursuit of the Kaminuriak barrenground caribou herd into its southern wintering ground, which used to overlap with the northern border of the Churchill River basin around Lake Athabasca and Reindeer Lake, is what brought Taltheilei groups into the area (Pentney, 2002: 68). Taltheilei sites are well known among subarctic archaeologists for being ephemeral, a trait which archaeologists often associate with high residential mobility (Pentney, 2002: 68).

Taltheilei material culture also appears throughout the lower portions of the Churchill River basin, especially in northern areas surrounding South Indian Lake, which have also been known to fall within the winter range of the Kaminuriak herd (Dickson, 1980:93; Kroker, 1990: 154). However, the presence of Taltheilei groups appears to have been much more restricted in this part of the basin. With the exception of northern portions of the South Indian Lake area, assemblages recovered from the lower Churchill River basin are largely dominated by materials attributed to Shield Archaic peoples by ~3000BP (Dickson, 1980:88; Kroker, 1990:151-152).

The Shield Archaic was first formulated by Wright (1972a) as the material culture signature of culturally homogenous groups of mobile hunter-gatherers whose territories stretched from the Kivaliq district of Nunavut through the boreal forests of Manitoba,

Ontario and Quebec to Labrador from 6000-2000BP. Wright (1972a) defined Shield Archaic assemblages as dominated by flaked stone knives, scrapers, small, side-notched points and, in heavily forested regions, large flaked adzes, and lacking the ground stone tools present in assemblages produced by neighbouring groups. The validity of this material culture categorization – which was originally based on a sample of only 800 artifacts from a few, mostly undated sites spread over most of the Canadian Shield – and the degree to which it represents the archaeological remains of a single cultural group has come under severe and justified criticism (Buchner, 1979; Hanna, 1980). More recent cultural chronologies treat the Shield Archaic more as a loosely similar, broadly distributed group of material culture signatures produced by potentially related groups practicing similar, boreal forest adapted subsistence and mobility strategies (Hanna, 1980; Kroker, 1990:152). This rather cautious framing is more appropriate than Wright's (1972a) confident categorization, given the sparse distribution and poorly understood chronology of these materials. Additionally, there is a degree of variability exhibited by some materials attributed to the Shield Archaic, especially in areas on the 'fringe' of Wright's (1972) defined distribution of this material culture signature, this suggests that regional variants of the Shield Archaic tradition may have developed through interaction with surrounding, economically and technologically different, groups. For example, lithic assemblages identified as Shield Archaic in the lower Churchill River basin do resemble materials from Shield Archaic sites as far away as the Northwest Territories, leading both Wright (1972:87) and Dickson (1980:148) to suggest that they were brought to the area by people migrating south into the Churchill River basin. However, other materials also assigned to the Shield Archaic in the lower Churchill area exhibit stylistic

similarities to earlier material culture assemblages recovered from the area identified as Plains and Parkland Archaic (e.g. Hanna, 1975: 26). This leads Kroker (1990: 151-152) to suggest that, in this area at least, some Shield Archaic assemblages may have been produced by the descendents of plains or parkland adapted peoples who altered their economy and technology to better address ecological changes associated with the development of the boreal forest, possibly with influence from other, more northern shield-adapted groups.

Shield Archaic groups occupying the lower Churchill River basin are thought to have been year-round residents of the boreal forest, unlike earlier groups who may only have come into the area seasonally (Kroker, 1990: 152). Caribou, moose and deer are present in faunal assemblages associated with Shield Archaic materials in the lower Churchill River basin (Kroker, 1990:152). Based on the recovery of elaborate, well-made bone and antler harpoon heads from the Shield Archaic Victoria Day burial, located near Threepoint Lake, MB, fishing also appears to have been important (Brownlee, 2006:65). These groups are thought to have pursued a relatively diversified subsistence strategy, consistent with adaptation to a resource-diverse forest environment (Cleland, 1976), involving extensive fishing as well as hunting. The scanty distribution, poor chronology of Shield Archaic materials in the lower Churchill River basin, as well as the lack of preserved faunal remains conclusively associated with Shield Archaic occupations prevents more firm conclusions regarding land use and resource procurement from being drawn at this point.

Throughout the later part of the period during which Shield Archaic materials dominate assemblages in the lower Churchill area, isolated recoveries of Hanna and

Pelican Lake projectile points more consistent with material culture from southern plains and parkland sites indicate that there may have been some contact between boreal forest groups and their southern neighbours (Kroker, 1990: 153). However, whether this material arrived in the boreal forest through trade or through northern travel on the part of southern groups is currently unknown.

2.3.3 The Arctic Small Tool tradition (ASTt)

The Arctic Small Tool tradition (ASTt) is a term used to describe a lithic tradition originating in Siberia that spread rapidly through Arctic regions of Alaska, Canada and Greenland. Regional manifestations of the ASTt recovered in Manitoba are attributed to Pre-Dorset and Dorset populations. The Pre-Dorset were the first occupants of the Canadian Arctic, arriving in the western arctic c.3700BC, during the relatively warm Subboreal period. Populations spread rapidly, expanding throughout the Arctic from Alaska to Greenland in only 500 years (Maxwell, 1985:44). The Pre-Dorset are widely believed to have followed a dual economy, seasonally exploiting both terrestrial and marine resources (e.g. Bielawski 1988; McCartney and Helmer, 1989; McGhee 1990; Maxwell 1985; Milne 2003). The relatively light construction of Pre-Dorset residences, coupled with this diverse exploitation, suggests a high degree of residential mobility (e.g. McGhee, 1981; Murray, 1999).

Between 800 and 500BC, Pre-Dorset populations were succeeded by the Dorset, who generally pursued more coastally-focused economies and, as a result, were generally less residentially mobile than the Pre-Dorset (e.g. McGhee 1981,1996; Murray 1999; Odess 1998; Darwent 2004; LeMoine 2005) – although this is not uniformly the case

(e.g. Milne et al., 2012). Widespread Dorset occupation of the Canadian Arctic persisted until roughly 1000AD, at which point the whaling Thule, ancestors to today's Inuit populations, began to colonize the region.

At least four sites in northern Manitoba – Thyazzi, Twin Lakes, Burton Rock, and Seahorse Gully – show definitive signs of occupation by members of the Arctic Small Tool tradition – including flaked burins, microblades, and characteristic side and endblades (Nash, 1969; Anderson and Hodgetts, 2007). These sites are located in the northeastern corner of the province, outside of the Churchill River basin – although two, Seahorse Gully and Burton Rock, are located on or very near to the mouth of the Churchill River itself. Evidence for inland occupation of Manitoba by members of the ASTt is more limited. Stylistic attributes of lithic artifacts at Rock Lake – located roughly 30km north of Thompson, MB – indicate ASTt influence (Nash, 1969:139).

Attribute analysis of material from one of the quarry sites analyzed for this dissertation (Grandfather Quarry, Section 5.1.1.1) is also suggestive of ASTt influence, if not direct use of the quarry by ASTt populations. This evidence includes the presence of microblades, microblade cores, and a flaked burin (Beardsell, 2013). Excluding Rock Lake, this may be the southernmost evidence for ASTt occupation of Manitoba, and one of the only known occurrences of ASTt in the boreal forest.

2.3.4 The Woodland Tradition (2000-300BP)

Approximately 2000 years ago, ceramic technology appeared throughout the lower Churchill River basin, and 500 years later began to appear at sites in the eastern portions of the upper Churchill River basin (Meyer and Smailes, 1975:58; Tisdale,

1977:8; Kroker, 1990:150; Meyer, 1995: 56; Pentney, 2002: 78-79). The earliest ceramic ware to appear in these areas is Middle Woodland Laurel ware (Kroker, 1990:154; Malasiuk, 2001:12). Laurel pots are characteristically large, coil-constructed, conoidal, thick walled, and decorated with diversely applied stamping and impression techniques for about a quarter to a third of their height below the rim (Malasiuk, 2001; 13). Laurel ceramics tend to be associated with small stemmed, side-notched or triangular projectile points and relatively high frequencies of side and end scrapers (Wright, 1967: 93; Janzen, 1968; 1010; Malasiuk, 2001: 14). This type of pottery is widespread throughout the boreal forest and parkland areas of Manitoba and the boreal forest and Boundary Waters areas of Ontario and Minnesota (Pettipas, 1996:87) and is associated with groups practicing a diverse subsistence strategy involving exploitation of game, fish and plant resources from both the boreal forest and adjacent aspen parkland (Boyd and Surette, 2010: 119). In the Churchill River basin, Laurel ceramics tend to be found more frequently – although still in low overall proportions – in southern portions of the lower basin (Malasiuk, 2001: 22). Malasiuk (2001: 22) interprets this restricted distribution as a result of infrequent seasonal use on the part of mobile, ceramic-using groups better adapted to survive in southern boreal forest/northern parkland interface environments as well as the restraining influence of territoriality on the part of Taltheilei groups who were already established in western and northern portions of the basin at the time of Laurel's fluorescence.

There is some debate as to whether the introduction of these ceramics to the Churchill River basin represents the effects of migration or diffusion. Wright (1972b) maintains that the spread of Laurel material culture resulted from diffusion as Shield

Archaic inhabitants throughout the boreal forest grafted ceramics onto their existing technological repertoire. Other authors maintain that Laurel ceramics were brought to northern Manitoba and Saskatchewan by populations moving north out of the Great Lakes (Hanna, 1980). Still other authors refuse to commit to an opinion (Malasiuk, 2001: 13; Pentney, 2002:80). This problem might be resolved if Laurel ceramics could be strongly associated with other material culture remains recovered from the basin, as this would indicate whether ceramics were initially grafted on to the Shield Archaic tradition or were accompanied by the sudden influx of an entirely new toolkit. However, because of the poor stratification of archaeological sites in the Churchill River basin, these associations are difficult to make (Hanna, 1980). Further investigation in the basin aimed at clarifying the shift from Archaic to Woodland material culture is necessary before this question can be definitively addressed.

Laurel ceramic wares persisted in northern Manitoba and Saskatchewan assemblages until around 1000 BP, much later than in southern regions of the boreal forest (Kroker, 1990:154). Toward the end of the Laurel period, at around 1300 BP, there is evidence for contact between groups in the Churchill River basin and groups to the south, who were utilizing a new kind of ceramic technology that produced thin-walled, globular, flared rim pots, known as Blackduck vessels (Malasiuk, 2001: 14). A few sherds of such pots have been recovered from sites around South Indian Lake (Francois *et al.*, 1995:10) and the eastern upper Churchill River (Pentney 2002: 89). Most scholars agree that these pots likely represent trade vessels that may have contained dried maize or rice, which Blackduck groups are known to have farmed and collected (Flynn, 2002; Boyd and Surette, 2010:120). Strong evidence for early maize trade

between Laurel-producing boreal forest groups and groups to the south has been recently established by Boyd and Surette (2010), lending support to this hypothesis.

Starting at around 1000 BP, groups in the Churchill River basin appear to have adopted ceramic manufacture techniques similar to those employed by Late Woodland groups to the south to produce thin walled, large, globular vessels known as Selkirk ware (Kroker, 1990: 157-159; Meyer, 1995: 56-57; Malasiuk, 2001; 17-21; Pentney, 2002:90). These vessels are widely distributed in several different stylistic forms, including the Kame Hills, Clearwater Lake, Pehonan and Kisis complexes, throughout both the upper and lower Churchill River basin, and were manufactured until they were replaced by vessels obtained through trade with Europeans. At well stratified and single-component sites, Selkirk ware is associated with a broad range of lithic and bone tools including small, thin, side-notched and triangular projectile points, barbed bone harpoon-heads, notched and unnotched bifaces, and chipped, ground adzes (Kroker, 1990: 157; Malasiuk, 2001:18). Use of exotic lithic raw materials in Selkirk assemblages is limited; most lithic tools appear to have been made out of local materials, with quartz becoming dominant as sites get farther from the chert deposits of the Hudson Bay Lowlands. However, non-local copper, brown chalcedony, catlinite and marine shell do occur in small quanities (Dickson, 1980: 151; Malasiuk, 2001: 18). The presence of these materials in Selkirk assemblages is attributed to participation in long-distance exchange networks by late precontact groups in the Churchill River basin (Malasiuk, 2001:18).

The emergence of Selkirk ware and related material remains is generally accepted as an indigenous northern boreal forest cultural development resulting from contact between groups in the area with members of other late precontact groups, either through

trade or intermarriage, rather than the result of a population influx (Malasiuk, 2001:17). However, some scholars urge caution in making this kind of assertion, stressing the difficulties inherent in directly linking specific cultural phenomenon to changes in material assemblages (Hanna, 1980). The successful spread of Selkirk-producing groups into northern and western portions of the basin where Laurel ware has not been recovered is explained by Malasiuk (2001:22) as the result of northern shift in the treeline, 1000 years ago, which decreased the Taltheilei presence in the area.

Based on ethnographic information regarding the distribution of Cree populations at contact, which overlaps consistently with the distribution of archaeological sites producing Selkirk ceramics, it is generally acknowledged that this style of pottery was produced by the ancestors of the modern Cree (Wright, 1971; Meyer, 1987; Smith, 1987:439; Kroker, 1990:158; Pentney, 2002:98). Selkirk ceramic sherds and other artifact types associated with occupation during this later precontact period are recovered far more frequently than artifact types associated with earlier periods of occupation in the Churchill River basin. It is suggested that this reflects increasing population density in the boreal forest during the late precontact period (Malasiuk, 2001:19). Sites associated with Selkirk ware vary in size (Dickson, 1972: 46). It is possible that larger sites represent the remains of multi-group summer aggregations, where people came together to exploit relatively predictable fish runs, while smaller sites represent winter hunting camps occupied by smaller hunting groups. This land use model is consistent with ethnographic information on Cree resource procurement and mobility patterns by Smith (1981: 260).

2.4. The Churchill River basin: interpretation beyond culture history?

The systems of social, technological, and economic organization selected by the people producing the artifacts upon which the above culture history is based are difficult to reconstruct through traditional analysis of artifact assemblages recovered from the central Churchill River basin. This is partially a result of the practical issues involved in interpreting boreal forest sites mentioned in section 2.2. Minimal stratigraphy prevents the clarification of occupation size at large, potentially multicomponent, sites. Poor organic preservation limits the feasibility of a broad seasonality study to investigate seasonal resource procurement patterning or the geographic extent of the annual round of populations in the basin. Lack of preserved organics for radiocarbon dating limits archaeologists' ability to clarify whether material culture change in the basin was the result of independent invention, ideological diffusion or immigration of groups out of surrounding areas (Dickson, 1980: 9, Hanna, 1980:67-68; Kroker, 1990: 146). Additionally, some of the more esoteric aspects of social organization in the central Churchill River basin, including the degree of shared identity and worldview experienced by individuals in the region over its human history, are difficult to reconstruct archaeologically even under the best circumstances of deposition and preservation.

To a limited degree, shortcomings in material culture-based reconstruction of social and economic organization in the central Churchill River basin can be made up for through application by direct analogy of information drawn from ethnographic sources. These include Fur Trade-era ethnographies (e.g. Drage, 1982 [1748]), as well as oral histories collected through more recent ethnographic field work in the Churchill River basin (e.g Brightman, 1993; 2007). Both contain information relating to mobility,

settlement, land tenure, division of labour, ideology and relationships with groups surrounding the basin that would be difficult, if not impossible, to replicate through traditional analysis of artifacts recovered from the area. However, the degree to which *all* of this information can be applied to directly interpret social and economic organization in the Churchill River basin throughout its 8000 year human history is contentious. Modern *Asiniskaw Ithiniwak* populations in the central Churchill River basin are undoubtedly the direct descendants of archaeological populations in the region dating back over 1000 – and possibly 6000 – years (Smith, 1987, Kroker, 1990:158; Linklater, 1994:10, 16-17, 34). However, active participation in the Fur Trade beginning in the 1700s had an indisputable effect on certain social and economic strategies selected by individuals and groups in the Churchill River basin, especially those related to mobility, technology and subsistence (Brightman, 1993: 247-250; Linklater, 1994:20-21). These changes definitely affect the suitability of European Fur Trade-era descriptive accounts for accurately interpreting the totality of behavioural organization in the more distant past. While oral narratives are a more robust source of information on social and economic organization in the ancient Churchill River basin, and can be used to clarify organizational changes caused by European contact, they simply do not describe some facets of past behaviour of interest to archaeologists and communities alike in sufficient detail to allow clear reconstruction. For example, like many other parts of the world, selection of lithic technological strategies in the basin is not described in either Fur Trade accounts or oral narratives. In the former case, this is likely a result of the abandonment of lithic technology shortly after steady access to metal implements and firearms was established. In the latter case, the omission is likely due to the non-lithics related

research foci (primarily human-animal relationships and the preservation of core narratives in the case of Brightman 1993; 2007 and settlement, mobility and origins of Cree groups in the case of Smith [1981]) of the ethnographers who collected said oral accounts.

The results of basic typological, functional and taxonomic analysis of archaeological assemblages recovered from the central Churchill River basin coupled with information contained in ethnographic accounts and oral narratives collected in the past from the basin have considerably enhanced our knowledge of past lifeways in the region. However, general understanding of some aspects of social and economic organization – including mobility, intergroup interaction – and many aspects of lithic technological organization, remain ambiguous. To some extent, ongoing analysis of material from the region employing novel techniques – such as macroscopic attribute analysis tailored to quartz debitage, which makes up the bulk of assemblages in the Churchill River basin (Beardsell, 2013) – is moving in the right direction to remedy some of these issues. However, strategies employed in lithic technology (specifically the selection, procurement and transport of lithic raw materials from particular sources), as well as the actual geography of group mobility in the basin, cannot be adequately addressed through macroscopic debitage analysis alone (Rankama *et al.*, 2006: 249). In other contexts where archaeologists are faced with similar questions about past populations and large assemblages primarily composed of stone tools and debitage, such as those from the Churchill River basin, lithic raw material provenance studies have proven useful for clarification. Data resulting from these studies have been successfully employed to research choices made during lithic procurement, and the spatial patterning

and extent of group mobility in archaeological contexts from Neolithic Iran to early Precontact Ontario (Julig *et al.*, 1987; Negash *et al.*, 2006; 2007; Bressy *et al.*, 2008; Eerkens *et al.*, 2008 date; Milne *et al.*, 2009; Niknami *et al.*, 2010; Healan, 1993; Weisler, 1994; Weisler and Kirch, 1996; Weisler and Woodhead, 1995; Insoll *et al.*, 2004; Fraser *et al.*, 2005; Phillips and Speakman, 2009; Evans *et al.* 2010).

Quartz is the most common lithic raw material in lithic assemblages in the Churchill River basin. Moreover, it is the only material type used in this region for which known procurement sites exist. Therefore, it is the material best suited to be the subject of a geographically broad characterization study within the Churchill River basin. Given the practical issues associated with dating assemblages in the boreal forest, undertaking a raw material provenance study of quartz assemblages in the basin will allow me to investigate only very basic aspects of the relationship between social and environmental factors, and quartz technological organization in the region, without any temporal resolution. However, even basic information about the integration of material from various quarries to toolkits in the region, and the distance over which quartz was transported will constitute a new contribution to our knowledge of mobility and quartz technological organization in the Churchill River basin.

3.0 Lithic provenance studies

Lithic provenance research consists of linking lithic artifacts to the quarry or deposit they were initially procured from by identifying physical, structural or chemical characteristics of their raw materials that differ detectably between different sources. Lithic provenance studies have been fundamental in reconstructing past resource procurement and utilization strategies (Bressy et al., 2008; Eerkens et al., 2007; Julig et al., 1987; Milne et al., 2009; 2011; Negash et al., 2006, 2007; Niknami et al., 2010) and testing hypotheses regarding aspects of social organization such as trade and mobility (Healan, 1993; Insoll et al., 2004; Evans et al. 2010; Fraser et al., 2005; Milne et al. 2011; Phillips and Speakman, 2009; Weisler, 1994; Weisler and Kirch, 1996; Weisler and Woodhead, 1995).

Significant improvements to the quality of geochemical equipment have resulted in rapid development of new techniques for establishing lithic raw material provenance. The list of 'sourceable' archaeologically exploited lithic raw materials now includes obsidian (Frahm et al., 2012; Glascock et al., 1993; Shackley, 1995), microcrystalline quartzes (Evans et al., 2010; Hoard et al., 1993; Luedtke, 1979; Malyk-Selivanova et al., 1998; Milne et. al, 2009; Milne et al, 2011), jade (Chen et al., 2004; Wang, 2011), basalt (Mallory-Greenough et al., 1999; Weisler and Kirch, 1995; Weisler and Woodhead, 1995), marble (Herz, 1987; Maniatis et al., 2010), and turquoise (Hull et al., 2008; Thibodeau, 2012; Hull, 2012), among others.

The earliest lithic provenance research generally consisted of little more than stray observations of physical qualities – such as colour, lustre, or texture – of lithic raw materials that were thought to be characteristic of certain sources. The identification of

these qualities in recovered materials or quarry deposits was largely unstandardized, and subjective, with descriptions of similar materials, or definitions of material qualities varying from observer to observer (Ives, 1984). Over the past century, a number of studies have questioned the validity of this approach (eg. Luedtke, 1979; 1993; Julig *et al.*, 1991; Ives, 1984). Either through chemical reanalysis of previously visually 'sourced' raw material sample sets (Julig *et al.*, 1991), or visual identification tests involving multiple specialists (Luedtke, 1993), these studies have demonstrated that qualitative visual analysis is often not a reliable technique for characterizing even supposedly visually 'distinct' raw materials, although exceptions occur (Braswell *et al.*, 2000).

These issues, combined with development of more reliable and accessible quantitative physical and chemical characterization techniques, have rendered qualitative macroscopic visual analysis nearly obsolete as a stand-alone approach to lithic sourcing. However, visual analysis can be a valuable first step in organizing large, diverse lithic samples into useful categories for further analysis by other, more reliable techniques. Milne *et al*. (2009; 2011), for example, use Munsell colour chips to visually classify a large sample of chert debitage from the southern interior of Baffin Island into color categories prior to trace element analysis by SIMS and ICP-MS. While SIMS analysis demonstrated that material colour and trace element chemistry were not strongly related in this material, colour categorization did allow the authors to design an organized approach to chemical analysis of the material (Milne et al., 2009; 2011).

The research discussed in this dissertation uses macroscopic visual analysis in a similar manner – as a first step to organizing samples prior to geochemical analysis.

Visual analysis was qualitative – all materials were organized into one of three colour categories, while artifacts for analysis were selected from the Manitoba Museum collection based on visual assessment of material quality. A more in-depth discussion of these approaches is described in sections 8.2 and 8.4 of this dissertation.

In some cases, lithic raw materials from different sources will exhibit differences in mineralogy and structure that are visually detectable on the microscopic scale (Mason and Aigner, 1987; Hermes and Ritchie, 1997; Pollock *et al.*, 1999; Pitblado *et al.*, 2007; Bressy *et al.*, 2008). Within a given raw material type, these differences may arise due to variation in the origin, history, and/or depositional environments of the sources being analyzed (Dong *et al.*, 1995; Hermes and Ritchie, 1997; Pitblado *et al.*, 2007). Microscopic visual analysis of lithic materials for provenance assignment is normally carried out on thin sectioned archaeological and geological samples using a transmitted light petrographic microscope. Pitblado and colleagues (2008), for example, utilize petrographic analysis as part of an integrated petrographic-geochemical protocol aimed at characterizing quartzite sources in the Gunnison basin of Colorado. Traits such as sediment grain size, sorting, shape and composition, cement composition, texture and presence/absence of mineral inclusions were ascertained through petrographic analysis and were found to vary between some geologically sampled quartzite sources and within the archaeological sample set considered, allowing provenance statements to be made – although a small proportion of these were later refuted by geochemical data (Pitblado, 2007:759,760). The structural and mineralogical variability observed by Pitblado and colleagues (2007) in their quartzite sample set is almost certainly a result of intersource variability in the sandstones from which the quartzites formed. Because sandstone is

composed almost entirely of the weathered, transported remains of other sedimentary, igneous or metamorphic rocks, its composition is highly dependent on the geology surrounding the area where it was deposited (Pitblado *et al.*, 1997). The mineralogy of authigenic cements forming after sediment deposition may also reflect source specific environmental conditions, enhancing discrimination between quartzites based on petrographic analysis (Pitblado *et al.*, 2007:757)

In the above case, petrographic analysis is an appropriate tool for source characterization because microscopically observable variability in quartzite texture and mineralogy is directly linked to factors which differ somewhat consistently between the raw material sources considered (Pitblado *et al.*, 2007). However, many raw materials fail to exhibit microscopically observable intersource variability. Structurally or chemically homogenous raw materials, including quartz, will appear very similar from source to source when viewed through a petrographic microscope (Götze *et al.*, 2005). Even where source-linked petrographic variability is identified, the qualitative, somewhat subjective data produced by petrographic analysis may not be sufficient for establishing accurate artefact source provenance. For this reason, most studies incorporating petrographic analysis as a sourcing tool do so using an integrated petrographic-geochemical approach, in which qualitative microscopic data are used to shape geochemical sourcing approaches and aid in interpreting resulting data (Pollock *et al.*, 1999; Pitblado *et al.*, 2007; Bressy *et al.*, 2008; Milne *et al.*, 2009). Because it represents a relatively simple, rapid tool for assessing the contents and structure of samples, which directly impacts the selection of appropriate geochemical sourcing techniques, petrographic analysis of materials to be sourced is almost universally

considered an important first step in any lithic provenance research design (Tykot, 2004:408).

3.2 Geochemical provenance studies

Most lithic provenance studies carried out in archaeological contexts today are based on geochemical, rather than visual or physical characterization of raw material sources and/or artifacts. In these studies, stable isotope ratios and trace element concentrations are the two most common material parameters relied upon for source characterization. Some studies – such as this one – utilize both to establish and/or rule out artifact provenance. Today, provenance researchers have access to numerous instruments capable of performing many different types of isotopic or elemental assays. This unprecedented climate of choice, combined with the exigencies of most archaeological budgets, makes the selection of a material-appropriate technique for source characterization extremely important. Deciding on the proper geochemical technique for establishing raw material provenance requires strong working knowledge of the geology of the lithic material in question, and how processes at play during its evolution can impact different aspects of its chemistry.

3.2.1 Trace element characterization

Trace element analysis – i.e. quantification of elements at concentrations <100ppm – is the most common type of geochemical assay employed to characterize archaeological lithic raw materials. Depending on the instrumentation required to quantify trace elements in a given material, trace element assay can be reasonably

inexpensive relative to other chemical assays, such as stable isotope analysis. Moreover, it has demonstrated efficacy for characterizing common lithic material types, including obsidian (e.g. Glascock et al, 1993; 1999, Eerkens *et al.*¸2007; Duff *et al.*, 2012) chert (e.g. Glascock, 2004; Evans *et al.*, 2007; 2010; Milne *et al.*, 2009; 2011), and basalt (Weisler and Kirch, 1996; Kirch *et al.*, 2012; Gluhak and Rosenberg, 2012). Concentrations of trace elements in rock and mineral deposits result from a variety of natural processes at play in the different geological settings under which they are formed. In some cases, these processes vary significantly enough during the formation of different raw material sources to produce detectable, source-specific variation in material chemistry (e.g. Murray *et al.*, 1990; Murray, 1994; Foradas, 2003; Larsen *et al.*, 2004). When this is the case, trace element analysis can form the basis of a robust material provenance technique. However, there is no 'one size fits all' trace element technique for sourcing lithic materials. Knowing which elements will optimally distinguish between deposits of a given raw material requires good working knowledge of its geochemistry – i.e. the interplay between specific geological processes known to affect the material and material chemistry. Elemental analysis capable of characterizing igneous raw material sources will likely not be suitable for application to sedimentary materials, and *vice versa*.

For example, certain elements, known as incompatible elements are, due to either their size or charge, or a combination of both, highly incompatible with solid phase rocks or minerals. Other elements, known as compatible elements, are much more compatible with solid rock phases. In magma chambers, where both solid and molten phases are present, incompatible elements will be strongly concentrated in the liquid component,

while compatible elements will be strongly concentrated in the solid component. Fractional recrystallization or melting events occurring during the magma's evolution prior to its solidification will alter the relative concentrations of compatible and incompatible elements in both the solid and liquid components present in the magma chamber (Weisler and Woodhead, 1995:1882; Shackley, 2005:10-15). Therefore, relative compatible and incompatible trace element concentrations in lithic materials formed from solidified lavas or magmas are dependent on the original incompatible element contents of parental magmas and surrounding rocks and minerals as well as events occurring during magmatic evolution. The result of this is that sources of igneous lithic raw materials formed from compositionally different magmas that underwent different courses of evolution prior to solidification, tend to exhibit different incompatible element signatures (Weisler and Kirch, 1996:1383; Shackley, 2005:11).

Obsidian sourcing is by far the best known and most successful application of incompatible trace element analysis to archaeological provenance research. Obsidian is igneous in origin, and forms when silicon and aluminum-rich magma with a low volatile content is extruded to the earth's surface and cools rapidly into a glass. Obsidian lava is derived from magma formed during high temperature (~1000°c) melt reactions below the earth's surface. The liquid and solid products of these reactions are chemically identical, with the exception of compatible and incompatible elements. This initial disparity is altered by fractional crystallization, which can introduce compatible elements into the magma, and further melting events, which will preferentially introduce incompatible elements. Therefore, the proportion of incompatible elements, which are distributed homogenously within the resulting obsidian, is highly specific to each primary source

(Glascock, 2002; Shackley, 2005: 10-15). Thus, instrumental techniques capable of producing quantitative data regarding incompatible and compatible trace element concentrations in analyzed samples form the foundation of obsidian sourcing methods (Glascock, 2002).

While incompatible elements may be used to accurately characterize igneous lithics, like obsidian, in which they are concentrated in detectable amounts, it would be an expensive waste of time to quantify them in an attempt to characterize non-igneous lithic materials, which form under dramatically different conditions. Instead, other trace element constituents that *are* known to be affected by potentially source-specific environmental conditions under which the material is formed should be the subject of analysis. For example, rare earth elements – consisting of Yt, Sc and the lanthanide series – constitute another group of trace elements that have received attention from archaeologists seeking to develop sourcing protocols for lithic materials, especially chert (Hess, 1996; Malyk-Selivanova, 1998; Malyk-Selivanova *et al.*, 1998; Foradas, 2003: 101; Evans *et al.*, 2007). Relative concentrations of these elements in silicate raw materials formed in marine sedimentary systems, like chert, are affected by ocean water conditions, and thus have the potential to vary between raw material sources (Murray *et al.*, 1990, 1992; Foradas, 2003).

Trace element analysis can be a valuable tool for differentiating between archaeologically exploited sources of some lithic raw materials. However, it is *not* a universally applicable sourcing tool. For some raw materials, factors influencing trace element composition do not vary on fine enough scale to allow accurate source characterization by this method (Woodhead and Weisler, 1995; Cackler *et al.*, 1999). For

others, these factors may vary on *too* fine a scale, leading to intrasource trace element variability in excess of intersource variability, rendering it impossible to match artifacts to a single source based on trace element data (Roll *et al.*, 2005). Other materials may not not contain detectable quantities of the trace elements that should, according to geochemical theory, differentiate between sources. Establishing provenance for these materials, therefore, requires the application of techniques other than trace element analysis that are capable of distinguishing between archaeologically exploited sources.

3.2.2 Stable isotope characterization

Archaeologists are increasingly recognizing the utility of stable isotope analysis for characterizing sources of Si-rich lithics that cannot be differentiated based on physical criteria or elemental concentration data (Weisler and Woodhead, 1995; Smith and Pell, 1997; Meighan *et al.*, 2003; Christensen *et al.*, 2006). As sensitive, accurate, minimally-destructive stable isotope measurement techniques continue to be developed and refined, applications of stable isotope analysis to problems of lithic sourcing will only increase (Shackley, 2008: 195; Resano *et al.*, 2010:59). The following section of this dissertation will present the theoretical foundations underlying the application of the two stable isotope systems most commonly used in lithic sourcing studies, oxygen and lead.

3.2.2.1 Oxygen stable isotopes

Isotopes are atoms that vary in mass as a result of variation in the number of neutrons present in the nucleus. The nuclear configuration of most known isotopes is unstable (Hoefs, 2009:1). Unstable isotopes are known collectively as radioactive

isotopes. In some cases these unstable isotopes decay at a predictable rate to form stable daughter products. When both the rate of decay and the original ratio of radioactive parent to stable daughter isotopes are known, this decay can form the foundation of radiometric dating techniques (e.g. carbon-14 and argon-argon dating), employed in both archaeology and the geosciences.

Isotopes which do not decay over time are referred to as stable isotopes. Subtle quantitative differences in chemical and physical properties result from mass differences between stable isotopes of the same element. These differences, known as isotope effects, are most pronounced for isotopes of lighter elements, where mass differences between stable isotopes constitute a significant percentage of overall atomic mass (Hoefs, 2009:35). The distribution of stable isotopes in nature is not uniform, and is largely altered by two processes. The first of these is the decay of radioisotopes, which elevates concentrations of stable daughter isotopes over time. The second of these is isotope fractionation, or the differential partitioning of isotopes of the same element between two substances or substance phases (Hoefs, 2009:5). Isotope fractionation can occur either as a result of kinetic isotope effects that occur during diffusion, evaporation and biological reactions, or through isotope exchange between two substances at equilibrium (Hoefs, 2009:6-11). In general, the magnitude of isotope fractionation that occurs through equilibrium isotope exchange is inversely related to temperature: greater fractionation occurs at lower temperatures and *vice versa* (Hoefs, 2009:7). In some cases, factors affecting isotope distribution cause different deposits of the same material to exhibit different relative isotope concentrations. When this occurs, isotopic analysis can form the basis of a material characterization and artifact sourcing protocol.

Stable isotope data are presented either as ratios of the concentration of the less abundant isotope against the concentration of the more abundant isotope, or as δ values. A δ value represents the isotope ratio of the sample normalized against the isotope ratio of a universal standard of known composition and is expressed in parts permil (‰). This normalization ensures comparability among data from different samples, instruments and laboratories.

Oxygen is the most common element in the earth's crust and is a major component of most archaeologically exploited lithic materials. Oxygen occurs naturally in three stable isotopes, ^{16}O, ^{17}O, and ^{18}O. The most common of these is ^{16}O, which makes up 99.76% of naturally occurring oxygen, followed by ^{18}O (0.21%) and ^{17}O (0.038%). In most studies, oxygen isotope data are expressed as $\delta^{18}O$ values, representing sample $^{18}O/^{16}O$ normalized against $^{18}O/^{16}O$ for standard mean ocean water (SMOW).

In certain geological regimes, factors influencing lithic $\delta^{18}O$ values have the potential to vary on an archaeologically significant scale, rendering stable oxygen isotope values a good provenance indicator for materials formed in these contexts. These factors include the oxygen composition of parental fluids or sediments (Taylor, 1983: 127; Blatt, 1987; Smith and Pell, 1997:773; Meighan *et al.*, 2003:246), temperature conditions during formation (Taylor, 1968:63-64; 1983; Knauth and Epstein, 1976; Matthews and Beckinsale, 1979; Blatt, 1987; Meighan *et al*., 2003:246) and the isotope chemistry of nearby fluids or minerals (Longstaffe *et al.*, 1981:86; Valley and Graham, 1996: 231). Theoretically, oxygen isotope data should distinguish between archaeologically exploited lithic sources where one or several of these factors vary significantly between them.

Materials, such as chert, which are formed in large deposits and/or under isotopically and thermodynamically similar regimes usually will not exhibit varying $\delta^{18}O$ values on a scale of use to archaeologists and should be characterized using other methods.

In spite of its potential to discriminate between different sources of certain lithic raw materials, oxygen stable isotope analysis has received little application to lithic material provenance studies, beyond application to sourcing archaeological marble (Herz, 1987; Maniatis, 2007; Shackley, 2008:200). This is likely related to the relatively high price tag and labour time associated with isotopic analysis and sample preparation in general, as well as the success of cheaper, faster trace element analysis for sourcing many lithic raw materials. Despite these issues, two relatively successful raw material characterization studies employing oxygen isotope data have been published over the past fifteen years, both focusing on quartz. The first, carried out by Smith and Pell (1997), uses $\delta^{18}O$ data from detrital quartz grains in red ochre to characterize ochre source regions in central Australia and assign regional source provenance to an archaeological ochre sample from the nearby Puritjarra rock shelter. The second, published by Meighan and colleagues (2003), is an oxygen isotope sourcing study of hydrothermal quartz facades from the Newgrange megalithic tomb in the Boyne Valley, Ireland. This study will be discussed more thoroughly in section 3.4, as it constitutes the only published macrocrystalline quartz provenance study outside of my dissertation research.

3.2.2.2 Lead stable isotopes

Since the late 1960s, stable lead isotope analysis has been extensively applied by archaeologists to establish source provenance for native and smelted metals (Stoss-gale *et*

al., 1997; Srinivasan, 1999; Sayre *et al.*, 2001; Baker *et al.,* 2006) glass (Brill and Wampler, 1967; Brill, 1970; Henderson, *et al*, 2005) and ceramic glazes (Habicht-Mauche *et al.*, 2002; Wolf *et al.*, 2003). The application of lead isotope-based sourcing techniques to provenance studies of lithic materials has been far more limited. This restricted application is likely a result of the same factors limiting the application of oxygen isotope sourcing to lithic analysis: time, cost and the widespread, successful application of trace element-based sourcing techniques. However, in cases where intersource chemical and physical homogeneity precludes sourcing based on visual analysis or elemental concentration data, stable lead isotope data can serve as an important provenance indicator (Woodhead and Weisler, 1995; Christensen *et al.*, 2006).

Lead occurs naturally in four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Of these, only ^{204}Pb is non-radiogenic. ^{206}Pb, ^{207}Pb and ^{208}Pb are the final daughter products of the radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively. In materials with appreciable levels of U and Th, concentrations of radiogenic lead isotopes will increase relative to ^{204}Pb at a predictable rate over time. Therefore, relative concentrations of lead stable isotopes will vary between material deposits according to the initial Th, U and Pb chemistry of parental sediments, melts or fluids and the age of the deposit (Hemming *et al.,* 1994; Weisler and Woodhead, 1995; Faure and Mensing, 2005:256). Pb isotope data are normally presented as ratios of radiogenic isotope concentrations over ^{204}Pb. Due to differences between the half lives of ^{238}U and ^{235}U, ^{207}Pb/ ^{206}Pb values are also often presented as age indicators that have the added benefit of being resistant to the effects of lead loss over time, as the two isotopes are resistant to fractionation during loss (Faure and Mensing, 2005:219).

Weisler and Woodhead (1995) use Pb stable isotope analysis to characterize fine-grained ocean island basalt from fifteen sources located on eight island groups in Polynesia to establish source provenance for imported basalt artifacts recovered from Henderson Island in the eastern Pacific. Ratios of incompatible trace elements have been used successfully in some contexts to accurately characterize archaeologically exploited basalt sources (Weisler, 1994; Weisler and Kirch, 1996). However, basaltic magmas in eastern Polynesia tend to undergo similar patterns of fractional crystallization and crustal assimilation prior to extrusion, resulting in widespread intersource incompatible trace element homogeneity (Weisler and Woodhead, 1995). However, basalt formations in different island groups, and in some cases on different islands within groups, do vary in age, resulting in measureable differences in lead stable isotope composition. Through their analysis, Weisler and Woodhead (1995) link artifacts recovered on Henderson Island to two basalt formations on Pitcairn Island and one in the Gambier Islands.

3.3 Quartz structure, chemistry, and formation

Unlike many lithic raw materials encountered by archaeologists, quartz is a mineral, rather than a rock. Minerals are composed of a structurally-ordered arrangement of elements, which means they can be represented as a chemical formula. Rocks, on the other hand, are aggregates of minerals; they cannot be represented in formula and do not have regular internal structure. Quartz is the second most common rock-forming mineral in the earth's crust; it is a common component of igneous, sedimentary, and metamorphic deposits. Quartz is part of a family of minerals know as silicates, and is represented by the formula SiO_2. Silicon and oxygen in quartz are arranged in a lattice of spiralling,

interconnected chains of Si-O tetrahedra. These chains are oriented parallel to the long, or c-axis of the quartz crystal, and are each connected to two other chains. The resulting structural arrangement of silicon and oxygen is responsible for quartz' characteristic chemical and mechanical behaviour.

Quartz lattices are very tightly bonded, admitting few trace element impurities during crystallization, with the result that most natural quartz is composed of upwards of 99% SiO_2. Structurally incorporated trace element impurities that *do* occur in quartz come in two forms: substitutional and interstitial (Müller *et al.*, 2003; Götze, 2009). Substitutional defects occur when trace elements replace Si in the quartz crystal structure. Substitutional trace elements, usually Al, Ti, and Ge, must have a relatively small ionic radius and must either carry the correct charge (4+) or occur with a charge compensator (like H^+, Li^+ or K^+ for Al^{3+} or Fe^{3+}) in a nearby interstitial position (Müller *et al*., 2003; Götze, 2009). Interstitial impurities in quartz tend to be composed of these charge compensating cations. Other trace elements, including Ba, Cr, Cu, Hg, Mg, Mn, Nd, Pb, Rb, Sr, U, and REE, tend to be incorporated into quartz non-structurally, as components of fluid or micromineral inclusions (Götze *et al.*, 2004).

Concentration levels of trace elements incorporated structurally and as inclusions in quartz are influenced by environmental factors at play during quartz crystallization. The rate of Al substitution in quartz has been tied to temperature, with concentrations increasing roughly 1ppm for each 3.6˚C increase in temperature (Dennen *et al.*, 1970; Rusk *et al.*, 2008). Ti concentration in quartz deposits is also influenced by temperature, as well as Ti activity and pressure (Wark and Watson, 2006; Thomas *et al.*, 2010; Behr *et al.*, 2011). When pressure and Ti activity are known, Ti concentrations in quartz can

serve as a geothermometer with accuracy of ~5˚C (Wark and Watson, 2006). Similarly, the size and type of fluid and micro-mineral inclusions in quartz, and therefore, their trace element chemistry, is influenced by environmental variables including the chemistry of nearby minerals, parental fluid chemistry, and temperature during crystallization (Götze, 2009).

Most of the colour variation observed in natural quartz is a product of quartz trace element anomalies. Amethyst's purple colour is the result of high concentrations of Fe (Hassan and Cohen, 1974; Lehmann, 1975). The pink colouration of rose quartz can be caused either by Mn, Fe, or Ti impurities, Al substitutions with compensating interstitial P cations, or micro-inclusions of duomortierite (Cohen and Mahkar, 1983, 1985; Maschmeyer and Lehmann, 1983; Ma *et al.*, 2002; Larsen *et al.*, 2004; Farias and Wantanabe, 2012). Smoky quartz is created when Al defects with compensating cations are converted to optically active AlO_4 defects through X- or γ-Ray bombardment by nearby radioactive elements (Götze, 2009).

In addition to trace element chemistry, quartz stable isotope ratios are impacted by formation environment (Taylor, 1983: 127; Blatt, 1987; Smith and Pell, 1997:773; Meighan *et al.*, 2003:246). Pb and O stable isotope systems, in particular, are affected by environmental parameters to the extent that geologists and archaeologists have used them to reconstruct quartz provenance – albeit on a large geographic scale (e.g. Hemming *et al.*, 1994; Smith and Pell, 1997; Meighan *et al*. 2003). Factors influencing the relative concentration of O stable isotopes in quartz deposits include the isotopic composition of parental fluids or magmas (Taylor, 1983: 127; Blatt, 1987; Smith and Pell, 1997:773; Meighan *et al.*, 2003:246), temperature conditions during formation or deposition

(Taylor, 1968:63-64; 1983; Knauth and Epstein, 1976; Matthews and Beckinsale, 1979; Blatt, 1987; Meighan *et al*., 2003:246) and the isotopic composition of surrounding fluids, rocks or minerals (Longstaffe *et al.*, 1981:86; Valley and Graham, 1996: 231). Lead isotope ratios in quartz are related to the same factors listed for trace element and O isotopes. However, because three of the stable isotopes of Pb are products of radioactive decay of U and Th, as mentioned in section 3.2.2.2, relative Pb isotope concentrations in quartz are also related to the age of the Pb source (Hemming *et al.*, 1994).

Selecting an appropriate technique for determining quartz provenance in any given archaeological context requires working knowledge of how the quartz forms and how formation parameters may vary across and between deposits. Quartz mineral deposits large enough to be of use for making stone tools generally form through one of two mechanisms: solidification of highly evolved granitic magmas, which produces pegmatite quartz, or precipitation of silica from fluids running through cracks in host rocks, which forms hydrothermal vein quartz.

Hydrothermal vein quartz is formed when silica is precipitated out of solution in hydrothermal fluids flowing through cracks and fissures in host rocks. Quartz veins may range from centimetres to kilometres in length and tend to produce coarse to fine-grained quartz and/or massive milky quartzes (Ballin, 2008:47). Quartz precipitation in hydrothermal systems occurs at a wide range of temperatures, between 50 and 750˚C (Rusk et al, 2008). As a result, hydrothermal quartz can exhibit a wide range of values for temperature-dependant chemical variables, including Ti concentration ranging from 11-200ppm (Rusk et al, 2008) and $\delta^{18}O$ values that range from less than zero to +18‰ (Aléon *et al.*, 2002). When environmental conditions change during quartz

crystallization in hydrothermal systems, internal chemical zoning of individual quartz crystals, or zoning across a quartz vein can occur. Variations in trace element chemistry of >100ppm can occur over as little as a few hundred microns within a hydrothermal quartz deposit (Rusk *et al.*, 2008). Fine-scale variation in hydrothermal quartz $\delta^{18}O$ values is also possible when temperature, pressure, or fluid chemistry changes during crystallization (Conrad and Chamberlain, 1992; Rusk and Reed, 2008). Using spatially resolved laser microprobe analysis, Kirschner and colleagues (1993), for example, detected $\delta^{18}O$ variability of >7‰ over areas of 2mm in quartz vein deposits in central Australia.

Knappable quartz can also form as a component of granitic pegmatites. The quarries discussed in this dissertation all exploit deposits of pegmatite quartz. Pegmatites are igneous mineral bodies, and are the last phase to crystallize from granitic magmas (Simmons et al. 2003). As a granitic body differentiates and crystallizes out of its parent magma, some elements that are incompatible with the crystallizing minerals due to their valence state or large ionic radius – known as 'incompatible elements' – become concentrated in the residual melt. In some cases, this residual melt is extruded into cracks and fissures in surrounding country rock and crystallizes to form a pegmatite. Pegmatites are internally zoned and, as a result of elemental enrichment, tend to be mineralogically complex (Simmons et al. 2003). The formation of a single granitic pluton may produce only one pegmatite, or may lead to the formation of an entire field of related pegmatites. Pegmatites are very coarse-grained, with individual crystals of component minerals, including quartz, ranging from centimeters to meters in size (Larsen *et al.*, 2004). Quartz is generally the last phase to crystallize out of pegmatite magma, and is generally

enriched in ^{18}O compared to other mineral phases (Taylor and Epstein, 1982; Taylor, 1983). Pegmatite quartz also tends to be very low in trace elements, as these are incorporated into minerals forming prior to quartz crystallization, although structurally bound impurities, like Al, Ti, Ge, Li, Na, and K are usually present (Götze *et al.*, 2004, 2005). Original, parental magmatic composition, fractional crystallization and crustal assimilation events during magmatic evolution, as well as the trace element chemistry of surrounding country rock influence the trace element composition of minerals contained in any given pegmatite, including quartz and any micro-mineral inclusions, which may be trapped within the quartz matrix (Simmons et al. 2003). O isotope chemistry of pegmatite quartz is influenced by oxygen isotope composition of parental magma, temperature conditions, and crustal assimilation events occurring during magmatic evolution. Pb isotope chemistry of pegmatite quartz is influenced by the same factors, as well as the age of the source rocks.

3.4 Provenance studies of quartz

Numerous provenance studies have been carried out on raw materials with a large quartz component, including microcrystalline and microfibrous quartz (i.e. flint, chert, and chalcedony) and quartzite (Julig *et al.*, 1987; Evans *et al.*, 2007; 2010; Milne *et al.*, 2009; 2011; Gaultier *et al.*, 2012; Pitblado *et al.*, 2008, 2013). However, only one published provenance study has been carried out on archaeologically exploited macrocrystalline quartz. Meighan and colleagues (2003) use a combination of macroscopic material observations and oxygen isotope data in an attempt to establish source provenance for hydrothermal quartz samples from the Newgrange megalithic

tomb in Ireland. For their study, O isotope analysis was carried out on rolled quartz pebbles and the white hydrothermal quartz facades from the tomb. As mentioned above, hydrothermal quartz $\delta^{18}O$ values tend to be quite variable and are governed by the oxygen isotope chemistry of hydrothermal fluid and wall rock, temperature conditions during crystallization, and, to a lesser extent, crystal growth rates (Kirschner *et al.*, 1993; Onasch and Vennemann, 1995). These are factors which can vary significantly between hydrothermal infilling events, which should lead to $\delta^{18}O$ heterogeneity between vein quartz sources deposited during different events (Meighan *et al.*, 2003:246). Meighan and colleagues (2003) suggest that this variability could allow characterization of hydrothermal quartz sources using $\delta^{18}O$ values. Source samples for comparison to quartz facades from Newgrange were taken from vein quartz outcrops in the Wicklow Mountains to the south of the site, as well as two beaches, Rathcor and Bray, located to the north and east of the Newgrange site, respectively (Meighan *et al.*, 2003).

Based on the results of their analysis, the authors state that hydrothermal quartz outcrops in the Wicklow Mountains are more chemically consistent with quartz from Newgrange than the beach quartz samples, although, no specific outcrop in the Wicklow Mountains could be strongly linked to the Newgrange materials based on their oxygen isotope data (Meighan *et al*, 2003:249-250). Indeed, their samples from the Wicklow Mountains have $\delta^{18}O$ values that overlap with those from Newgrange (11.9-17.7‰ and 9.0-12.2‰ respectively), while the beach samples are significantly more enriched in ^{18}O ($\delta^{18}O$ = 13.7-20.0‰). If their conclusions are correct, the absence of an exact oxygen isotope match between the Newgrange quartz and the Wicklow Mountain material sources sampled by Meighan *et al*. (2003) likely has more to do with their sampling

strategy than any shortcomings of the technique. Quartz outcrops in the Wicklow Mountains and at the Rathcor and Bray beaches are represented by only one or two samples each. In the case of the Wicklow Mountains, this represents alleged characterization of a 50km long series of quartz outcrops based on the analysis of only four samples. If the Wicklow Mountains did provide the quartz for the facades at Newgrange, it is not unsurprising that a matching source was not uncovered through this extremely limited sampling. Unfortunately, very little can be said about the utility of oxygen isotope analysis for sourcing archaeological vein quartz based on this small study. It is possible that convergence between values obtained from the three geological quartz sources would occur with further sampling of outcrops in the Wicklow Mountains or sampling and analysis of more than three potential sources. It is also possible that distinct signatures would persist; the sample set analyzed is simply too small to confidently draw any conclusions at this point.

Geological provenance studies of quartz are more common than their archaeological counterparts. However, these studies are generally aimed at distinguishing between detrital quartz grains produced in igneous, metamorphic, or sedimentary systems (e.g. Suttner and Leninger, 1972; Blatt, 1987; Hemming *et al.*, 1994; Bruhn *et al.*, 1996; Aléon et al., 2002; Boggs *et al.*, 2002; Agustsson and Reker, 2012) rather than distinguishing between sources of macroscopic quartz within these systems. A study of pegmatite quartz carried out by Larsen and colleagues in 2004 provides one exception. By measuring substitutional and interstitial trace element impurities in quartz from pegmatite fields in southern Norway, Larsen *et al.* (2004) were able to detect significant chemical differences between quartz samples from the Evje and

Froland fields. Further, the authors noted trends in trace element chemistry *within* these fields dependant on whether quartz crystallized early in magmatic evolution, or later, under lower temperature conditions. This study provides promising support for the utility of trace elements for establishing fine-scale provenance for igneous quartz, in spite of the low levels at which many trace elements are concentrated in this material.

4.0 Raw material variables, procurement, and the organization of technology

Stone tools have been recognized as important clues regarding human behaviour since the origin of archaeology as a discipline. People made them throughout human history on all six inhabited continents. The tools are well preserved in almost all depositional contexts, and through morphological, functional, technological, and chemical studies, can be used to answer questions about behavioural and environmental factors that framed the lives of their makers.

Until the latter half of the twentieth century, lithic analysts focused on stylistic or functional concerns as the primary generators of lithic assemblage variability. Descriptive morphological, residue, and use wear analyses abounded as researchers sought to investigate links between cultural identity, stone tools, and the tasks they were used to carry out (Frison, 1968; Wilmsen, 1968; Tringham *et al.*, 1974; Brose, 1975; Close, 1978). Depending on the dominant theoretical paradigm of the day, stability or variability in morphological traits or use wear exhibited by recovered stone artifacts was interpreted as the direct result of either environmental or behavioural systems. In all of these approaches, however, the focus was on recovered artifacts as static objects, rather than the end result of a series of choices on the part of toolmakers and users.

Beginning in the late 1960's, archaeologists began to realize that lithic analysis could have far broader implications for understanding the lives of tool users if those tools were viewed as more than simply finished objects. Increasingly, archaeologically recovered stone tools were recognized as the final products of artifact life histories, each consisting of a series of stages from raw material procurement to production, to use, to discard (Frison, 1968; Binford, 1979; Bamforth, 1986; Shott, 1986; Kuhn, 1991; Nelson,

1991; Andrefsky, 1994a; Carr, 1994; Odell, 2000). At each of these stages, specific choices were made by the individual creating, curating and using the tools. Taken together, these choices constitute a technological strategy (Nelson, 1991: 57).

At its most basic level, the study of technological organization is concerned with exploring how technological strategies are interrelated with the environments in which they are enacted, and the social and behavioural frameworks they facilitate (Kelly, 1988:717; Nelson, 1991: 57-58). Organization of technology research is also focused on how technological strategies, in turn, impact artifact form and distribution through choices related to design and spatial patterning of tool-related activities (Rolland and Dibble, 1990; Nelson, 1991:58; Kelly, 1992; Baales, 2001; Blumenschine, 2008; Bradbury *et al.*, 2008).

Raw material provenance studies are of particular utility in reconstructing the effects of environmental and social factors on the implementation of technological strategies related to material procurement. By revealing which raw material sources were selected for quarrying, and how material from different sources was incorporated into lithic toolkits, provenance studies allow archaeologists to understand the impact of environmental factors like material quality and availability, and human behaviours like group mobility on technological strategies in different archaeological contexts. Further, by allowing archaeologists to track the movement of lithic raw materials, provenance studies can be used as an indicator of a group's geographic range or the extent of trade networks where other approaches to clarifying these are not fruitful. Following sections will discuss the impact of lithic resource availability and quality on technological strategies, using examples to illustrate the utility of provenance information in

demonstrating these effects. Following this will be a discussion of provenance studies used to assess hunter-gatherer mobility through reconstruction of procurement ranges.

4.1 Effects of raw material quality and abundance on procurement

Lithic material quality is a product of both intrinsic material variables and contingent human needs (Gould and Saggers, 1985; Goodyear, 1989; Nelson, 1991:75; Taçon, 1991; Gilfoyle, 2009). The most important factor determining a material's quality as toolstone is predictable fracture (Goodyear, 1989; Nelson, 1991:76; Reher and Frison, 1991; Seeman, 1994). If stone does not break in a predictable way when struck, it is exceedingly difficult to produce any type of useable tool from it. Functionally dependent raw material qualities, which make some materials suitable for certain applications, but not for others, include hardness (Bamforth, 1991; Nelson, 1991:76; Yonkekura *et al.*, 2008; Yonekura and Suzuki, 2009), edge retention, and package size (Brantingham and Kuhn, 2001; Wenzel and Shelley, 2001; Wilson, 2007).

Raw material quality is also assessed through the lens of culturally specific worldviews related to, for example, spirituality, kinship, and/or aesthetic preference (Gould, 1985; Reher and Frison, 1991; Taçon, 1991; Gilfoyle, 2009). In some cases, physical properties of certain material types, or locations where it outcrops may make them especially desirable for tool manufacture. For example, ethnographic evidence as well as a stylistic analysis of Aboriginal rock art in the western Arnhemland region of Australia strongly suggests that high frequency of quartzite utilization in the area c. 6000-1000BP results from cultural interpretation of the materials' iridescent lustre (Taçon, 1991). In Aboriginal artistic traditions, iridescence is used to channel the power of

ancestral beings; Taçon (1991) hypothesizes that similar power-channelling properties would have been attributed to naturally iridescent raw materials, such as quartzite, making them an attractive and specially sought-after choice for the manufacture of hunting tools.

Material abundance refers to the degree of access toolmakers had to lithic raw materials. Availability may be determined simply by the frequency and geographic distribution of outcrops of toolstone within a given area, but would logically also be affected by the accessibility of raw material deposits and technology available for resource extraction (Andrefsky, 1994a). In addition, social constraints may be placed on material availability, for instance when family or other related groups control access to one or more raw material sources (e.g. Ballin, 2008:74-76).

According to Andrefsky (1994:23), "The availability of lithic raw materials may be the most important factor in the organization of technology." Material quality and abundance have a direct effect on the selection of technological strategies at all stages of tool life histories, from procurement, through manufacture, use, and discard. The effect of quality and abundance on procurement strategies is most pronounced in situations where sources of lithic material with either physically or socially desirable qualities are scarce. In areas where useable toolstone is either rare, of poor quality, or both, high quality raw materials are far more likely to be the subject of direct procurement – that is, expeditions made for the sole purpose of obtaining lithic raw material, as opposed to procurement embedded in other activities – or trade networks spanning large distances (e.g. Seeman, 1994; Gould and Saggers, 1985). This is especially the case when lithic raw materials are required for reliable tools to be used in subsistence activities involving

rapid, unpredictable encounters, like big game hunting. Lithic components of these tools generally need to be manufactured with a high degree of precision to ensure proper function in resource encounters where tool failure is unacceptable (Nelson, 1991:67); execution of this type of technology on poor quality raw materials is exceedingly difficult, if not impossible, making high quality materials, when available, preferred for the manufacture of this kind of toolkit (Beck and Jones, 1990).

An example of this phenomenon is observed in the lithic assemblage recovered from Nobles Pond, a multi-component early Holocene occupation site in Stark County, Ohio. The occupants of this site were likely residentially mobile, and depended, at least in part, on early Holocene megafauna for subsistence (Seeman, 1994). Outcrops of reasonably high quality lithic raw material are available in all directions around Nobles Pond. However, the results of Seeman's (1994) comparative visual analysis of lithics from the South Field area of the site shows that ninety-six percent of recoveries were manufactured from exceptionally high-quality microcrystalline silicates from two sources, both located over 100km from the site (Seeman, 1994:280). Instead of engaging in procurement at multiple sources randomly encountered during the expansive yearly round of early Holocene hunter-gatherers, the homogenous raw material assemblage at Nobles Pond suggests that occupants of the site were undertaking intensive, direct procurement of specific sources of very high quality, non-local raw materials (Seeman, 1994). Seeman (1994) uses his provenance data to support the hypothesis that these outstanding raw materials were preferred over relatively lower quality toolstone for the manufacture of the reliable tools necessary to take advantage of high-risk/high payoff hunting encounters with megafauna (Seeman, 1994).

Gould and Saggers (1985) present an archaeological example of the effects of more esoteric aspects of raw material quality on lithic procurement choices. Adzes recovered from the Puntjarpa Rockshelter, a woodworking site in Australia's Western Desert, are mostly fabricated from functionally well-suited local raw materials. However, a significant portion of the adzes are made from functionally inferior exotic chert (Gould and Saggers, 1985). The authors argue that these functionally inferior raw materials were directly procured and used because of their social significance, possibly stemming from the location of the outcrop they were quarried from (Gould and Saggers, 1985). Gould and Saggers go further and state that risk avoidance strategies involving the maintenance of strong inter-group social ties during periods of resource stress may have been embedded in the long-distance direct procurement of socially significant lithic raw materials (Gould and Saggers, 1985).

Material quality and availability also affect the *type* of tools that will be manufactured in different contexts. Andrefsky (1994) summarizes this relationship. Using a series of archaeological and ethnographic examples, he demonstrates that toolmakers tend to produce informal tools – unstandardized tools with minimal effort expended in manufacture and considered disposable (i.e., for short-term use) – from materials of poor quality, regardless of abundance, due to mechanical constraints placed on knappers by material quality. When toolstone is of high quality, but low abundance, it will be reserved for formal tool production – standardized tools with additional effort put into manufacture to ensure proper tool performance and/or potential for reuse or repurposing. Andrefsky (1994) illustrates these relationships using lithic assemblages recovered from Calispell Valley, a region where local raw materials are of low quality

and low abundance, but high quality non-local materials could be accessed. As expected, local raw materials were primarily used in the manufacture of informal tools, while formal tool classes are dominated by imported, higher quality raw materials.

In contexts where lithic raw material is both high quality and locally abundant, it will be used in the production of both formal and informal tools. As an example of this phenomenon, Andrefsky (1994) presents lithic data from sites in Piñon Canyon, CO. High quality lithic raw materials are locally abundant throughout Piñon Canyon; lithic assemblages at sites in the region are made up of roughly equal proportions of informal and formal tools manufactured from local raw materials. This pattern holds at sites occupied by both residentially mobile and relatively sedentary groups, demonstrating that raw material availability played a more significant role than mobility in the organization of technology in this context (Andrefsky, 1994a).

Strategies of tool curation – a measurement of the degree to which a tool's total utility is exhausted through use and repair prior to discard (Shott, 1996; Andrefsky, 2009) – are also affected by raw material abundance and quality (Bamforth, 1986; Beck and Jones, 1990; MacDonald, 2008; Andrefsky, 2009). Put simply, the decision to continue resharpening, refurbishing and reusing a stone tool as it wears out is highly conditioned by the accessibility of materials of sufficient quality to make a replacement (Binford, 1980; Kelly, 1988; Blades, 2003; Andrefsky, 2008). For example, when residentially mobile groups – that is, groups who often move their primary residential unit from place to place – move from an area where good quality raw materials are abundant into areas where available raw materials are of lower functional quality, tools made from high quality materials are often not immediately replaced with functionally inferior local

materials upon damage or dulling, but tend to have a more of their potential used life extracted prior to discard. For instance, MacDonald (2008) examines the relationship between curation, and raw material quality and availability in a lithic assemblage from the Skink Rockshelter in West Virginia. In this area, the local lithic landscape is dominated by medium to low quality Kanawha chert. A much higher quality raw material, Upper Mercer chert, is available at outcrops and in secondary pebble form 60-85 km distance from Skink Rockshelter. Upper Mercer chert was brought into the area by residentially mobile groups in the form of retouched flake tools. Retouched flake tools were also manufactured at the site out of low quality local materials. However, archaeologically recovered flake tools made from non-local, high quality chert show signs of more extensive retouch than functionally similar tools manufactured from low quality local chert (MacDonald, 2008). The people using Skink Rockshelter were more apt to discard and replace retouched flake tools manufactured from functionally inferior Kanawha chert than to discard tools made out of superior Upper Mercer Chert and replace them with local, poor quality material.

Andrefsky (2008) combines materials provenance analysis with an assessment of blade resharpening levels to examine how resource availability conditioned curation of obsidian projectile points in logistical toolkits – toolkits designed for long distance resource procurement forays away from a base camp – at a camp site in southeast Oregon. Points made from obsidian sources within a two-day journey of the camp show minimal signs of resharpening and fall out of use as soon as they are broken. Points made from obsidian procured further away from the camp show signs of resharpening or reconfiguration into other tool types after damage (Andrefsky, 2008:200). Andrefsky

(2008) associates projectile points manufactured from more distant sources with logistical journeys over longer distances. During these longer trips, individuals would have been more likely to find themselves in parts of the landscape far from the residential camp or obsidian sources where material for fabricating replacement tools was available. Therefore, they were more apt to respond to tool breakage or the dulling of tool edges with repair, rather than discard (Andrefsky, 2008).

In some cases, tool curation will continue until a suitable source of material to manufacture replacements is at hand. This can result in recovery of assemblages of highly curated tools manufactured from exotic materials at quarry sites, a sign that hunter-gatherer groups may have come to these sites specifically to "retool" (Gramly, 1980; 1984).

4.3 Provenance studies and mobility

One of the most straightforward applications of raw material provenance data lies in the evaluation of hunter-gatherer mobility through reconstruction of the range over which material was transported between procurement and discard (Shackley, 1986[in Freund]; Roth, 2000; Evans *et al.*, 2007, 2010; Freund, 2012; Hull, 2012; Kirch *et al.*, 2012). However, such application must be done with the caveat that raw material transport distance is *indirect* evidence for human mobility. Without analysis of typological, temporal, and/or spatial data – which can be used to control for other transport mechanisms, like intergroup exchange – provenance data can only show that a piece of raw material travelled from point A (site of procurement) to point B (site of discard), not how it got there. When such information is lacking, and mobility patterns

have not been well established through other avenues, long-range mobility and exchange must be considered as potential transport mechanisms when provenance data indicates long-distance movement of lithic raw materials (Roth, 2000; Freund, 2012).

Roth's (2000) application of obsidian characterization data to reconstructing Archaic mobility patterns in the Tucson Basin of southern Arizona is a good example of this kind of provenance study. Roth (2000) hypothesizes declining mobility during the area's middle and late Archaic periods based on a drop in exotic obsidian at late Archaic sites relative to earlier middle Archaic sites – although he notes the difficulty in differentiating between long-distance direct procurement and exchange in middle Archaic contexts. In an innovative application of provenance data, Evans and colleagues (2010) carry out geochemical characterization of archaeologically-exploited chert from northern England to resolve patterns of what they describe as 'social partitioning of space' in the region. By demonstrating that chert from northern sources was poorly represented at southern sites within the study area, Evans *et al.* (2010) challenge the model of hunter-gatherer mobility proposed for the region in which inland and coastal groups were mobile in a north-south direction. Instead, their data support a model in which hunter-gatherers living in the northern and southern portions of the study area were socially distinct and moved from costal to inland sites during their seasonal round (Evans *et al.*, 2010).

Researchers should be cautious when selecting tools for provenance analysis to reconstruct group mobility. Attention to the effects of raw material abundance and quality on technology within a given research context is essential in selecting a raw material type and artifact sample set to focus on when addressing questions of mobility. For example, in areas where lithic raw material is abundant and of high quality, frequent

opportunities to replace damaged tools *could* lead to reduced curation of some tool types, making distance between sites of procurement and discard for these tool categories a poor indicator of overall group mobility. In areas where local raw materials are of poor quality for tool manufacture, the production of expedient, informal tools with little capacity for repair or repurposing might lead to a similar reduction of curation, with the same results for the meaningfulness of provenance data for reconstructing group mobility. Formal tools recovered from contexts in which a certain degree of raw material stress was in effect make good candidates for sourcing to reconstruct mobility, as they are more likely to be highly curated. Formal artifacts that were potentially obtained through exchange should also be avoided in provenance studies aimed at reconstructing mobility.

4.4 Quartz as toolstone

As mentioned above, to be of any use in the manufacture of stone tools, lithic raw materials have to fracture predictably during knapping (Goodyear, 1989; Nelson, 1991:76; Reher and Frison, 1991; Seeman, 1994). The fracture mechanics of quartz crystals are determined to an extent by their chemical structure, described in section 3.3. Interhelical planes running parallel to the long axis of quartz crystals make it easier to achieve predictable fracture when force is applied in this direction (Reher and Frison, 1991). Force applied perpendicular to this axis often results in stepped fracture and the detachment of useless, blocky flakes (Reher and Frison, 1991). Force applied to large crystals of quartz can also be redirected by internal crystal defects or mineral inclusions, leading to failure in flake production during knapping (Reher and Frison, 1991). Additionally, its rigid crystal structure renders macrocrystalline quartz more brittle than

other materials used for tool manufacture, and less tolerant of misdirected force (Reher and Frison, 1991). Striking a quartz crystal in the wrong direction, with too much force, or with the wrong type of percussor can cause a crystal to shatter into a heap of useless debris. These factors combine to make crystal quartz a more difficult material to knap than more isotropic materials, such as obsidian or microcrystalline quartz (Reher and Frison, 1991). With practice, however, conchoidal fracture is possible in all directions on large, inclusion and defect-free quartz crystals (Reher and Frison, 1991).

Quartz formed under different conditions varies from poor to moderately high quality in terms of its utility as a raw material for tool manufacture. Pegmatite quartz generally forms in large, inclusion-free crystals. This type of quartz can be fashioned into both formal and informal tools by experienced knappers and is often incorporated into efficient core technologies (Blanton, 1984; Reher and Frison, 1991). Large crystals of pegmatite quartz are particularly well suited for manufacture into blade cores, as the crystal's mineral structure can facilitate blade flake removal when the striking platform is placed perpendicular to the crystal's long axis (Reher and Frison, 1991). Some fine-grained or massive hydrothermal quartz can also be knapped predictably and are suitable raw materials for fashioning most types of tools (Ballin, 2008; 47-48). Where relatively high quality hydrothermal or pegmatite quartz is available, it tends to be incorporated into hunter-gatherer toolkits according to its availability and group mobility in patterns similar to other moderately high quality raw materials. When it is abundant, it is generally used in the production of both formal and informal tools, which tend not to be extensively curated (Blanton, 1984; Ballin, 2008). When it is not abundant, it generally appears, if at all, in the form of highly curated formal tools (Reher and Frison, 1991).

In contrast to megacrystalline and fine-grained quartz, coarse-grained hydrothermal quartz has very poor flaking properties and is difficult to reduce into formal tools (Reher and Frison, 1991; Ballin, 2008:49). When aggregations of small quartz crystals, such as those making up hydrothermal quartz, are struck, fractures occur along grain boundaries, making controlled reduction of this type of material challenging for even the most skilled knapper (Reher and Frison, 1991). This places a rather obvious constraint on how this material can be incorporated into lithic technologies. Coarse-grained quartz tends to be manufactured into informal tools and is generally used expediently (Reher and Frison, 1991; Ballin, 2008:49).

In addition to material quality, deposit type can make quartz easier or more difficult to exploit as a lithic raw material (Ballin, 2004; 14; 2008:64-67). Quartz from pebble deposits, for example, is relatively easy to acquire; procurement of small amounts of material from these sources does not entail the use of special tools or great expenditures of effort, and could easily be embedded in other activities (Ballin, 2008:64). However, extensive quarrying of large deposits of hydrothermal or pegmatite quartz requires considerable planning and the use of specially prepared tools and equipment, meaning that procurement at these sources is technologically complicated, and likely direct (Ballin, 2004:12-13). At the Cnoc Dubh vein quartz quarry on the Isle of Lewis, for instance, scaffolding had to be built to allow access to the highest parts of the vein, while large hammerstones and wedges were employed to drive apart slabs of quartz (Ballin, 2004: 12). Both the infrastructure preparation and actual quarrying carried out at this site were labour intensive and necessitated importation of foreign materials to the quarry. It is unlikely that this type of behaviour would have been a component of a

casual, embedded procurement strategy. Such direct, intensive quartz procurement would strongly indicate that higher quality lithic materials were scarce or unavailable in the surrounding area.

In some archaeological and ethnographic contexts, quartz has been ascribed special material qualities and is used and/or recovered in ritual contexts (Reher and Frison, 1991; Meighan *et al.*, 2003; Ballin, 2008:66; Hanna, 2009). Gould and Saggers' (1985) ethnoarchaeological research demonstrated the lengths that hunter-gatherers will go to in order to procure ritually or socially significant lithic raw materials. Given these factors, it is possible that ritual or social importance attributed to quartz may have contributed to its incorporation into some hunter-gatherer toolkits.

4.5 Quartz in the Churchill River basin

Hydrothermal and, to a lesser extent, pegmatite quartz deposits are a common component of the rocky boreal shield landscape of the Churchill River basin (Wood, 1983:26). It is unsurprising, then, that quartz is a nearly ubiquitous component of archaeological lithic assemblages in the Churchill River basin, and tends to be the dominant raw material in most lithic tool classes (Dickson, 1983:124-152, 1980: 180-270; Hanna, 1975:49-57; Malasiuk, 2001:127; Pentney, 2002:154-162; Speidel and Syms, 2000). However, at many sites projectile points tend to be manufactured from chert (e.g. Dickson, 1980: 183-188). In general, deposits of lower quality hydrothermal quartz are more frequently encountered than sources of megacrystalline pegmatite quartz. Although high quality, non-quartz raw materials were incorporated into local lithic technologies, deposits of these materials in the study area appear to be rare. Chert tools

have been recovered at sites in the Churchill River basin (Malasiuk, 2001: 167). This material has much better knapping qualities than all but the highest quality pieces of quartz, making it a better raw material for the manufacture of tools, like projectile points, used in unpredictable, rapid resource encounters. However, chert likely had to be imported into the area from the distant Hudson Bay lowlands (Malasiuk, 2001: 167); there are no known chert procurement sites in the study area. Other materials found in lithic assemblages in the study area, like basalts and other pyroclastics were also likely imported (Malasiuk, 2001: 167). It should be noted, however, that without a full survey of the study area, the exact distribution of raw material sources remains unknown.

Quartz procurement behaviour in the Churchill River basin is poorly understood. Quarry sites are recorded in reports from surveys carried out in the basin (Dickson, 1972; Meyer and Smailes, 1975; Wilson and Light, 1980; Pentney, 2002) but few have undergone archaeological investigation beyond mapping and surface collection. Both hydrothermal and pegmatite quartz sources were exploited by toolmakers in the Churchill River basin (Wilson and Light, 1975; Hanna, 2002; Pentney, 2002). Quarries exploiting hydrothermal veins of quartz tend to be small, and the material produced of relatively low quality for flintknapping, indicating that this material was primarily exploited for the manufacture of informal, expedient tools. In contrast, quarries exploiting deposits of pegmatite quartz tend to be large (>1 m in smallest dimension) or consist of multiple smaller excavation features (Brownlee *et al*. 2008; 2010; ten Bruggencate *et al.*, 2013). These quarries are characterized by macrocrystalline to megacrystalline quartz, which could be considered of moderate to high quality for the purposes of flintknapping.

Excavations have been carried out at two pegmatite quartz quarries in the Churchill River basin, HbMd-4 (Grandfather) and GcNc-1 (Pickerel Bay). Attribute and mass analyses have been carried out on debitage recovered from Grandfather quarry, and indicates manufacture of formal tools at this site, in spite of the material's moderate quality (Beardsell, 2013). Use of this material in formal tool production strongly implies scarcity of higher quality raw materials in the area. Such scarcity is also implied by the implementation of bifacial reduction at the quarry – an efficient strategy employed to create useful packages of raw material that are highly curateable (Andrefsky, 1994b). Given this, it is probable that formal quartz tools were manufactured at Grandfather quarry with relatively long-term curation in mind, as material to manufacture replacement tools would have been difficult to come by. Provenance data from formal quartz tools manufactured from pegmatite quartz should be a good indicator of procurement range, therefore, as these tools were likely carried for longer periods of time, and would be more likely to be discarded in an exhausted form away from their quarry of origin.

The social or spiritual significance of quartz to ancient toolmakers in the Churchill River basin is currently not well understood. Quartz and quartz procurement sites definitely have special meaning to modern populations in the region. For example, quartz is incorporated into rattles used in sweat lodge ceremonies, due to its tendency to spark when two pieces are struck together (Hanna, 2009). Furthermore, two of the quartz procurement sites sampled for this dissertation are associated with important stories for members of the Granville Lake community. However, this is extremely tenuous evidence for attitudes of archaeological populations in the Churchill River basin toward quartz and its quarrying. The recovery of a hammerstone smeared with ochre – which is often

applied to spiritually significant objects or human remains in archaeological contexts (Bishop and Smith, 1975:58; Nicholson and Nicholson, 2007) – inside the Grandfather quarry pit during excavations in 2009 lends some support to the idea that quarrying may have been viewed as more than just an economic activity. Again, however, this evidence is tenuous. For the purposes of interpreting the data presented in this thesis, the spiritual significance of quartz to toolmakers in the Churchill River basin will not be discussed further.

5.0 Materials

5.1 The Granville Lake and Lac La Ronge Quarries

One approach to developing a lithic raw material characterization technique begins with analyzing samples obtained through controlled collection from known archaeologically exploited raw material sources. From these analyses, it is determined which, if any, physical or chemical parameters can be used to distinguish between samples from different sources. This approach, in contrast to cluster analysis of chemical data from unprovenanced artifacts, has the added benefit of providing the researcher with a partial database of 'fingerprinted' sources against which any subsequently obtained artifact or quarry data can be compared.

To develop a technique for characterizing igneous quartz, samples from several known quarry sites in the Churchill River basin of Manitoba and Saskatchewan were obtained. Quarry sampling was carried out over the course of two field seasons (2007, 2009) as part of the Social Sciences and Humanities Research Council of Canada-funded Granville Lake quarries project. This project began in 2006, when Kevin Brownlee, Curator of Archaeology at the Manitoba Museum, was invited to document oral histories, cultural landscapes, and ancient heritage in the traditional territory of the *Asiniskaw Ithiniwak* (Rock Cree) in the Granville Lake region of the central Churchill River drainage basin. During this documentation, several culturally significant heritage sites were made known to him, including three major quartz quarries that have remained spiritually and socially important to the community (Brownlee *et al.*, 2008). These quartz quarries, which were utilized prior to European colonization, are the largest recorded within the western boreal forest of Canada (Brownlee *et al.*, 2010).

In 2007, the Granville Lake quarry project interdisciplinary team was assembled to research the archaeology, geology and ethnohistory of the quartz quarries in the Granville Lake area and surrounding portions of the Churchill River basin. I joined this team formally at the commencement of my doctoral studies in the Fall of 2008, one year after the first quarry samples from the Churchill River basin were obtained.

During the 2007 and 2009 Granville Lake quarry project, 17 quartz extraction sites were visited and sampled. Early bulk analyses of quartz collected through the project (described in sections 6.3.1.1 and 6.3.1.2) included samples from all of these potential sources. However, during later stages of technique development, a more streamlined research design was adopted. Analysis was restricted to samples taken from 'major' quarries. For the purposes of this research, a major quarry is defined as one in which material extraction features are

- larger than 1m in their smallest dimension (i.e. length, width or depth) and/or,
- are comprised of multiple archaeological resource extraction excavations within a 50m radius.

These criteria were chosen to focus analysis on quarries exploiting large quartz deposits, which, in the Granville Lake region tend to be composed of relatively high-quality pegmatite quartz. This strategy has two advantages. First, ensuring the quarry sample is composed of only pegmatite quartz considerably simplifies the development of a sourcing technique, as processes involved in only one type of formation environment have to be considered when selecting potential characterization parameters. Second, the decision to focus on larger quarries, with their greater individual potential to supply raw

materials for toolmakers in the area, was also made to increase the chance of a positive match with the artifact sample.

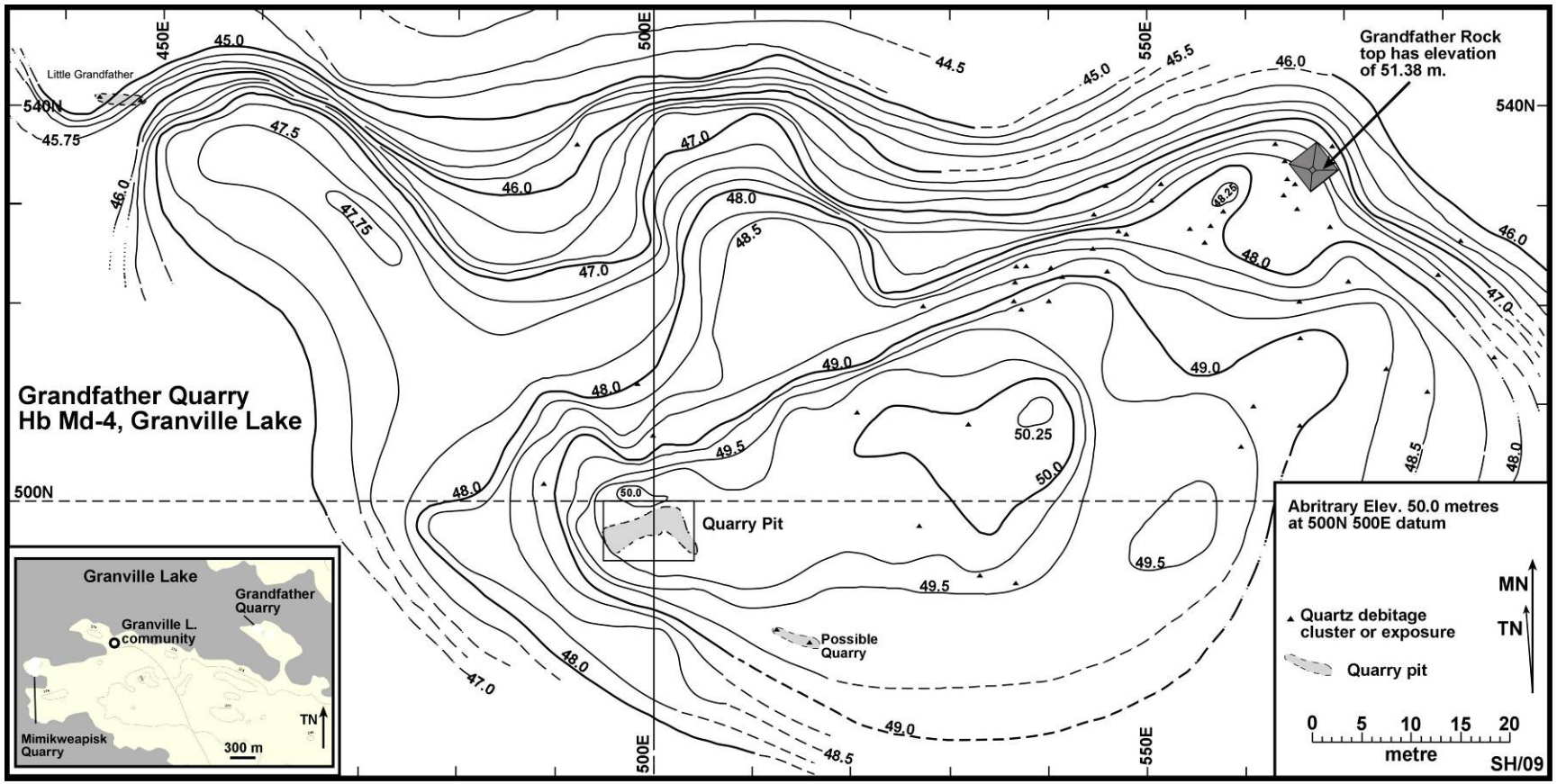
The following sections will consist of a brief description of all of the quartz extraction sites sampled during the 2007 and 2009 field seasons. To respect the wishes of the community leaders and participants of the Granville Lake quarry project, UTM coordinates or other information which would provide readers with the exact geographic location of the extraction sites visited are omitted. All of the Granville Lake extraction sites are located within the 'Granville Lake quarry district' depicted on Map 1.1.

5.1.1 Grandfather quarry (HbMd-4)

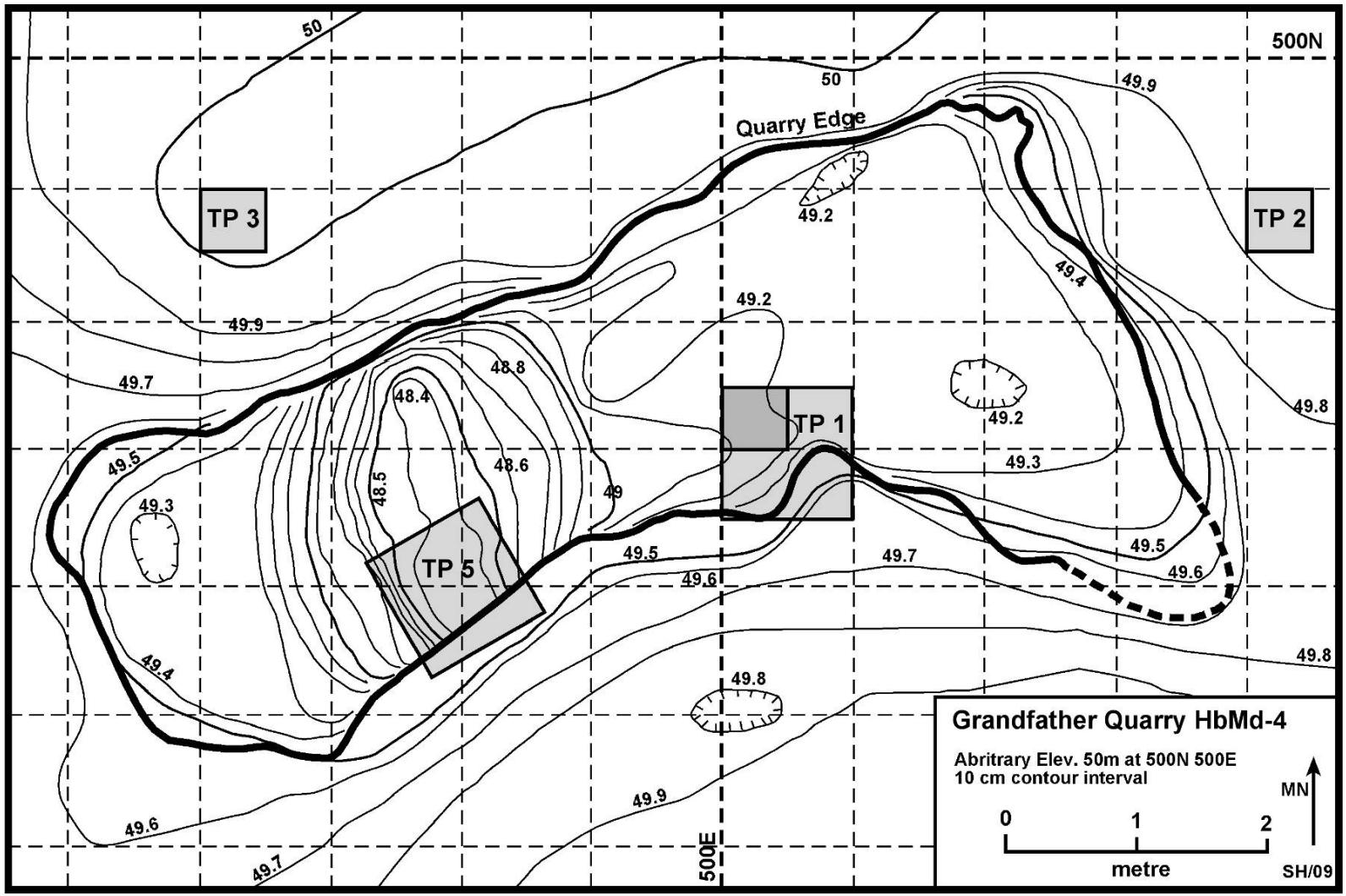
Grandfather quarry is located on top of a rocky prominence to the east of the community of Granville Lake. The name of the quarry is derived from the presence of a large glacial erratic to the northwest of the quarry. In the oral history of the *Asiniskaw Ithiniwak*, this rock, known as the Grandfather, is a man turned to stone to forever watch over nearby Granville Lake (see Map 5.1). The main pit at Grandfather quarry consists of an excavation into a metasediment-hosted pegmatite deposit measuring approximately 12 m long, at least 2 m deep, and 4 m across at its widest point (Map 5.2). To the south of the quarry pit is a much larger depression in the bedrock which may constitute more extensive quarry workings, however this has not been confirmed by excavation (Map 5.1). The main quarry pit has become infilled with a mixture of vegetation, soil matrix, quartz fragments weathered from the quarry walls, quartz debitage, quartz tools, and a number of probable schist anvils and hammerstones (see Figure 5.1). The quarry pit is surrounded on all sides by extensive scatters of quartz debris and debitage, which were

exposed by forest fire activity at the site roughly 20 years ago. In 2007, numerous test pits were placed around the man quarry pit, and one was placed inside the quarry itself (Map 5.2). A more thorough excavation of the quarry interior was carried out during the 2009 field season. Two 1 m^2 excavation units were placed within the quarry pit (TP 1 and TP 5 on Map 5.2). Due to the inward slope of the interior quarry wall on the south wall of unit 1, an additional 1 m x 0.5 m unit was opened directly to the north (the north half of TP 1 on Map 5.2). Debitage and other artifacts recovered through these excavations were transported to Winnipeg and housed at the University of Manitoba. Compared to other known quarries in the Granville Lake district, Grandfather quarry is both large and geologically complex. The inner walls of Grandfather quarry are made up of large crystals of feldspar, mica, smoky quartz, and white quartz (Figure 5.2, Maps 5.3-5.8). Additionally, quartz from the walls of Grandfather quarry shows varying degrees of banding, caused by fluid inclusions. In the metasediment host rock surrounding the quarry pit, distinct generations of quartz can be seen crosscutting each other, and it is highly probable that multiple generations of quartz contributed to the material extracted from Grandfather quarry.

A number of radiocarbon and optically stimulated luminescence dates have been obtained from Grandfather quarry. These are presented in Appendix 7.



Map 5.1 Large scale view of Grandfather Quarry. Note positions of the possible quarry SE of the main pit, and Little Grandfather (top left) and *Mimikweapisk* (inset) quarries



Map 5.2 Close up view of main pit at Grandfather quarry. Note position of test pits and excavation units.



Figure 5.1 Photo of Grandfather pit facing west. Note debris and vegetation infilling of quarry pit and quartz debris scatter surrounding pit.

5.1. 2 Little Grandfather quarry

Little Grandfather quarry is located roughly 70m to the northwest of the main quarry pit at Grandfather quarry (Map 5.1). Much smaller than nearby Grandfather quarry, Little Grandfather consists of three approximately 1m x 1m x .5m excavations into an outcrop of metasediment-hosted pegmatite quartz. The excavations at Little Grandfather are oriented roughly 30˚ from the vertical on a north-facing slope leading down into Granville Lake. For this reason, they were not infilled with soil. Both smoky and clear quartz are exposed in the walls of two of the extraction features making up Little Grandfather quarry. The western most pit presently only contains white/clear quartz. Given the proximity of Little Grandfather to Grandfather quarry, it is likely that quartz deposits at these sources are related.

5.1.3 *Mimikweapisk* quarry (HbMd-5)

The second largest of the known quarries in the Granville Lake quarry district is known in Cree as *Mimikweapisk* quarry. This quarry is located on a rocky promontory adjacent to the community of Granville Lake and consists of eight caves excavated into a metasediment-hosted pegmatite deposit (see inset in Map 5.1). These caves are distributed on three levels down the face of the promontory. Some of the caves have become infilled with soil matrix and vegetation, while one cave on the bottom-most terrace is usually flooded (Figures 5.3-5.5)

The caves of the *Mimikweapisk* quarry are recorded in local oral history as the former home of the *Mimikwesiwak*: small, forest-dwelling creatures with fish-like skin. It is said that the *Mimikwesiwak* lived in the caves at *Mimikweapisk* until contact with

Europeans. Disgusted by the poor manners of Europeans visiting the nearby community of Granville Lake, the *Mimikwesiwak* decamped for Manitou Island, an island in Granville Lake less frequently visited by human beings of any descent (Brightman, 2007:130).

Quartz exposed in the quarry walls at *Mimikweapisk* is predominantly rose, interspersed with small veins of opaque white quartz. Like Grandfather and Little Grandfather quarries, there is no known habitation or workshop site associated with *Mimikweapisk* quarry, and no diagnostic artifacts or debitage have been recovered. Organic materials suitable for radiocarbon dating have not been recovered from *Mimikweapisk* quarry, either, making it impossible to temporally situate quartz procurement activities at the site.

5.1.4 Wheatcroft quarry (HbMd-13)

Wheatcroft quarry consists of three depressions excavated into metasediment-hosted deposits of pegmatite quartz spread over a roughly $17m^2$ area (Map 5.9). The northernmost of these depressions had become infilled with soil, quartz debris, and vegetation, which had to be removed to expose the quarried area (Figure 5.6). The quartz from this depression is opaque white. The other two depressions at Wheatcroft quarry produce quartz similar in appearance to material from *Mimikweapisk* – namely, large crystals of rose quartz interspersed with small veins of opaque white quartz. These depressions had become partially infilled with soil and quartz debris.

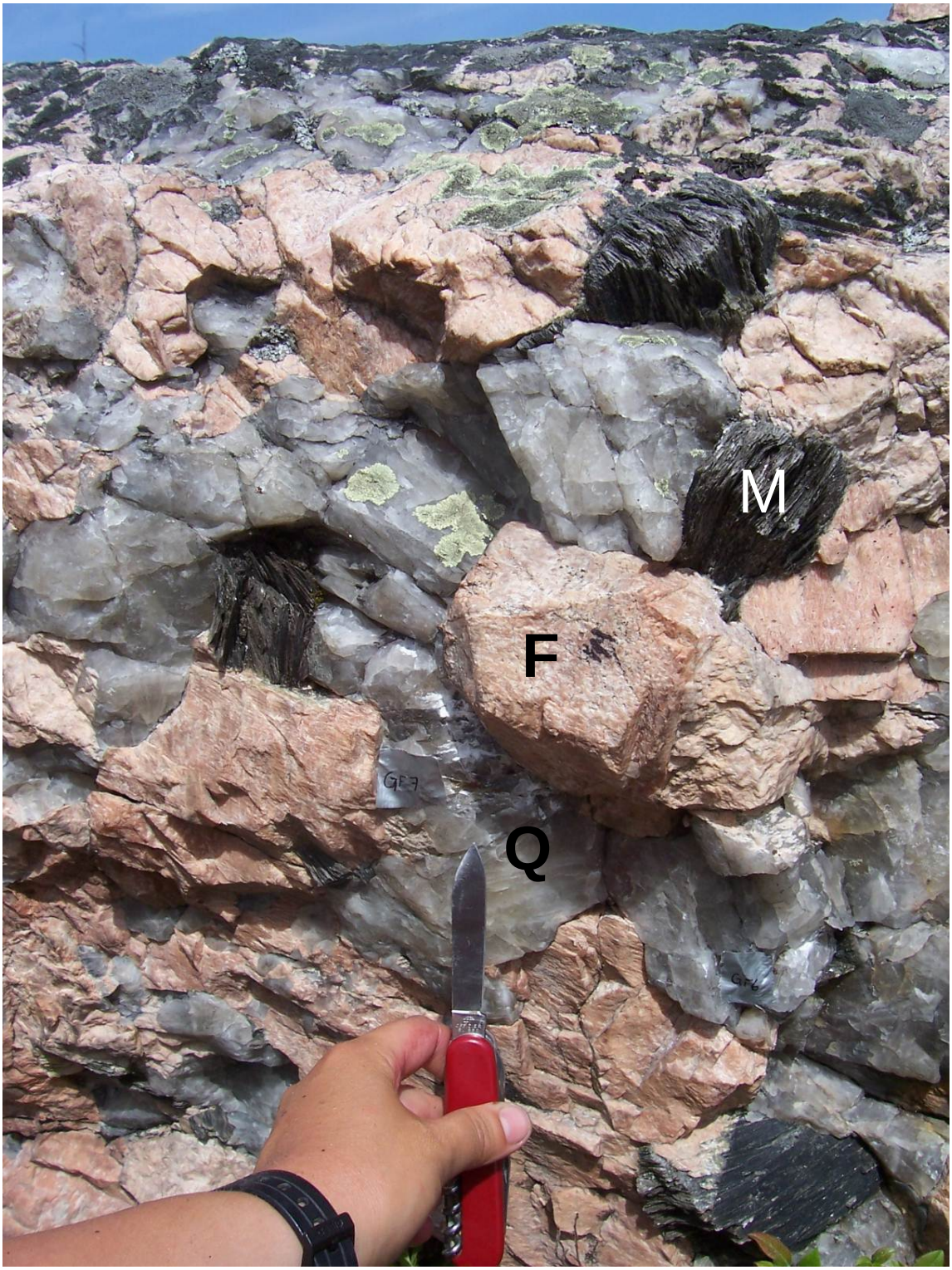
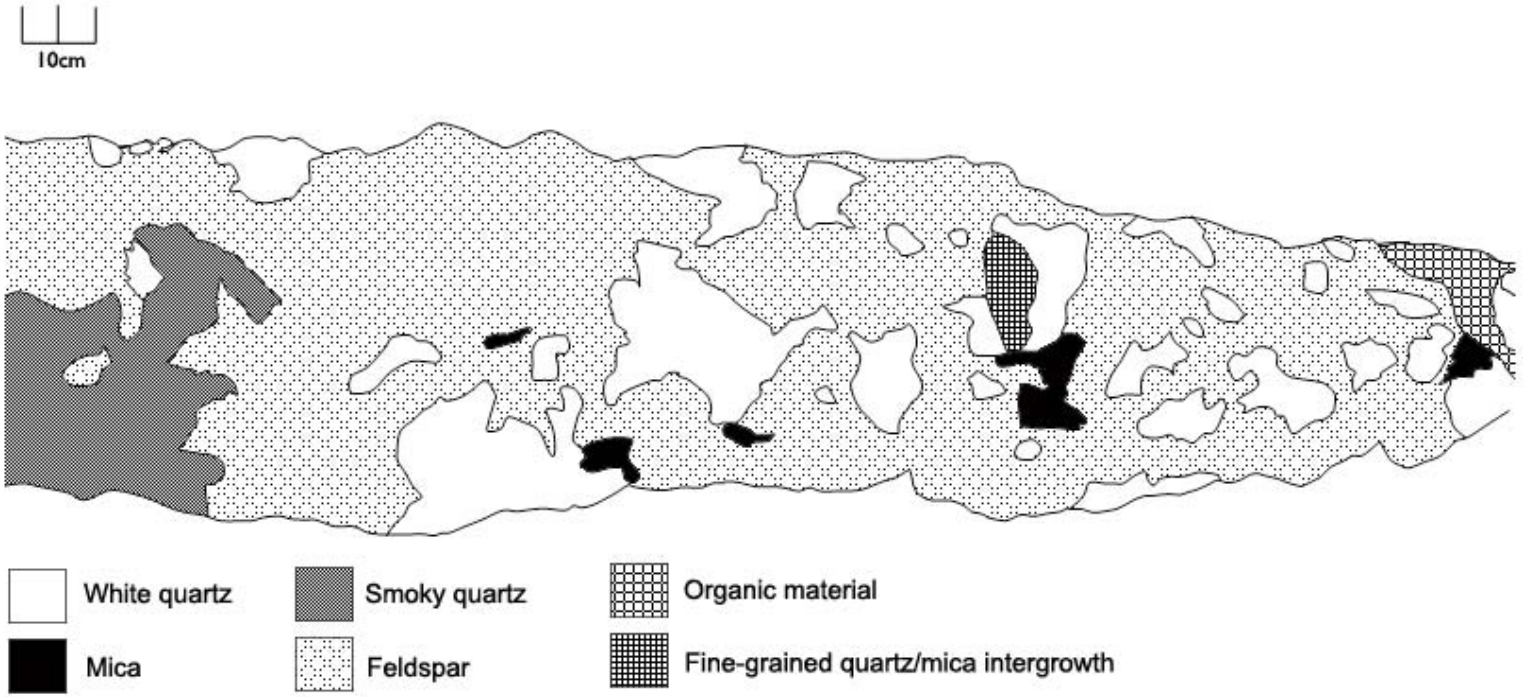
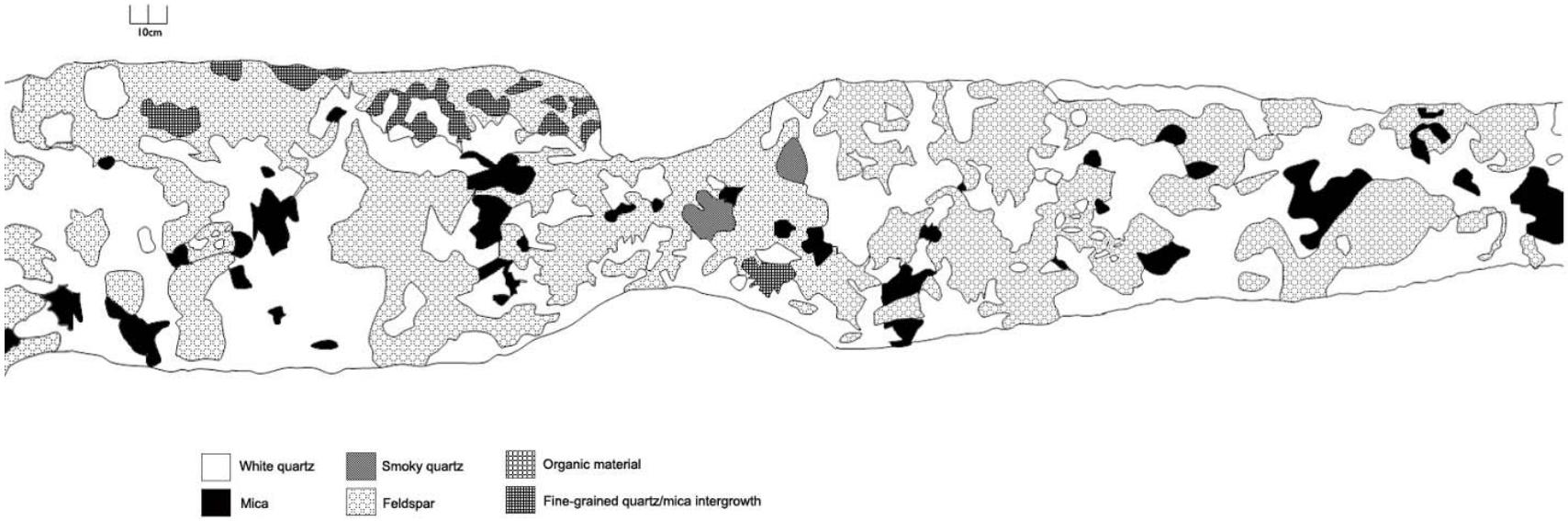


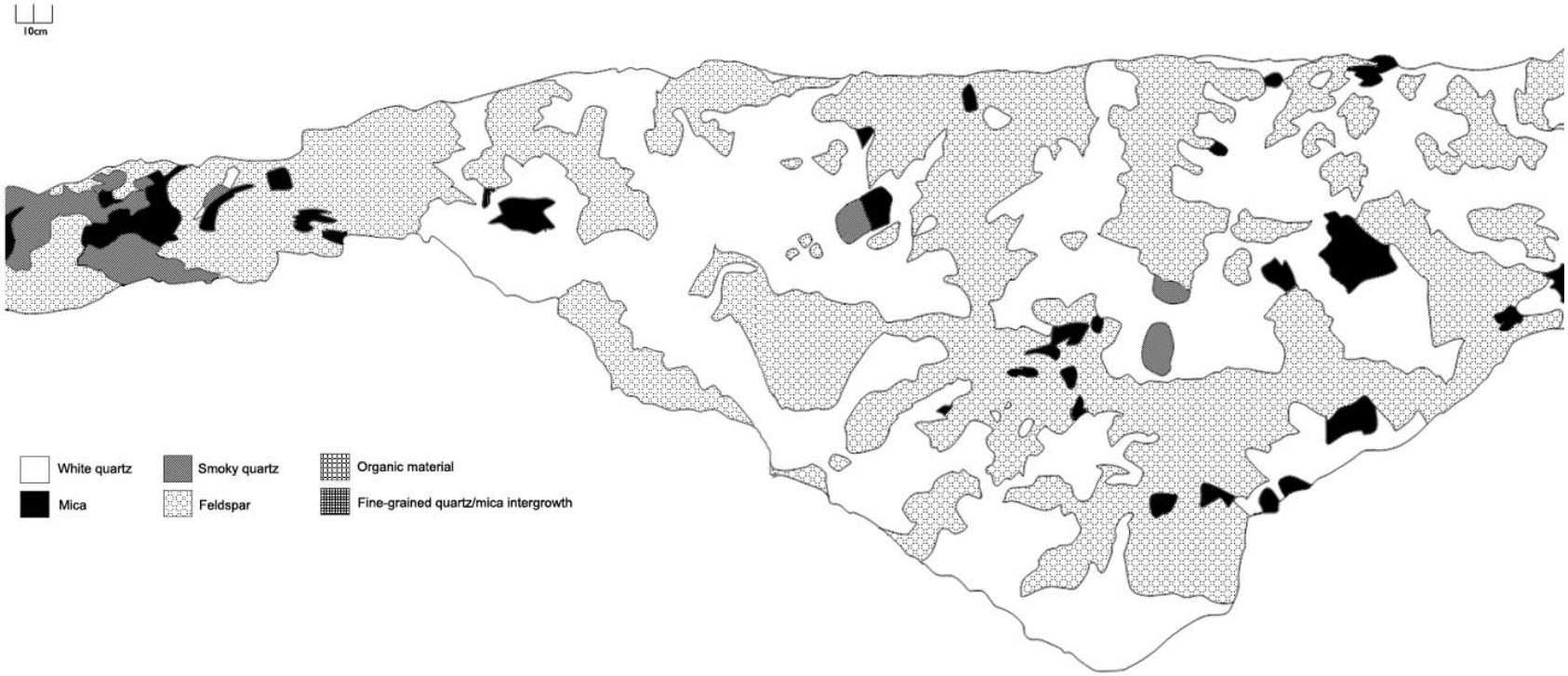
Figure 5.2 Photograph of inner wall of Grandfather quarry pit showing quartz (Q) with feldspars (F) and mica (M)



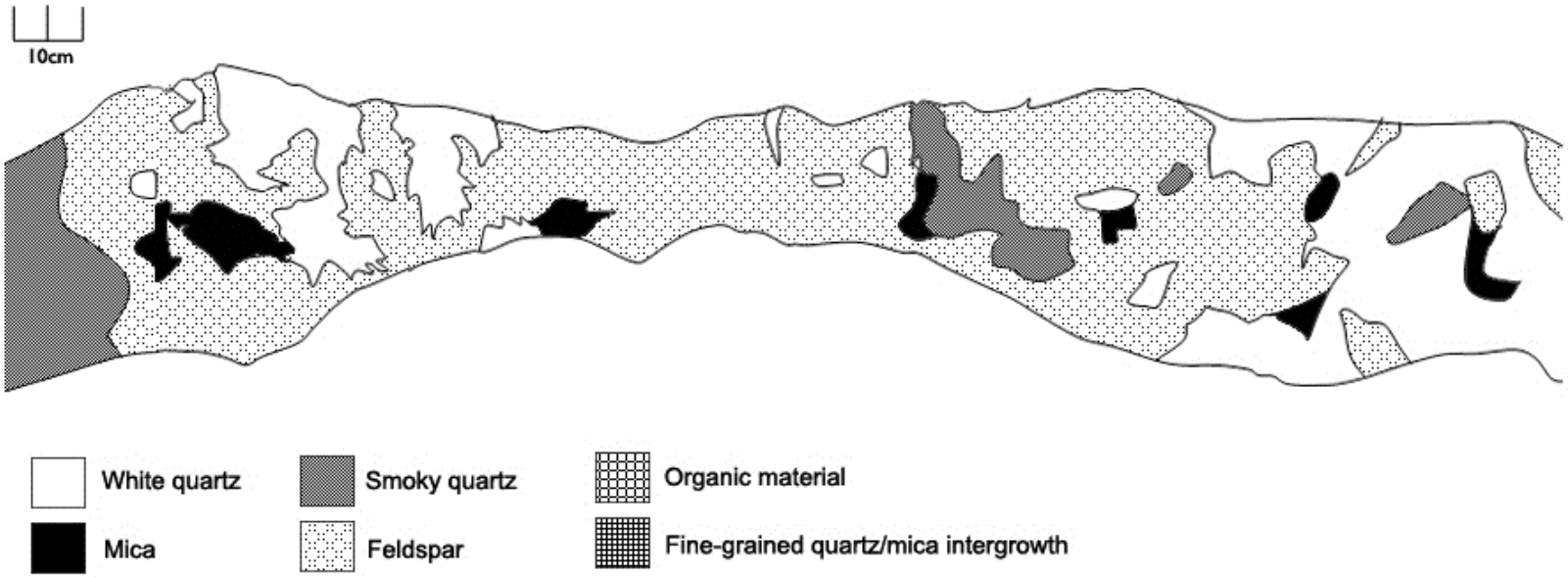
Map 5.3 Sketch map of interior east wall of Grandfather quarry pit



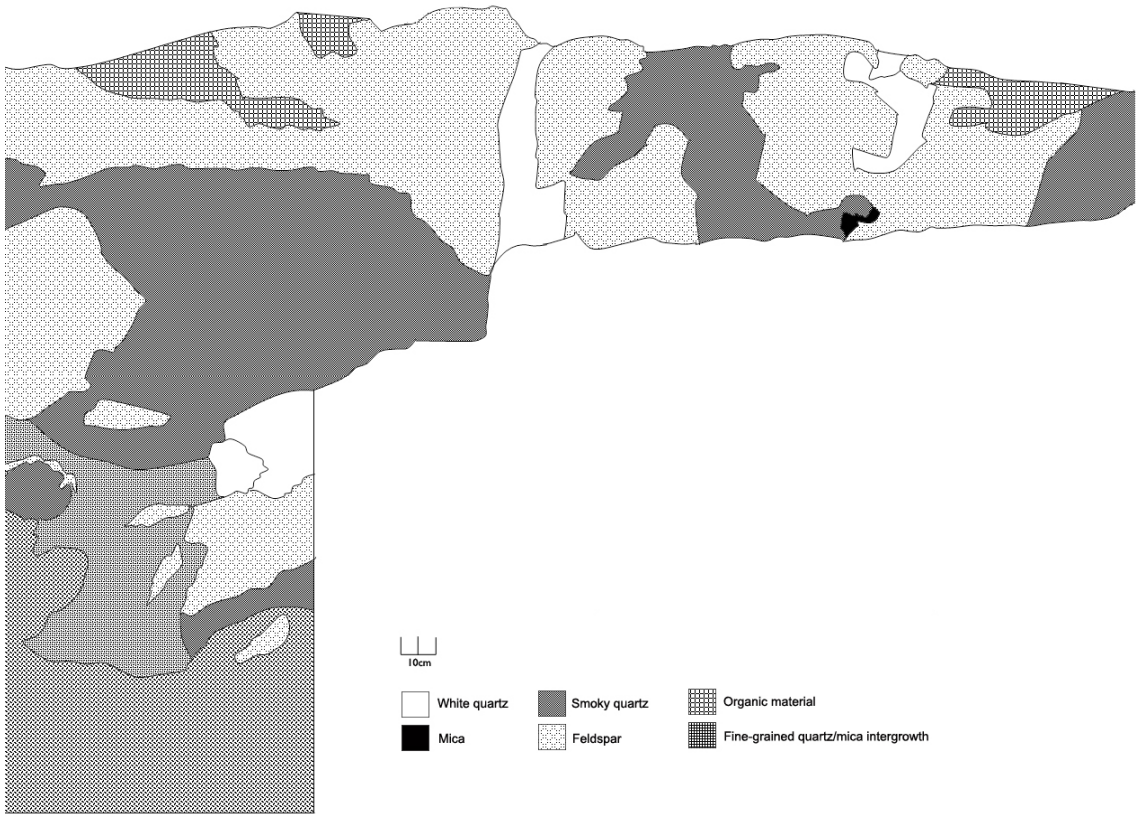
Map 5.4 Sketch map of the east half of interior north wall of Grandfather quarry



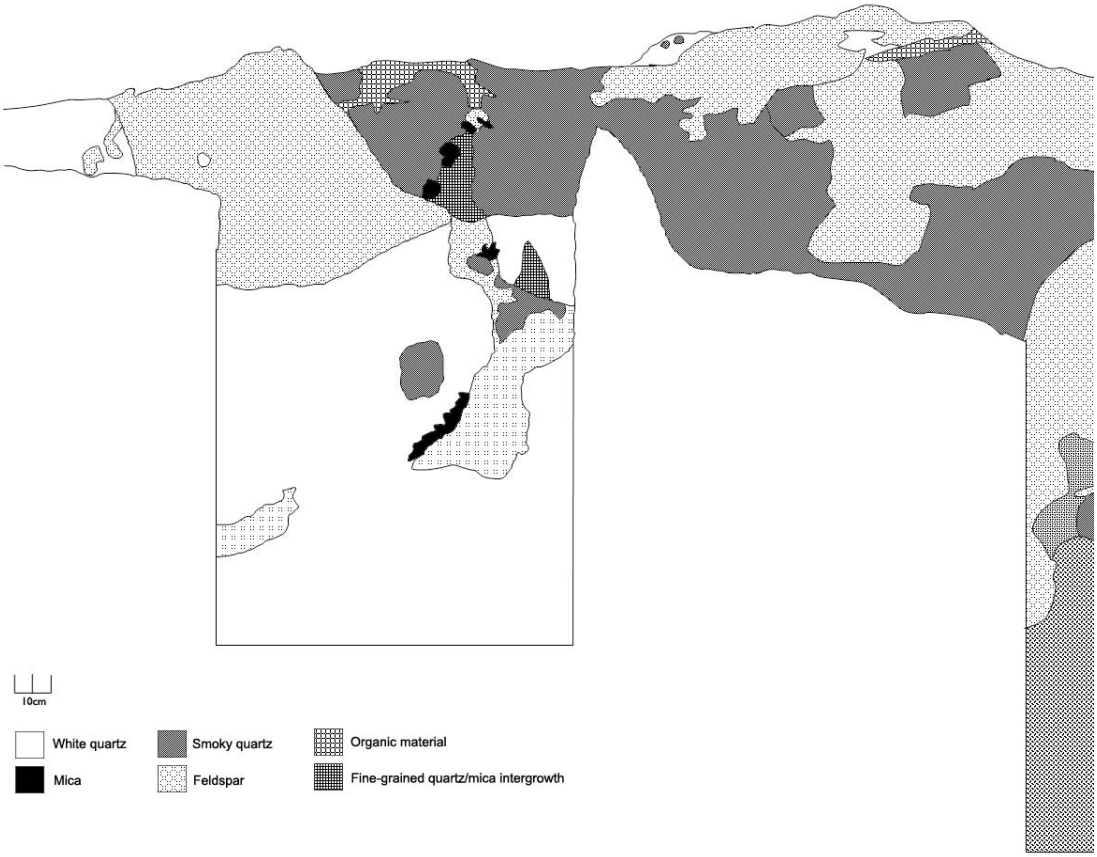
Map 5.5 Sketch map of the west half of interior north wall of Grandfather quarry



Map 5.6 Sketch map of the western interior wall of Grandfather



Map 5.7 Sketch map of west half of south interior wall of Grandfather quarry



Map 5.8 Sketch map of eastern half of interior south wall of Grandfather quarry

5.1.5 Floating Island Bay quarry (HcMe-2)

Floating Island Bay quarry exploits a deposit of pegmatite quartz located on the side of a steep ridge on a peninsula jutting into Granville Lake. The quartz outcropping at this quarry is almost entirely composed of large crystals of smoky quartz, although some small deposits of opaque white quartz are present. The quarry itself is composed of a vertical rock face, with an overhang created by quartz procurement activities (Figure 5.7).

5.1.6 Smoky Quartz quarry (HcMe-1)

Smoky Quartz quarry is located on the opposite shore of the same peninsula as Floating Island Bay quarry. Smoky Quartz quarry is similar to Floating Island Bay quarry in that the main extraction feature at the site takes the form of a flat exposure composed predominantly of smoky quartz (Figure 5.8). Several potential smaller quarry pits were identified up the hill to the south of this main quarry feature, where deposits of smoky quartz appeared to have been pecked away (Figure 5.9). These pits had become infilled with soil and quartz debris, which had to be removed prior to sampling.

5.1.1.7 Pickerel Bay quarry (GcNc-1)

Pickerel Bay quarry is located on the west-facing side of a peninsula jutting into the eastern waters of Lac La Ronge in north-central Saskatchewan (Map 1.1). This site was originally excavated and reported on by Dr. Margaret Hanna of the Royal Saskatchewan Museum in 2002. The quarry consists of a roughly 1 m deep pit excavated almost vertically into a deposit of pegmatite quartz underlying a thick feldspar overburden (Hanna, 2002:42). Prior to excavation in 2002, the quarry pit was infilled with soil and 'an extensive and thick layer of lithic debris' (Hanna, 2002).



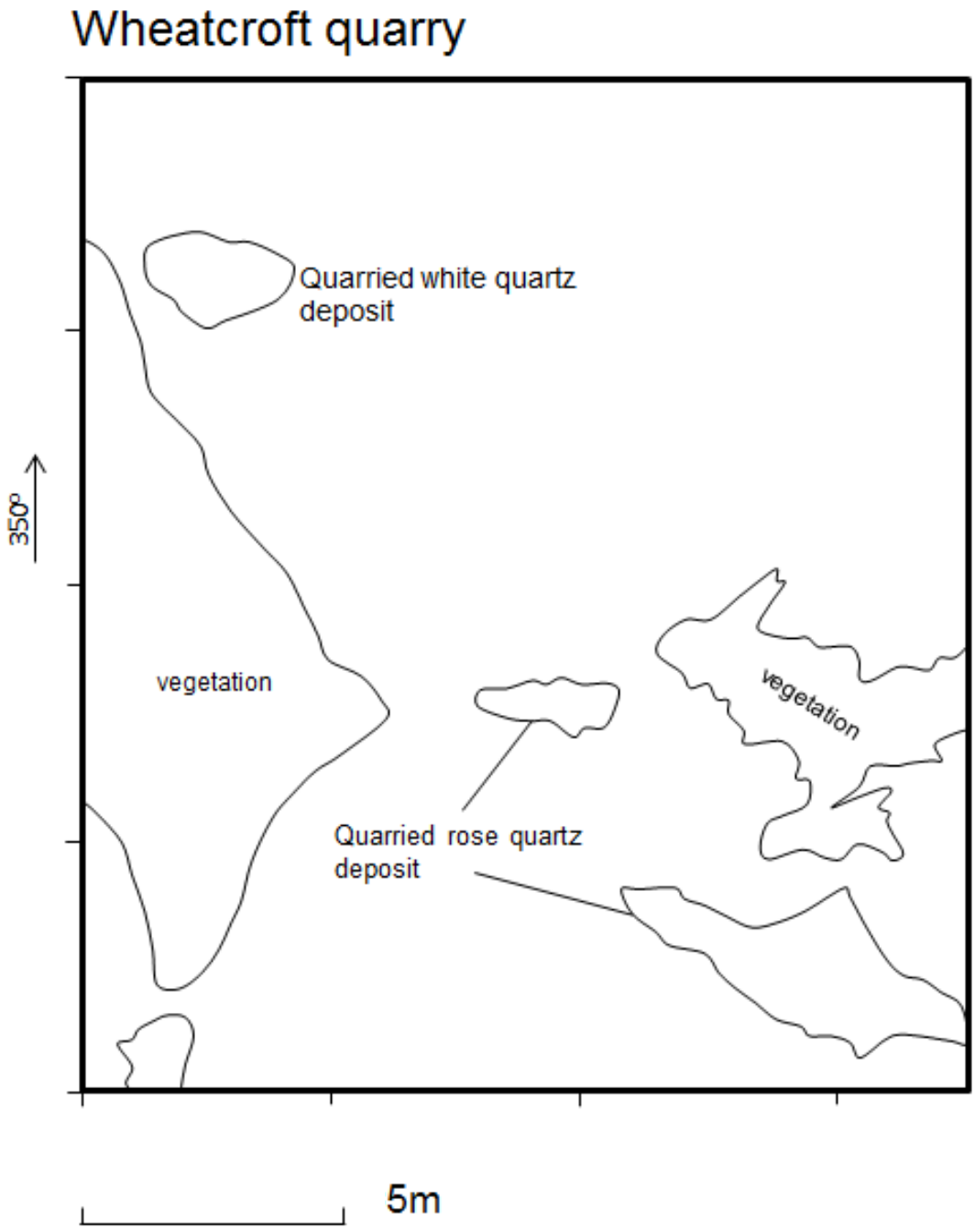
Figure 5.3 Sampling at *Mimikweapisk* 2009. Note cave HR-CM1 in right background.



Figure 5.4 *Mimikweapisk* cave HR-CM1



Figure 5.5 Flooded cave (FC) at *Mimikweapisk* quarry



Map 5.9 Sketch map of Wheatcroft quarry pits



Figure 5.6 The quarried white quartz deposit at Wheatcroft

Extending to the northwest of the quarry pit is what Hanna (2002:43) identifies as a triangular 'tailings-milling-lithic reduction area.' Artifact deposits in this area are primarily composed of quartz debitage; however, flaked quartz tools, and granite and schist cobble tools were also recovered. In contrast to quarries in the Granville Lake district, quartz procurement at Pickerel Bay is associated with a nearby habitation site where culturally diagnostic artifacts were recovered. These artifacts consisted of ceramic sherds from Clearwater Punctate and Laurel vessels (Hanna, 2002: 47). Culture phases associated with these vessel types date to 350-650BP and 700-900BP in north-central Saskatchewan, respectively. However, thermoluminescence dates in excess of 2500BP obtained from quartz debris in basal strata at the Pickerel Bay quarry itself indicate that quartz procurement at the site may have begun much earlier than this. Hanna (2002:48) hypothesizes that the Pickerel Bay quartz quarry was intermittently exploited over a long period of time during the precontact era. While the original report on the quarry at Pickerel Bay identifies the source of quartz exploited at the quarry as a vein, subsequent visits by a geologist have confirmed that the quartz at this quarry is part of a pegmatite deposit. Visually, quartz from Pickerel Bay is unlike quartz extracted from pegmatite deposits in the Granville Lake district; it is made up of much smaller individual crystals of quartz, giving it a more opaque, grainy appearance. Upon petrographic analysis, quartz from Pickerel Bay shows signs – such as straining of quartz crystals – of having undergone metamorphism (Figure 5.10), which is not the case for quartz from the Granville Lake quarries.



Figure 5.7 The quarried smoky quartz deposit at Floating Island Bay quarry



Figure 5.8 Vertical exposure of quartz at Smoky Quartz quarry



Figure 5.9 Sampling of quarry pit at Smoky Quartz quarry

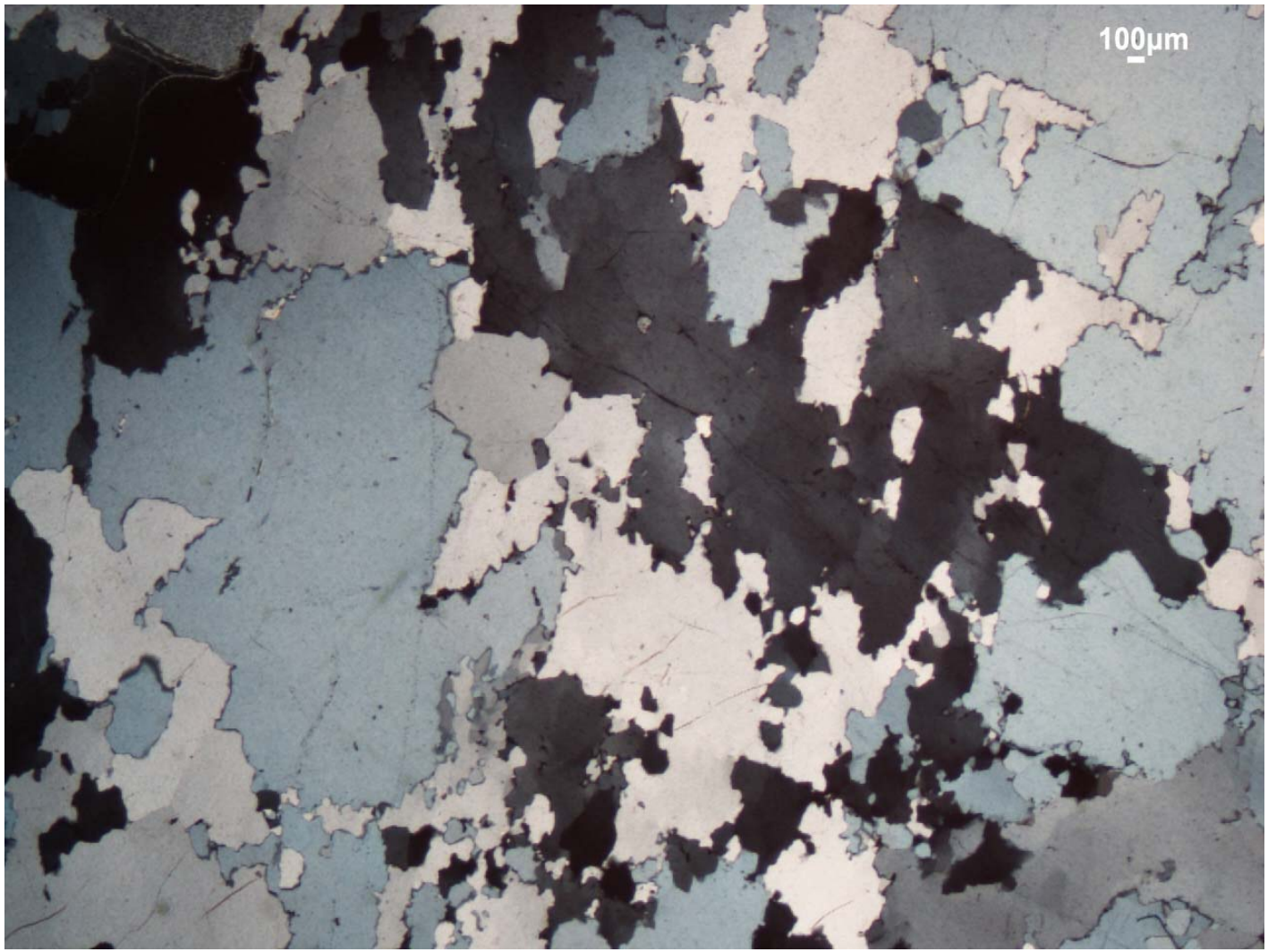


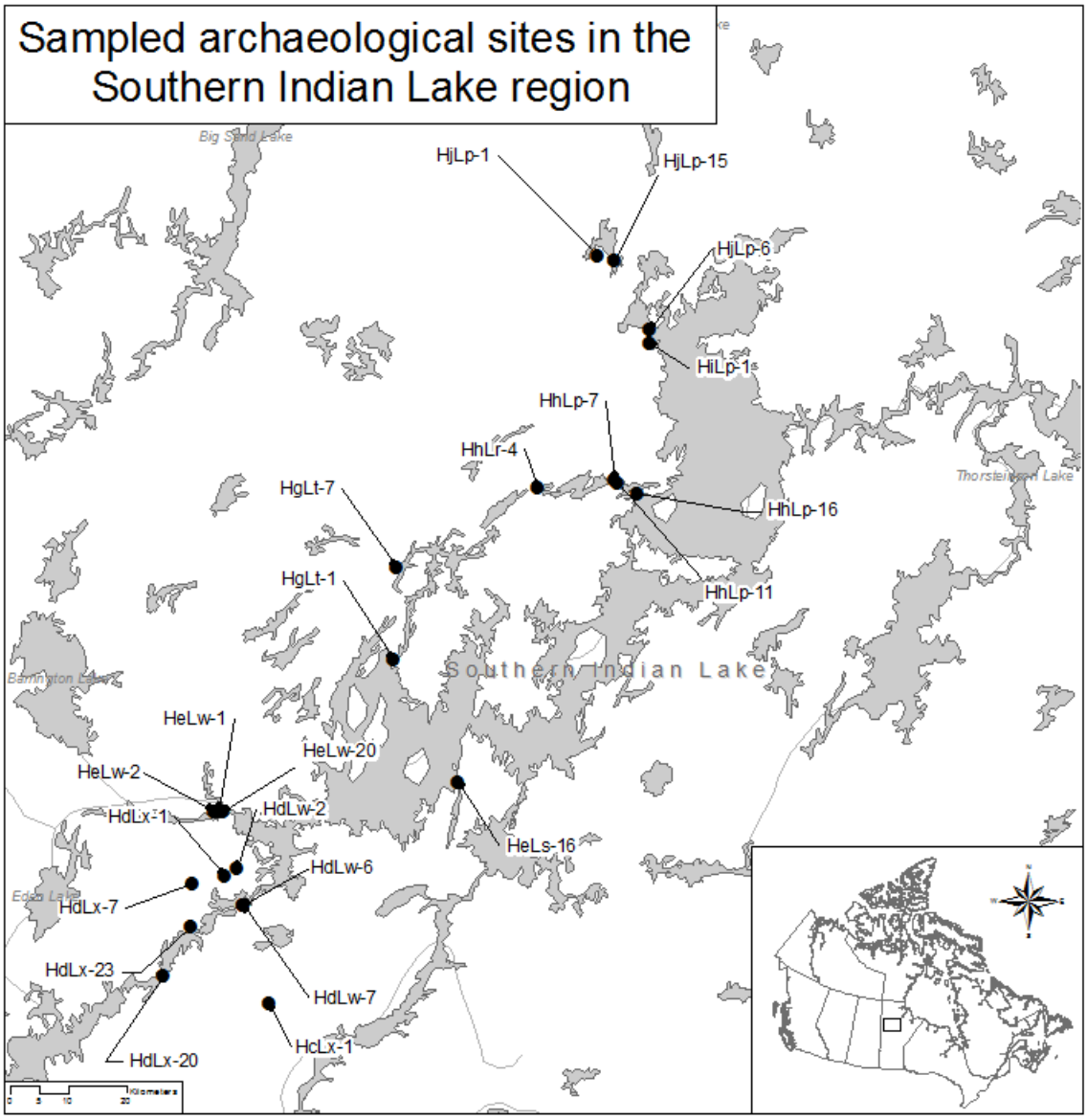
Figure 5.10 Pickerel Bay quarry sample SW2-02 viewed in thin section

5.2. Archaeological sites

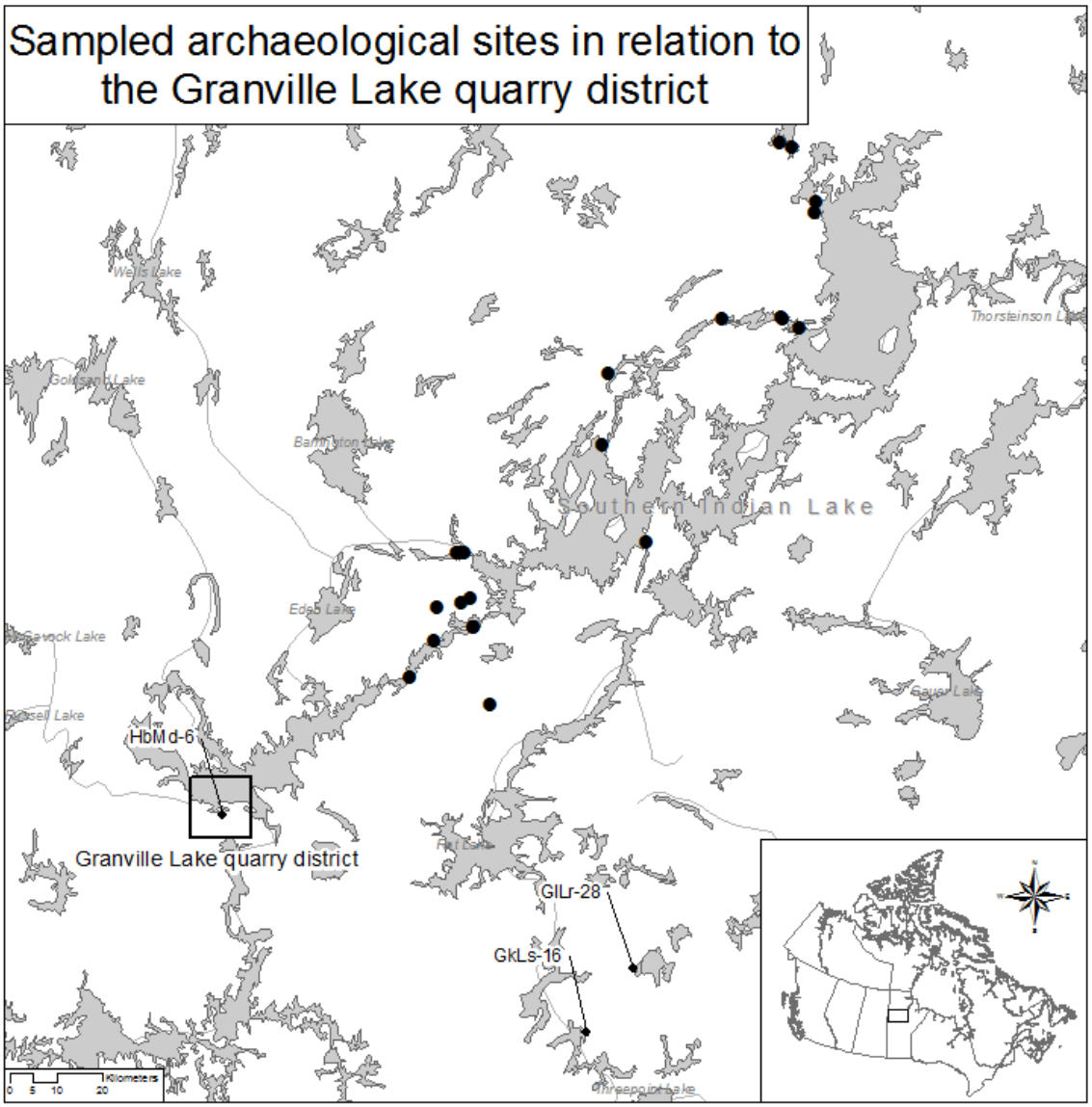
The following section will consist of a brief description of the sites from which artifacts were selected for analysis as well as the artifacts themselves. These archaeological sites were primarily identified during the different stages of the Churchill River Diversion Archaeological Project and lie within that project's study area around South Indian Lake, to the north of the Granville Lake quarry district. Unless otherwise noted, site details are taken from site report forms on file at the Manitoba Museum. Details of the artifact sample, including recovery and metric attributes are located in table form in Appendix 3.

5.2.1 HbMd-6 (*Wewe* Point)

HbMd-6 is the only site contributing to the artifact sample located within the Granville Lake quarries region. It is located midway between Wheatcroft and Grandfather quarries on the Laurie river, approximately 2km from Granville Lake. Both pre- and postcontact materials, including precontact ceramics, lithic tools, and metal artifacts were recovered from the site during survey and excavation in 2007 and 2008. *Wewe* point constitutes an interesting convergence between archaeology and toponomy in northern Manitoba; its name translates to 'Marriage Point.' During site testing in 2007, a Jesuit ring was recovered from the site, supporting oral histories indicating that it was a setting for marriage ceremonies for local residents.



Map 5.4: Archaeological sites in the Southern Indian Lake region providing artifacts for analysis.



Map 5.5: Archaeological sites providing artifacts for analysis in relation to the Granville Lake quarry district

5.2.2 HcLx-1 (Leaf Rapids Portage or Leaf Falls)

HcLx-1 is located at the portage around Leaf Rapids, at the southern end of Southern Indian Lake (Wood, 1983). This portage constitutes one of the few navigable paths into or out of Southern Indian Lake for those travelling by foot, sled, or canoe, regardless of season, as the rapids remain open during most winters. Survey and testing in 1969 indicated that the site was stratified and contained relatively early diagnostic

cultural material. The site was chosen for more thorough excavation under the CRDAP mandate. In total, 180 m^2 were excavated along the entire length of the portage. Precontact materials, including bifaces, scrapers, and Middle to Late Woodland ceramic sherds were primarily concentrated at the ends of the portage. Post-contact materials, including beads, clay pipe fragments, nails, and metal housewares tended to be concentrated at the centre of the portage. Hearth features were recorded throughout the site; an especially deep hearth was selected for radiocarbon dating. The date returned (160BP±90) was much younger than expected, placing the hearth's construction during the postcontact period.

The site was revisited in 1992 under the renewed CRDAP mandate of resurveying sites for eroding burials. No human remains were encountered, but an uncontrolled surface collection of the site yielded additional Middle and Late Woodland ceramic sherds, and stone tools including scrapers, a biface, a retouched flake and knapping debris. At the time of this last visit, Leaf Rapids Portage showed signs of 'considerable erosion due to flooding and damage by modern use'.

5.2.3 HdLw-2 (Bill Anderson site)

HdLw-2 was first identified during survey in 1969. The site is located on a southwest facing beach directly to the south of the junction of the Vermillion and Churchill Rivers. Surface collection at the site in 1969 and 1992 resulted in the recovery of both pre- and postcontact material culture including stone tools, lithic flakes, precontact ceramics, a gunflint, and chinking. HdLw-2 was also the site of a recent cabin belonging to the Anderson family of Leaf Rapids. According to a site update form filed

at the Manitoba Museum, the Bill Anderson site was 'considerably damaged by flooding' when last visited.

5.2.4 HdLw-6 (Rusty River Camp site)

The Rusty River Camp site is located on a high, relatively flat area on top of the northwestern tip of a long point north of the junction of the Vermillion and Churchill Rivers. When visited in 1992, it was noted that the area had been cleared and a cabin – belonging to one of the local community members participating in the survey – had been built on top of it. Activities associated with use of the cabin and the presence of dogs had caused some disturbance to the site, along with ongoing shoreline erosion. Artifacts associated with the modern era, the Fur Trade, the late precontact period, the Middle Woodland, and the Archaic period were recovered during uncontrolled surface collection at HdLw-6. In site forms filed at the Manitoba Museum, Riddle remarks that considerable subsurface cultural deposits likely remain at the site.

5.2.5 HdLw-7 (Broken Gear site)

HdLw-7 is located to the southwest of HdLw-6 on a point jutting into the Vermillion River close to its exit into the Churchill River. It is located on flat, high ground on the point behind a steep bank. Like many of the sites in the CRDAP area, erosion has impacted cultural deposits at HdLw-7, though site forms indicate that some subsurface material may remain at high points at the site. Uncontrolled surface collection at the site yielded metal, lithic and ceramic material culture associated with the Fur trade, the Woodland period, and the Archaic period.

5.2.6 HdLx-1 (Whacked in the Face)

Originally identified as three sites (SIL 9, 10, and 11), HdLx-1 is composed of 5 loci located on a small, south-facing stretch of shoreline at the point where the Island River joins the Churchill River just south of Fuller Lake (Dickson, 1972). The site was surface collected in 1969, 1992, and 2002. Recoveries included both pre- and postcontact artifacts including scrapers, bifaces, quartz debitage and cores, pre- and postcontact ceramics, ammunition, and metal scraps.

5.2.7 HdLx-20 (West Winter Road site)

HdLx-20 is located on a high, flat portion of the west bank of the Churchill River, approximately 3km upstream of the town of Leaf Rapids' fish processing plant. The site had at one time been cleared to form part of a now-abandoned winter road leading to Leaf Rapids, but was overgrown with poplar and spruce when it was visited by survey teams in 1992. Surface recoveries from the site consisted of non-diagnostic flaked and ground lithics and one piece of faunal material. No cultural affiliation could be attributed to the site due to the lack of diagnostic artifacts.

5.2.8 HdLx-23 (Roxy Stopped Here)

HdLx-23 is located on the east and southeast shore of the Island River just north of HdLx-1. The low, flat land on which the site is located had experienced some erosion when it was surveyed in 1992. Despite this erosion, the survey team was able to identify several fire pits and recover a number of lithic and ceramic artifacts, some of which were

diagnostic, placing at least one occupation of the site within the Terminal Woodland period.

5.2.9 HdLx-7

HdLx-7 is located on an island in the Churchill River roughly 10 miles north of the town of Leaf Rapids. The site consists of artifacts scattered along 20 m of the island's shoreline. Lithic artifacts were recovered through surface collection at the site in 1969; no cultural affiliation could be assigned as none of these artifacts were diagnostic.

5.2.10 HeLs-16

HeLs-16 is located on a south-facing mud beach on the east side of 42 Bay, just before it empties into Southern Indian Lake. The site shows signs of both recent use and archaeological occupations dating to the terminal Woodland period. Surface collection was undertaken at the site in 1992 and 1993. Precontact ceramic and lithic artifacts were recovered.

5.2.11 HeLw-1 (MacBride)

HeLw-1 falls within the MacBride-Barrington locale, one of the four locales initially selected for intensive archaeological investigation by the CRDAP (Hanna, 1975). MacBride-Barrington is located at the confluence of the MacBride and Barrington rivers, just over three kilometers northwest of the point where the Barrington River empties into Opachuanau Lake. The site is located on a point that forms the northern shore of the mouth of the Barrington River. A soil overburden entirely covers the bedrock underlying

the site, except at the very terminus of the peninsula on which the site is located, which consists of exposed bedrock.

HeLw-1 is the only site sampled for this analysis that was the subject of recorded excavations prior to the CRDAP. The site was visited by Wright (1971) during his 1965-1966 survey of the Southern Indian Lake region. At the site, Wright observed what he terms 'camp refuse' strewn about a 100 m x 20 m stretch of beach surrounding the point, and a large, exposed hearth feature (Wright, 1971:3). Wright excavated two units 4 m apart into this feature, recovering both precontact and postcontact material. These included decorated Woodland ceramics, flaked and pecked lithic tools, postcontact ceramics, and metal artifacts. Noting the collapsed stratigraphy of the feature, and the difficulty this presented for resolving the chronology of artifact deposition at the site, Wright collected two radiocarbon samples from the base of the hearth feature. These returned dates of 'post A.D. 1800 and A.D. 1590 ± 100'(Wright, 1971:3), which would associate the hearth feature with a late pre-contact and/or early to mid-contact period occupation of the site.

The site was visited again in 1969 by survey crews working for the CRDAP. Recovery of a large quantity of artifacts, including projectile points, from the shoreline and identification of an additional partially exposed hearth several meters inland during this survey resulted in HeLw-1 being chosen for further excavation. Two areas of the site, were chosen for this excavation: Area A, centred on the hearth feature, and Area B, located close to the beach near the rocky area of the point. Area A proved to be the more productive of the two areas; both pre- and post-contact artifacts were recovered from

Area A, including lithics, precontact ceramics, tin cans, a moccasin, a pair of doll eyes, leather pieces, and a musket ball. Area B was found to be sterile (Hanna, 1975).

The site was revisited in 1990 and 1993 by Mr. D. Riddle as part of the renewed CRDAP initiative to survey areas impacted by the Churchill Diversion for human remains and archaeological sites exposed by shoreline erosion. Riddle noted that the site had experienced erosion, but remained in overall good condition, although he was 'almost certain' that sport fishermen making recent use of the site have collected and removed artifacts.

Other temporal indicators at HeLw-1 include a projectile point indicative of Middle Woodland Laurel occupation of the site, and Late Woodland Clearwater Punctate sherds recovered during excavation in 1973 and surface collection in 1990.

5.2.12 HeLw-2 (Cabin site)

HeLw-2 is located on top of a terrace on the eastern tip of a point that forms the western boundary of the bay making up the Barrington-MacBride locale (Hanna, 1975). The area of the peninsula where HeLw-2 is located had been an island a few years prior to the 1969 CRDAP survey, when the channel running between it and the mainland became silted up and densely vegetated. This site was chosen for excavation because of dense deposits of lithic artifacts observed eroding out of terrace banks above the beaches of the peninsula during the 1969 pedestrian survey of the site. A grid of units was placed along a 48m transect oriented along the peninsula's long axis, from which 30 2 m^2 units were randomly selected for excavation. The five units located at the centre of this

distribution, immediately to the east of the cabin yielded the most artifacts, while the other units were nearly sterile.

Initial survey and excavation at HeLw-2 uncovered both pre- and postcontact artifacts, including rifle and musket ammunition, household items, a stone pipe bowl, unifacially retouched flakes, bifaces, projectile points, and late Woodland ceramic sherds. Additionally, four partial hearths were encountered by excavators in the central portion of the site. One of these was judged to be modern, based on the presence of tin foil fragments, while the other three were associated with lithic debitage, burned and calcined bone, ceramic sherds, and stone tools.

The site was revisited in 1990 by Riddle as part of the renewed CRDAP. During this visit, areas of the peninsula's beach that are now flooded in all but extremely low water years were surface collected. Ceramic sherds, lithic flakes, a scraper and a recent pin were recovered during this survey. A further reassessment and surface collection took place in 2002, both recent and precontact materials were collected.

5.2.13 HeLw-20 (Flicker site)

HeLw-20 is located on the northern shore of the MacBride river about a kilometer north of the river's exit into Opachuanau lake. The site is situated on a roughly 2 m high terrace behind a 20m wide gently sloping clay beach. The densest artifact concentrations were encountered between 5 and 15cm DBS in a 120m^2 area of the site. Hanna (1975:22) notes that the site shows no stratigraphy, preventing excavators from placing undiagnostic artifacts within a site chronology. Artifact recoveries from HeLw-20 included historic beads and ceramics, six side-notched projectile points, scrapers, a

biface, retouched flakes, a hammerstone, an antler spear or harpoon head, and a number of precontact ceramic sherds. Several hearths were encountered during excavation at HeLw-20, some of which were directly associated with artifact concentrations. No radiocarbon dates were obtained from these features (Hanna, 1975:23).

5.2.15 HgLt-7 (Onaykowow River Exit)

HgLt-7 is located on an eroded, southeastern- facing shoreline at the point where the Onaykawow River exits into Mulcahy Lake. The site is described in Riddle's field forms as in 'fair' condition, despite erosion. Recoveries made during uncontrolled surface collection in 1990 include Late Woodland ceramic rim sherds, lithic flakes, a stone knife, a spokeshave, and a combination end-side scraper.

5.2.16 HhLp-11 (Copper Thing site)

HhLp-11 is located on the northern and eastern shores of Nowan Island, located at the northwestern entrance to Shallow Lake. Prior to flooding caused by the Churchill River diversion, Nowan Island was connected to the mainland and located next to a series of rapids that have since been submerged by high water levels. Artifact deposits on both shores of the island consist of concentrations of precontact ceramics and lithics. Uncontrolled surface collection was carried out in 1990 and 1999. Recoveries included flaked lithic tools, such as bifaces and scrapers, flakes and cores, a flaked and ground trihedral adze, and Late Woodland ceramics. Recent use of the site is indicated by the recovery of a white plastic button.

5.2.17 HhLp-16 (Ken Macleod site)

HhLp-16 is located to the southeast of HhLp-11, on a northeast facing sand beach making up the western shore of a narrows joining Shallow Lake to Southern Indian Lake. Like most of the sites visited as part of the renewed CRDAP, HhLp-16 has been impacted by considerable erosion. In forms filed at the Manitoba Museum, Riddle notes 'it's likely that only a small portion of the original site area is still present.' Recoveries made during uncontrolled surface collection in 1990 include Late Woodland ceramic sherds, bifaces, scrapers, as well as projectile points that Riddle attributes to Talthelei occupation of the site.

5.2.18 HhLp-7 (Leslie's Nice Rims site)

HhLp-7 is located across a small strait immediately to the northwest of HhLp-11. The site consists of a scatter of ceramics and lithics on the exposed lacustrine clays making up the eroded beaches in the area. During uncontrolled surface collection of the site in 1990, ceramic sherds, flakes, and a scraper were recovered. Riddle identifies the sherds as Late Woodland. The site was revisited in 2002, resulting in the collection of additional lithics and Late Woodland ceramic sherds.

5.2.19 HhLr-4 (Shallow Lake)

This site is located on the west bank of an unnamed river located to the northwest of Shallow Lake. A portage leading into the Shallow Lake system lies about 50m north of the site. Although Riddle remarks in site forms filed at the Manitoba Museum that the site likely extends back from the mixed sand and clay beach surveyed in 1990, only

materials on the eroding beach were surface collected. The artifact deposit at HhLr-4 consisted of scattered ceramic sherds, flakes, a biface, and two projectile points.

5.2.20 HhLt-6 (Nagami Bay Fish Camp)

HhLt-6 is located on the southern shore of a small island on the north side of Nagami Bay. The site is described by Brownlee in forms filed at the Manitoba Museum as 'large' (70mx20m). Surface artifact concentrations at HhLt-6 were dense, and included a relatively large number of chert tools and flakes, as well as Late Woodland ceramic fragments.

5.2.21 HiLp-1 (Kame Hills)

HiLp-1 is the largest site discovered through the course of the pre-diversion CRDAP. Unsurprisingly, it makes the largest contribution to the artifact sample analyzed in this study. The site is located on a large bay near the northern end of Southern Indian Lake, approximately 7 km to the south east of the mouth of the Muskwesi River (Dickson, 1980). Prior to the Churchill River diversion, the site was located in deposits on two terraces behind a sandy beach, and bordered on all sides by kames. The site was first noted in 1971 by two fishermen while setting up camp in the area. In 1972, a team of 13 archaeologists carried out survey and initial testing at the site. 148 surface artifact loci were noted during this survey. Due to this richness, combined with impending threat of severe inundation due to hydroelectric development, HiLp-1 was selected as a site meriting intensive excavation under the guidelines of the CRDAP.

In 1973, five 2 m^2 test units were placed on each of the terraces where the densest concentration of surface and subsurface artifacts and features were located. In 1974, a block of 79 2 m^2 units was opened directly adjacent to the most productive of the 1973 test pits. Additionally, two test units and 40 test pits were placed on the secondary terrace of the site, and one test unit was placed on one of the nearby kames in an area where artifacts had been found on the surface. Excavation of these units continued through the 1975 field season, at the end of which the operations were concluded.

Stratigraphic resolution at HiLp-1 site was poor, a feature which it shares with many boreal forest sites. Site stratigraphy consisted of a variably thick layer of moss, or in some places, sod overlying sand. Artifacts were recovered from both the moss/sod layer and the top 20-40 cm of the underlying sand. Artifact recoveries at HiLp-1 included lithic, faunal, and ceramic remains. Lithic tool categories recorded include projectile points (40), bifaces (135), scrapers (171), a drill, retouched flakes (183), utilized flakes (37), gravers (2), chithos (5), wedges (21), whetstones (8), adzes (2), hammerstones (8), and 'miscellaneous tools' (12). Among formal tool classes, chert is the preferred material (75% of projectile points, 44% of bifaces, 85% of scrapers), with quartz coming in second (15% of projectile points, 34% of scrapers, and 19% of scrapers).

In total, 48 features were encountered during survey and excavation. Forty-two of these are described as 'type 1 hearths', which Dickson (1980:23) defines as consisting of diffuse areas of ash, stained sand and humus, mixed with bone fragments, charcoal, and cobbles. They tend to be oval in outline, and a shallow basin shape in profile. Cultural materials, including lithic, faunal, and ceramic remains, tend to be found either in, or very

close to type 1 hearths. Of the 42 type 1 hearths, 27 were assigned, either through radiocarbon dating or artifact associations, to the terminal Woodland period, one was assigned to the Taltheilei tradition, one was assigned to the Shield Archaic tradition, four were recorded as unassigned precontact, while four were recorded as historic. These hearths tend to be found either directly below the moss layer or in the upper portion of the sand stratum at HiLp-1. The deepest recorded type 1 hearth at the site was encountered at 1-17cm DBS.

Of the remaining six features, three consisted of what Dickson (1980:23) terms 'type 2 hearths.' These consist of a circle of large cobbles around a concentration of smaller, broken cobbles intermixed with charcoal. Ash, burned bone, and artifacts are absent or scarce in and around type 2 hearths. These hearths were encountered at depths of 10cm, 29cm, and 38cm DBS at HiLp-1. All of these hearths were assigned to the Shield archaic tradition, either through radiocarbon dating, or artifact association. The other three features consisted of two unidentified hearths and one diffuse charcoal scatter. Recovery of *in situ* faunal remains and burned organics provided 15 samples for radiocarbon dating. Four of the samples returned younger dates than materials recovered above them and were rejected by Dickson (1980:13), although they are, in fact, likely indicative of the problematic stragigraphy of the site. The earliest date from HiLp-1 (3505±90 BP) was obtained from large mammal/large bovid remains recovered at a depth of 25cm DBS. These remains were not associated with any cultural material and were too poorly preserved for butchering marks, if any were present, to be noted. The earliest dates directly associated with human occupation of the site come from the three 'type two' hearths. These dates (3340±65BP, 3170±70BP, and 2695±600BP), place these

features within the Shield Archaic period in northern Manitoba. Both of these hearths contain lithic tools and debris, however, with the exception of one 'Taltheilei-style' point, none of these is culturally diagnostic. The validity of these dates was to some degree substantiated by the recovery of an middle Archaic corner-notched point stylistically dated to 2000-1300BP directly above one of the dated hearths.

Additional radiocarbon dates from HiLp-1 were taken from type 1 hearths with directly associated culturally diagnostic material culture. Samples taken at two depths within a hearth associated with an Archaic point and both early and late Woodland ceramics returned dates of 1290±150BP (which is consisted with terminal Archaic or very early Woodland finds in northern Manitoba), and 380±70BP (which is consistent with other radiocarbon dated late Woodland sites in northern Manitoba) (Dickson, 1976). A number of dates were obtained from 'type 1' hearths associated with late Woodland ceramics only. These range from 1010±95BP at the earliest to 340±90BP at the latest.

Unfortunately, none of the excavated or surface collected artifacts obtained from this site for this study can be directly associated with dated features at HiLp-1, and correlating non-associated artifacts using stratigraphy is not useful. As Dickson (1980: 106-107) notes, 'At a site such as HiLp-1, where the matrix is sand, at least six archaeological complexes are represented, and the culture bearing strata are shallow, it is almost impossible to associate these tools with the complexes.'

5.2.22 HjLp-1 (Moss Lake)

HjLp-1 is located on the eastern shore of Moss Lake in an area heavily impacted by erosion resulting from hydroelectric development in the area. The area to the north

and east of the site, which used to be above water, now forms a small bay, which is shielded by a sandy bar of land to the east during low water years. HjLp-1 was visited during the 1990 season of the CRDAP as a known burial site in danger of being destroyed by erosion caused by the Churchill River diversion. Upon survey, it was discovered that the burial had been completely washed away by rising and falling water levels; no human remains were observed at the site. During uncontrolled surface collection of the site, numerous ceramic and lithic artifacts were recovered, including decorated Late Woodland rimsherds, body sherds, bifaces, flakes, and a scraper.

5.2.2.23 HjLp-15 (Pierre Gagnon site)

HjLp-16 is located on a southwest facing boulder-strewn mixed sand and clay beach approximately 125m southeast of HjLp-1. The site shows signs of modern reuse in the form of an artificially maintained clearing containing the remains of a recent camp. Riddle identifies the site as a 'major multi-component camp,' and suggests that intact portions of the site might remain inland from the heavily eroded beach. Artifact recoveries made during uncontrolled surface collection of the site in 1990 include Late Woodland ceramics, and a Taltheilei projectile point. Additional surface collection at HjLp-15 was carried out in 2002.

5.2.24 HjLp-6

HjLp-6 is located on the tip of a south-facing point jutting into Moss Lake. When the site was visited by the CRDAP crew in 1971, it was the site of a modern cabin. Tree felling and cutting were noted as potential disturbances to surface deposits. A test unit

was placed both to the north and south of the cabin. As the Churchill River diversion had not yet been completed, deposits at the site had yet to be impacted by erosion. Stratigraphy at the site consisted of a thin layer of humus overlying sand. No surface deposits were observed at HjLp-6, however, artifacts were recovered from the humus and sand layers of both test pits. Artifact recoveries consisted of ceramic sherds, chert, quartz, and quartzite flakes, a biface, retouched and utilized flakes, a unifacially retouched tool, a wedge, and a scraper.

5.2.25 GlLr-28

Two artifacts sampled for this study were taken from sites outside the Churchill River basin (GlLr-28/11 and GkLs-16/152). These artifacts were selected for analysis from collections at the Manitoba Museum by Mr. Kevin Brownlee, curator, on the basis of their visual resemblance to raw materials from Granville Lake smoky and rose quartz sources.

GlLr-28 is located in on the western bank of Footprint River, roughly 1km to the southeast of the point where the river meets Osik Lake. These bodies of water are a part of the Nelson River basin, and lie approximately 100km to the southeast of the Granville Lake quarry district. This area was also impacted by the Churchill River Diversion, and was surveyed as part of the renewed CRDAP in the 1990s. Uncontrolled surface collection was carried out at GlLr-28 during this period.

5.2.26 GkLs-16

GkLs-16 is located on the Rat River between Wapisu and Threepoint Lakes. This site was surveyed and surface collected during the renewed CRDAP in the 1990s. This area of Threepoint Lake lies approximately 120km to the southeast of Granville Lake. Both pre- and postcontact material culture was recovered from GkLs-16.

6.0 Quarry, artifact, and geochemical sampling methods

6.1 Quarry sampling

The 2007 field season of the Granville Lake quarries project began on August 10th, 2007, and lasted a total of 11 days. Ten quarry sites were visited and sampled during this time. Six of these sites were later judged to be too small to fit the criteria for major quarries detailed above; samples from these sites were eliminated from further consideration. The four sites sampled in 2007 that *did* meet the criteria for analysis included Grandfather, *Mimikweapisk*, Wheatcroft, and Pickerel Bay quarries. For all of the quarries except Pickerel Bay, samples taken in 2007 were intended to serve as a preliminary sample set, from which some initial chemical data could be obtained to form an analytical protocol for sourcing quartz and help shape sampling strategies during the 2009 field season. For this reason, 2007 quarry sample sets – even those obtained from large, complex sites like Grandfather, *Mimikweapisk*, and Wheatcroft – are relatively small. Unless otherwise noted, all samples were collected directly from quarry walls using a steel geological hammer.

The 2009 sampling season in the Granville Lake district of the Churchill River basin began in early July and lasted a total of 28 days. In total, 166 quartz samples were taken from seven localities in the Granville Lake district. Of these, 98 were collected to support the development of a sourcing strategy (Appendix 2) the remaining samples were collected in support of other research. Unless otherwise noted, all samples were taken directly from quarry walls using a steel geological hammer.

6.1.1 Grandfather quarry sample

Four sample lots were taken from Grandfather quarry in 2007 (Appendix 1). One of these sample lots (GF-1) consists of an assortment of loose quartz debris collected from around the edges of the main quarry pit. The remaining three sample lots (GF-03 – GF-04) are made up of quartz struck from the walls of the main quarry pit.

Sampling strategies employed at each quarry during the 2009 field season were shaped by the quarry size and the geological complexity of the deposit exploited. At the Grandfather quarry, at least two generations of quartz can be seen crosscutting feldspars and host rocks (Figures 6.1 and 6.2). Moreover, the quartz itself varies visibly from clear to smoky, with each colour variety exhibiting variable levels of fluid inclusions in the form of banding. Because of this material variability, as well as the size of the quarry excavation, Grandfather quarry was mapped and sampled intensively. In total, 63 sourcing samples were taken from the Grandfather quarry (GF-04 – GF-66) (Appendix 2). Sampling was designed to be as representative of material variability at the site as possible. Samples of each visual category of quartz observed were taken at roughly ten centimetre intervals from each wall of the quarry where they occurred.

6.1.2 2009 Little Grandfather quarry sample

Sampling at Little Grandfather quarry was very straightforward. Both smoky and white quartz were exposed in the walls of the easternmost and central caves making up the quarry. One sample of each colour category was obtained from these two features (GFNW-10 – GFNW-13). Only white quartz was exposed in the westernmost cave; one sample was taken from this feature (GFNW-14)



Figure 6.1 Quartz vein crosscutting host metasediment to the north of the main pit at Grandfather quarry



Figure 6.2 White quartz crosscutting metasediment crosscut by feldspar-rich dike north of quarry pit at Grandfather quarry

6.1.3. *Mimikweapisk* quarry sample

The *Mimikweapisk* quarry is the next largest of the Granville Lake quarries after the Grandfather quarry and shows some visual heterogeneity potentially indicative of the presence of multiple generations of quartz within the exploited deposit. Seven of the eight caves making up *Mimikweapisk* quarry were sampled in 2007 (Appendix 1). One of these, cave HR-BM9, a roughly 1.5m long, 0.5m wide, basin shaped vertical depression, is located on a plateau on the top of the rocky slope that hosts the main complex of quarry caves. The other sampled caves, HR-CM1, HR-CM1A, HR-CM1-B, HR-CM1C, HR-CM2, and HR-CM3 are excavated laterally into the rocky slope. Rock chips were taken with a geological hammer at regular intervals inside HR-CM1, HR-CM1A, HR-CM1B, and HR-CM1C to ensure representative sampling. A single sample was taken from both HR-CM2 and HR-CM3.

Because all but one of the caves making up the *Mimikweapisk* site had already been sampled during the 2007 field season, a sampling regime to assess the level of variability encountered within the largest quarry cave was undertaken. Cave CM1 was selected for intensive sampling. Seventeen samples in total were obtained from the walls of CM1 (see Appendix 2). Fourteen of these samples were taken in support of sourcing research, while three were taken in support of other work. In addition, one sample (FC-16) was taken from the flooded cave not sampled during the 2007 field season.

6.1.4. Wheatcroft quarry sample

Six samples were taken from Wheatcroft quarry in 2007 (Appendix 1). One of these, WC2-A1 consisted of loose quartz rubble collected from around one of the quarry

pits at the site. Two of the remaining samples, WC2-01 and WC2-02, consist of quartz chips struck from the surface of the two quarry pits at the site that were exposed in 2007. WC-03 was collected from a plateau above the main quarry site and consists of quartz found underneath a layer of sphagnum moss that covers much of the area above the quarry.

At the Wheatcroft quarry, sampling during the 2009 field season was designed to obtain samples of each visual category of quartz observed in the different quarry pits (i.e. white and rose quartz) and to sample each pit encountered. Twenty-two samples were taken from the Wheatcroft quarry (WC-01 – WC-22) (Appendix 2). However, many of these were ill-suited for developing a sourcing protocol, as they came from sources other than the pit walls. Several samples, for example, came from the matrix overlying one of the quarry pits, while other samples were surface-collected loose quartz rubble. While it is highly probable that these samples were produced either by quarrying activity or subsequent weathering of the quarry pit walls, they cannot with 100% certainty be attributed to the Wheatcroft quarry, and were excluded from analysis.

6.1.5 Smoky Quartz quarry sample

Both the quarried vertical deposit of quartz and adjacent quarry pits at Smoky Quartz quarry were sampled during the 2009 field season (SQ-01 – SQ-06) (Appendix 2). The small number of samples taken from each feature was a product of their observable lack of geological complexity and small size.

6.1.6 Floating Island Bay quarry sample

Three sourcing samples were taken from the Floating Island Bay quarry during the 2009 field season (FIB-01 – FIB-03) (Appendix 2). One of these samples (FIB-01) was taken from a rocky plateau above the main quarry face, and consists of white quartz found in association with white feldspars. This sample was not associated with any quarrying activity. The remaining two samples (FIB-02, FIB-03) consist of pieces of smoky quartz. FIB-03 was obtained from the main quarry face, while FIB-02 was obtained from an unquarried smoky quartz outcrop several metres to the north of the quarry face. This sample was taken to assess the degree of variability that could be expected from a single colour category of quartz over a large area with little apparent geological complexity.

6.1.7 Pickerel Bay quarry sample

Three quarry features were sampled at Pickerel Bay in the summer of 2008 (Appendix 1). The main quarry pit at GcNc-1, discussed above, provided one sample (SW1-1). SW2-1, SW2-2, and SW3-3 were obtained from a more highly metamorphosed quartz deposit several kilometers' boat ride away from GcNC-1, on the basis of its dissimilarity to quartz at the main Pickerel Bay quarry. SW3-1 was obtained from another quartz outcrop located several kilometres' distance from GcNc-1

6.2 Artifact Sample

Forty-eight quartz artifacts from the 24 sites described in Chapter 5 were selected to be analyzed for comparison to quarry samples. These artifacts were selected from collections housed at the Manitoba Museum based on the following criteria:

- Distance between any visible flaws (e.g. fissures, macroscopic mineral inclusions) in material must be ≥2cm.
- Artifacts with largest dimension ≤2cm must be free of visible material flaws.
- Material must fit into rose, smoky, or clear (with or without banding) colour categories.
- Only formal artifacts (projectile points, bifaces or scrapers) will be accepted for analysis

This sampling strategy has several major benefits. First, because vein deposits observed in the study area do not produce quartz with the above characteristics, while pegmatite deposits do, this strategy restricts the artefact sample to quartz that is geologically similar to the quarry samples analyzed during technique development that form the comparative source database. This ensures that the technique developed from the quarry samples is suitable for characterizing the artifact sample, and increases the likelihood of achieving positive matches between quartz artifacts and sampled quarries. Although artifact chemical signatures plotting outside of known quarry chemical signatures can be informative, positive matches between artifact and quarry chemical signatures allow more concrete statements about quartz procurement and transport across the landscape to be made.

Second, these selection criteria limit my sample to formal artifacts manufactured from a relatively scarce, high-quality form of quartz. Compared to expedient tools or tools manufactured from lower quality materials, artifacts of this type have a greater likelihood of being highly curated (Andrefsky, 2009; Odell, 2000; Wenzel and Shelley, 2001; MacDonald, 2008). This makes them a better indicator of overall mobility when positive source matches are obtained through a raw material provenance study.

Ideally, culturally diagnostic artifacts, or artifacts recovered from securely dated contexts would be selected for a raw material provenance study to facilitate interpretation of diachronic shifts in observed procurement and/or material transport trends. However, it was not possible to meet these criteria when selecting a quartz artifact sample for this study. The only artifacts considered clearly diagnostic of different cultural phases in the Churchill River basin are projectile points and, during the Woodland period, decorated ceramics. Despite its relative scarcity in the area, toolmakers in the Churchill River basin show a marked preference for making projectile points from chert (Dickson, 1980, Hannah, 1975). The few quartz projectile points observed in the Manitoba Museum collection did not meet the other quality criteria for selection for this study, having been manufactured from opaque, granular quartz.

Securely dating archaeological materials in the Churchill River basin is complicated by the region's pedology. Soils in boreal forest contexts like the Churchill River basin are acidic, breaking down organic remains that could otherwise be radiocarbon dated (Meyer, 1995:54). Some sites in northern Manitoba, including some in the study area, have produced radiocarbon dates (Dickson, 1976), which will be discussed in the sections below. However, the collapsed stratigraphy typical of boreal forest soils

makes associating radiocarbon dates with artifacts recovered from other areas of the same site difficult (Meyer, 1995:54). Most of the artifacts analysed in this study were surface recoveries, found lying on the bare stone that makes up much of the shoreline in the Boreal Shield ecotone where the Churchill River basin lies. None of the artifacts can be directly associated with securely dated features or diagnostic artifacts. However, provenance data from these artifacts is still of broad interpretive significance to mobility and procurement in the pre-contact period. For a list of artifacts sampled for this study, including recovery and metric information, where available, please see Appendix 3.

6.3 Geochemical Sampling methods

Multiple geochemical techniques requiring a number of different instruments were explored before a viable protocol for sourcing igneous quartz was determined. Most of these approaches failed to distinguish between material from different quarries. For the purposes of discussion, the following sections consist of a brief summary of the physical and chemical principles of each of these techniques, as well as their strengths and weaknesses in application.

6.3.1 Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) was the first instrumental technique applied to the development of a quartz sourcing protocol in the course of my dissertation research. During analysis by ICP-MS, samples – usually in the form of an aerosol – are ionized using a high-temperature inductively coupled plasma. This plasma is normally generated from argon gas and free electrons in a quartz torch

surrounded by a copper induction coil (Taylor, 2001:16; Hill *et al.*, 2005: 1). The free electrons are introduced via an electric spark and accelerated by means of a radio frequency electrical current flowing through the induction coil. The accelerated electrons interact with the argon gas to form positively charged ions and more free electrons in equal proportions, creating a charged neutral plasma (Taylor, 2001:16, Hill *et al.*, 2005: 1; Ammann, 2007). The plasma formed by this process is roughly cone-shaped, exhibiting a hollow axial channel into which the sample is introduced. Samples are normally introduced in aerosol form, however, plasma torches may be modified to allow the introduction of solid or liquid samples in small volumes (Hill *et al.*, 2005:4). Regardless of state, the sample is rapidly ionized by the ICP – with most elements reaching 100% ionization almost instantly – and carried via the plasma stream into an attached mass spectrometer. Low pressures maintained within the mass spectrometer during analysis result in rapid cooling and expansion of the plasma and ionized sample as they enter. Ion optics consisting of a series of electrostatic lenses focus the resulting ion stream toward the analytic portion of the mass spectrometer, where ions of interest are isolated according to mass. In most single-collector ICP mass spectrometers, this separation is carried out through the use of a quadrupole mass analyzer (Taylor, 2001:34). The quadrupole consists of four metal rods, generally <25cm in length secured in a circular arrangement with a drilled ceramic plate. The two rods in each opposing rod pair are electrically connected and radio frequency (RF) and direct current (DC) voltages are run through them (Batey *et al,* 2005:30). Different voltage ratios permit ions of different mass/charge to pass along a stable trajectory through the quadrupole to the detector. In cases where ions of multiple different masses are to be measured, the voltage

ratio is altered sequentially to allow the different ions to reach the detector (Batey *et al.*, 2005: 33).

Some single-collector, and all multi-collector ICP mass spectrometers carry out mass filtering through the use of a magnetic sector field mass analyzer, rather than a quadrupole mass analyzer. Magnetic sector instruments utilize a magnetic field, rather than an electric field, to isolate ions according to mass/charge ratio (Batey *et al.*, 2005: 41). The magnetic sector analyser consists of a curved flight tube positioned between the poles of a strong electromagnet. Accelerated ions pass through the tube, and the magnetic field causes ions of different mass/charge ratios to assume different circular trajectories. A movable slit at the end of the flight tube is positioned to allow only ions of a specific mass/charge ratio to exit and reach the detector (Batey *et al.*, 2005). Multi-collector magnetic sector field instruments feature multiple detectors; during simultaneous multi-element analysis, the exit slit on the magnetic sector field analyzer is opened wide enough to permit the entire mass spectrum of elements under consideration to exit the flight tube. The collector array may be movable, allowing different collectors to be positioned in the path of desired ion streams, or variable dispersion zoom optics may be used to align ion beams of a given mass/charge ratio with the collector array (Batey *et al.*, 2005:57)

ICP-MS is sensitive to a majority of elements in the periodic table and is capable of detecting elements in incredibly low concentrations (Taylor [2001:2] gives a figure of 1-10ng of element in 1L of solution). In addition to detecting trace element concentrations, ICP-MS is also capable of measuring isotope concentrations and ratios for most elements (Taylor, 2001:2). Multicollector ICP-MS has proven particularly

valuable for this latter application. In a conventional, single collector mass spectrometer, ions of interest are isolated and counted sequentially. Fluctuations in ionization and plasma flow occurring during this sequential analysis can, therefore, introduce an unacceptable level of error in isotope ratio measurements. Because ion collection occurs simultaneously in a multi-collector instrument, any instrumental fluctuation will affect all measurements equally, resulting in more stable ratio measurements and much lower error (Batey *et al.*, 2005).

A wide variety of techniques may be used to transform solid lithic samples into aerosols for analysis by ICP-MS. Two of these were utilized in this analysis: acid digestion and laser ablation.

6.3.1.1 Acid digestion ICP-MS

One of the most straightforward ways to prepare solid lithic samples for trace element analysis by ICP-MS is by acid digestion. This method of sample preparation not only converts solid lithic samples to a liquid state suitable for nebulisation into an ICP mass spectrometer, but selective digestion can also be used to concentrate the trace element component of a sample by eliminating major element components. Methods for converting solid samples to solution vary depending on the nature of the sample, the detection limits of the instrument to be used, and the elements to be measured (Wray, 2005:432).

Sample dissolution may involve mixture with an alkali flux (normally in a 5:1 flux-sample ratio) prior to open vessel digestion in weak nitric acid (Wray, 2005:432). Nitric acid (HNO_3) is extensively used for sample digestion prior to elemental analysis

because its constituent elements are generally present as atmospheric contaminants during ICP-MS analysis, and therefore, it does not present a risk for additional mass interferences (Vogl, 2005; 152). While fluxing followed a by weak acid bath does result in thorough sample dissolution, the resulting sample solution must be strongly diluted to prevent build-up of flux materials inside the ICP-MS. When older instruments are used, this may put trace element concentrations below detection limits.

In some cases, the alkali flux may be omitted and the sample dissolved using a strong acid solution. Strong acid digestion requires less sample dilution and, therefore, produces a more concentrated sample solution (Wray, 2005: 433; Jarvis, 1992). However, this method of sample preparation does have its drawbacks. For instance, if a very strong acid, such as HF is employed to dissolve a sample, all instrument parts coming into contact with the sample prior to ionization must be made from acid resistant materials to prevent damage to the machine. Further, most strong acids are difficult, dangerous and unpleasant to handle. Additionally, if strong acid dissolution is carried out in an open vessel, extreme care must be taken to avoid environmental contamination of the solution. It should also be noted that some minerals, including zircon and chromite (Wray, 2010: 433; Motabar *et al.*, 2009), known as "resistate" minerals, are resistant to dissolution even in strong acid solutions. This may be problematic if a bulk lithic sample containing these minerals is to be chemically characterized. Microwaving may be used to eliminate environmental contaminants and ensure complete sample dissolution. However, microwave-assisted digestion is a longer process than either flux-acid or strong acid dissolution, and the size of the microwave chamber used places an upper limit on the number of samples that can be processed during each preparation run. In the end, the

dissolution technique employed will depend very much on the chemical composition of the material to be analyzed, as well as the time, equipment and finances available to the researcher.

Acid digestion ICP-MS is a bulk analysis technique. This means that it provides chemical data for the entire sample submitted for analysis with no internal spatial resolution. Bulk ICP-MS samples generally range in mass from 0.1g-10g (Wray, 2005:432), depending on digestion technique and ICP-MS instrumentation to be used. For heterogenous siliceous raw materials, such as the microcrystalline quartzes or basalt, bulk analysis may be beneficial to source characterization, as "whole rock" results might be more representative of the source as a whole. For example, Hess (1996) uses trace element data obtained through ICP-MS analysis, combined with data obtained through instrumental neutron activation analysis (INAA) to characterize known sources of microscopically complex cherts in the Columbia Plateau and to assign a local source provenance to chert artefacts from the Mack Canyon site. Additionally, the superb sensitivity of solution based ICP-MS (detection limits range from 0.001 ppm for certain elements to 0.01% for others) makes it a good choice for characterizing lithic materials – such as quartz – which exhibit relatively low trace element concentrations. Solution based ICP-MS can, of course, also be used to characterize internally homogenous siliceous raw materials exhibiting easily quantified intersource chemical variability, such as obsidian (Tykot, 1998). However, the destructive nature of the methodology, in which artefacts must be cut, crushed and digested, largely precludes its use where other, less destructive techniques may be employed.

Quarry samples from both the 2007 and 2009 field seasons were submitted for acid digestion ICP-MS. The 2007 samples were submitted as rough quartz nuggets, which in some cases contained grains of non-quartz minerals. The 2009 samples were carefully denuded of any visible non-quartz minerals using a geological hammer and a variety of steel hand-tools. Five hundred milligrams of each sample was submitted to Activation Laboratories for analysis, where it was powdered and digested in aqua regia (a mixture of nitric and hydrochloric acids) at 95°C in a microprocessor controlled digestion box for two hours. The resulting solutions were diluted and analyzed using a Perkin Elmer SCIEX ELAN 6100 or 9000. International standards USGS GXR-1, GXR-2, GXR-4 and GXR-6 were analyzed prior to and following sample analysis, while internal standards and a duplicate sample were analyzed after 10 sample runs to ensure consistency of results.

6.3.1.2 Laser ablation ICP-MS

Quarry samples from the 2007 field season were also analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). During LA-ICP-MS analysis, small masses of solid samples are converted into vapour for ICP-MS analysis using a focused laser beam. Thick sectioned, polished samples are placed surface-up on a mechanized stage inside a closed sample chamber which is flooded with either argon or helium gas (or a mixture of the two). The sample is exposed to the laser beam, which ablates and vaporizes atoms and molecules from a very small area (10-400μm) of the sample surface. The vapour is conveyed via a carrier gas stream – normally composed of Ar – to the plasma torch. Samples may be exposed to a single, short laser burst to

generate data with very high lateral and in-depth resolution, or a number of pulses may be administered to generate laterally resolved depth profile data (Taylor, 2001: 83). Additionally, if transect chemical data are desired, either to achieve more "bulk" chemical values for homogenous samples, or to asses zonal chemical variability in heterogeneous materials, the sample may be exposed to multiple rapid bursts while the mechanized stage is slowly moved in order to raster the laser over the sample surface (Taylor, 2001: 83). Frequencies for lasers used in LA-ICP-MS normally range from 1-50Hz, however new lasers capable of femtosecond pulse rates are currently under development (Resano *et al.*, 2010).

Early LA-ICP mass spectrometers utilized ruby lasers for sample ablation, however, instruments used today tend to employ more stable eximer or Nd:YAG lasers capable of generating shorter wavelength beams (Resano *et al.*, 2010: 55). Wavelength is an important characteristic of lasers used to ablate samples for elemental or isotopic analysis. Shorter wavelength lasers ablate most samples in a more controlled manner and are capable of ablating transparent materials, such as glasses, that would only be cracked or melted by long wavelength lasers (Resano *et al.*, 2010; Taylor, 2001:81). Additionally, elemental fractionation is reduced when shorter wavelength lasers are employed (Resano *et al.*, 2010:57).

Although the use of shorter wavelength lasers can dramatically reduce instrumental fractionation during sample ablation, fractionation will still occur to varying degrees during ablation, vaporization and ionization in all LA-ICP-MS analyses (Guillong and Günther, 2001; Resano *et al.*, 2010: 59). Therefore, data produced through LA-ICP-MS analysis must be calibrated against results obtained from standards of known

chemical composition. Some researchers attempting to characterize Si-rich archaeological materials through LA-ICP-MS use synthetic standard reference glasses of known composition prepared by the National Institute of Standards and Technology (such as NIST SRM 610, 612, 614, 616) as external standards (e.g. Barca *et al.*, 2008). While these reference materials have the advantage of being easily obtained, matrix differences between prepared glass standards and archaeological lithic materials, which may lead to differential fractionation between the two, make them less than ideal for calibrating LA-ICP-MS data in sourcing studies. Other researchers describe methods by which matrix-matched standards can be prepared, leading to more accurate calibration (Pereira *et al.*, 2001). Britta Pereira and colleagues (2001), for example, were able to more accurately calibrate LA-ICP-MS trace element data obtained from archaeological obsidian samples using an in-house synthetic obsidian standard for which trace element concentrations had been determined by acid digestion ICP-MS.

To correct for machine fluctuations during LA-ICP-MS analysis, trace element results are also normally calibrated against measured levels of a minor isotope of an element known to be abundant within the sample. This is known as internal standardization. For analysis of Si-rich lithic materials, including quartz, ^{29}Si is often used as the internal standard, although ^{42}Ca is also commonly employed for siliceous materials where that element is known to be abundant (Jackson *et al.*, 1992).

When proper procedures are followed, LA-ICP-MS can be used to rapidly generate accurate, spatially resolved trace element or isotopic profiles of lithic samples with only minimal destruction. Unless a raster scan is carried out, analysis craters are generally not visible to the naked eye and analysis consumes only a few nanograms of the

sample (Nelms, 2005: 235). Sample preparation for LA-ICP-MS analysis is minimal for samples small enough to fit directly inside the analysis chamber; some polishing may be required if a raster scan is to be carried out to ensure a constant distance between the sample and laser source during analysis. For larger lithic samples, LA-ICP-MS analysis is destructive as a piece small enough to fit within the sample chamber must be removed using a rock saw or drill. Specialized "bottomless" analysis chambers, in which a section of the sample itself forms the chamber floor, have been developed for the analysis of large artefacts, such as paintings, when destructive sampling is not an option (Resano *et al.*, 2010: 60). However, their application to lithic sourcing has not yet been explored.

Because of its relatively low detection limits and non-destructive nature, LA-ICP-MS has seen increased application to the sourcing of Si-rich lithic raw materials over the past two decades (Resano *et al.*, 2010:56). Between 1992 and 2008, for example, the number of sourcing studies based on LA-ICP-MS data published annually increased from one to sixteen (Resano *et al.*, 2010:56). Many of the studies published during this interval focus on assigning provenance to Si-rich lithic materials (Eerkens *et al.* 2008, Grenough *et al.*, 2001; Mallory-Greenough *et al.*, 1999; Jackson *et al.* 1992; Insoll *et al.*, 2004). Obsidian is particularly suitable for characterization by LA-ICP-MS, due to its internally homogenous chemistry and consistent inter-source trace element variability. For example, Eerkens and colleagues (2008) were able to successfully differentiate between obsidian samples taken from 12 sources in the American Southwest, some of which were located in the same volcanic field, based on LA-ICP-MS trace element data. Further, they were able to assign source provenance to obsidian artifacts recovered from archaeological sites in the region based on these data and methodology to explore

mobility pattern fluctuations in the area. Carnelian and basalt are two other siliceous materials for which sourcing using LA-ICP-MS trace element has been attempted, albeit with less conclusive results (Mallory-Greenough *et al.*, 1999; Insoll *et al.*, 2004)

LA-ICP-MS generated isotope ratio data are used less frequently for sourcing siliceous raw materials. The measurement of light isotope ratios (other than Li and B isotope ratios) by LA-ICP-MS is precluded by the relatively high levels of atmosphere normally present in the sample cell. Therefore, light isotope ratios of potential utility to sourcing Si-rich lithic material are best measured using other isotope-capable geochemical techniques such as AD-ICP-MS, or SIMS (discussed below). Isotope ratios for heavier elements, such as lead, which have shown promise for siliceous raw material sourcing in the geosciences, can be accurately measured using multi-collector LA-ICP - MS (LA-MC-ICP-MS) (Resano *et al.*, 2008; 2010; Schultheis *et al.*, 2004). However, in the archaeological literature, this technique has been primarily applied to determining source provenance for materials used to make ceramics and ceramic glazes (e.g. Habicht-Mauche *et al.*, 2002; Resano *et al.*, 2008). This represents an area of untapped potential for LA-MC-ICP-MS, which deserves further exploration as archaeological provenance research expands beyond traditionally considered materials.

To collect the LA-ICP-MS data discussed below, quartz samples were mounted in epoxy resin, sectioned, polished, and cleaned in an ultrasonic bath of deionised water for 30 minutes. Each sample was placed inside a solid sample chamber attached to a Thermo Electron Element II ICP-MS. The sample chamber was flushed with Ar gas for 15 minutes to purge atmospheric contaminants. A transect across the longest axis of each sample was ablated using a New Wave UP-213 213nm wavelength Nd:YAG laser. Beam

size was set to 100μm with a pulse rate of 20Hz and beam energy of 5.8J/cm^2. Six samples from three quarries (Grandfather [1], *Mimikwesiwak* [3] , and Pickerel Bay [2]) were analyzed for Nb, Hf, Pb, and Th. Results for isotopes ^{93}Nb, ^{179}Hf, ^{208}Pb, and ^{232}Th are given as trace element signals in counts per second, normalized against an internal standard element of known concentration (in this case ^{29}Si) and calibrated against external standard NIST 612 to give concentration data in parts per million (ppm).

6.3.2 Cathodoluminescence

When exposed to a focused electron beam, some materials emit photons with wavelengths within the infrared, ultraviolet, and visible light spectra. This phenomenon is known as cathodoluminescence (CL). The wavelength and intensity of light emitted by different materials when struck by the electron beam is dependent upon factors related to their chemical composition. Therefore, CL imaging is a powerful tool for rapidly visualizing chemical variation within and between samples with luminescent properties. Optical CL systems are normally mounted on a specialized light microscope and consist of an electron gun fixed to a vacuum chamber and aimed toward a sample stage. Above the stage is a small window which allows light emitted from the sample to pass into the microscope, either for viewing or photography with an attached camera.

Cathodoluminescence is a widely used petrographic technique in the geosciences. It has been applied to quartz, specifically, to characterize lattice and interstitial defect structures (Müller, 2000), reconstruct the formation environment of plutonic quartz grains (Rusk *et al.*, 2006), and to assess geochemical variability over the growth history of hydrothermal quartz crystals (Rusk and Reed, 2002). In archaeology, CL has found more

limited application. CL has been suggested as a provenance technique for chert (Akeridge and Benoit, 2001), a tool for sourcing Neolthic *spondylus* shell jewellery along with $\delta^{18}O$ values (Bajnóczi *et al.*, 2013), and has been used in conjunction with $\delta^{13}C$ and $\delta^{18}O$ data to establish source provenance for Mediterranean white marbles (Barbin *et al.*, 1992; Herrmann and Barbin, 1993). For this research, CL images were collected to detect whether chemical zoning or localized trace element impurities were present in Granville Lake quartz samples, and, if so, the extent to which these would have to be taken into consideration when selecting the spatial resolution of chemical sampling techniques.

CL images of thick sectioned samples also analyzed by LA-ICP-MS were obtained using a Technosyn Cold Cathode Luminescence Model 8200 Mk II cathodoluminescence system mounted on a Nikon Optiphot 150 binocular microscope with attached Nikon Coolpix 800 digital camera. Electron gun operational settings were maintained at 15kV and ~500μA. Digital images were obtained using the camera's infinite focus setting and an exposure time of one minute.

6.3.3 Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) combines the sensitivity and multi-element/isotope capabilities of mass spectrometry with a minimally destructive microbeam sampling technique. During SIMS analysis, solid samples are exposed under high vacuum to a focused primary ion beam. When primary ions strike the sample surface, their kinetic energy is transferred to the sample, which leads to the ejection of atoms, molecules and molecular fragments from the sample surface in a process referred

to as sputtering. A small fraction of these ejected particles (~0.1%) are ionized during the sputtering process, and are channelled via a series of electrostatic lenses toward a magnetic sector mass analyzer for separation according to mass/charge ratio as described above. Ion yields are detected using a Faraday cup for high yield (>$1x10^6$ counts/second) ions, or an electron multiplier for lower yield (<$1x10^6$c/s) ions.

SIMS is a highly sensitive technique for assessing solid sample trace element and isotopic chemistry, with detection limits for most elements in the ppm to sub-ppm range. In contrast to other mass spectrometry techniques discussed above, SIMS is also capable of light isotope quantification as it is carried out under high vacuum on unaltered solid samples. However, due to fractionation occurring primarily during sputtering and ionization, ion yields detected during SIMS analysis are not directly representative of sample chemistry (Ireland, 1995:10). To correct for this, standards of known composition must be analyzed at regular intervals during a run of analyses to generate a correction factor by which data can be calibrated. Because instrumental fractionation varies drastically between materials of different composition, standards should be as closely matrix-matched as possible to samples undergoing SIMS analysis. This may present some difficulty when samples are microscopically heterogeneous or of unknown composition. In these cases, it may be necessary to submit a few representative samples for external trace element or isotopic analysis.

Analysis craters generated by SIMS analysis are normally invisible to the naked eye, ranging in size from 2-200μm in diameter, and only nanograms of sample are ablated during a single analysis. However, it would be disingenuous to refer to SIMS as a completely non-destructive technique. Most SIMS sample chambers are designed to

house samples up to 2.5cm in diameter; larger samples must be cut and mounted in epoxy resin prior to analysis. Additionally, to ensure accuracy and comparability of SIMS data, samples must be as smooth as possible, and extensive polishing is usually carried out prior to analysis. Some archaeologists may not be willing – or allowed – to submit sensitive, irreplaceable artifacts to such a destructive preparation process. In some cases, where artefacts are smaller than 2.5cm in diameter and present a reasonably smooth surface, sectioning and polishing can be omitted, keeping in mind that data may be compromised.

Application of SIMS to sourcing siliceous raw materials has been limited. This is likely because less expensive, less sensitive techniques with lower sample preparation requirements are sufficient for assigning provenance to most archaeological materials. SIMS is usually only employed for provenance research where high sensitivity and/or high spatial resolution are required, or where accurate stable isotope data – particularly light stable isotope data – are desired. Hull et al. (2008), for example, highlight the isotopic capabilities of SIMS by employing it to measure copper and hydrogen stable isotopes in samples taken from archaeologically exploited turquoise sources in the American Southwest. Using this technique, they found that the turquoise sources analyzed exhibited distinguishable copper and hydrogen isotopic signatures. To test this method's utility for sourcing archaeologically recovered materials, seventeen turquoise artifacts from Ancestral Puebloan sites of Chaco Canyon and Guadalupe Ruin were analyzed using the same protocol. Of these, thirteen were found to have isotopic signatures matching known turquoise sources, effectively establishing their raw material provenance. In this instance, SIMS analysis was employed not only due to its light

isotope capabilities, but also the spatial resolution of the chemical data it produces. Mineral impurities within turquoise samples and artifacts analyzed by Hull *et al.* (2008), which would have constituted a considerable source of contamination in bulk analysis were avoided through the use of a ~20µm beam (Hull *et al.*, 2008:1358). In another study Milne et al. (2009; 2011) employ SIMS as part of their multi-technique protocol for source categorization of chert in a situation where *in situ* material sources had not been located. Concentrations of Al and Ga/Zr values for 18 pieces of chert debitage from a Palaeoeskimo site on Baffin Island, NU were measured using SIMS. In this case, spatially resolved analysis was necessitated by the structural complexity and presence of inclusions within the chert samples under consideration. It was found that Al and Ga/Zr values could be used to separate the 18 debitage samples into four visually heterogeneous, but chemically distinct groups, which are interpreted to be representative of different exploited chert sources (Milne *et al.*, 2009).

6.3.3.1 SIMS sample preparation and machine settings

A variety of geochemical techniques using SIMS were explored for this study. These include analysis of trace elements Nb, Hf, Th, U, Fe, and Al, as well as O, and Pb stable isotope analysis. All SIMS analysis of quarry samples from the 2007 field season was carried out on thin sectioned samples. Thirty micrometer polished thin-sections of Churchill River Basin quartz samples were prepared and hand-cleaned with a 95% ethanol solution. A ~200 Å thick Au coat was sputter deposited onto the surface of each thin section prior to SIMS analysis using an Ernest F. Fullham No. 18930 Effacoater. The sections were placed in stainless steel sample holders where surface conductivity was

approximately 5-10 ohms/cm. Immediately prior to analysis, each sample was placed in the SIMS sample airlock and brought to high vacuum.

All artifact samples and quarry material collected during the 2009 field season were prepared as thick sections for SIMS analysis. Quarry samples were reduced to ~0.5 cm pieces using a geological hammer. Samples were immersed for 20 minutes in successive ultrasonic baths of distilled water, deionized water, 95% ethanol and 200-proof anhydrous ethanol. One fragment from each sample was selected and embedded in resin in a drilled 2.5 cm diameter aluminum mount. Artifact samples were prepared in a less destructive manner – a small wedge of quartz was removed from each artifact using a diamond wafering blade mounted on a Buhler slow-speed rock saw. Artifact samples were cleaned and mounted in the same manner as quarry samples. Mounted samples were polished, cleaned again using the protocol described above, and sputter-coated with a 25Å Au coat to dissipate electrical charging produced during SIMS analysis.

Initial SIMS analysis of Nb, Th, Hf and Pb trace element concentrations was carried out using a Cameca ims 7f with an O^-, 25μm ~25nA primary beam. The secondary ions $^{93}Nb^+$, $^{232}Th^+$, $^{178}Hf^+$ and $^{208}Pb^+$ were sequentially detected using an electron multiplier and measured as ratios against detected ^{29}Si. A typical analysis lasted ~4 minutes, comprising 30 analysis cycles. Prior to each analysis, samples were pre-sputtered for 10 minutes to remove the Au coat. Three analyses were carried out on each sample to account for possible intrasample trace element variability. All results were calibrated relative to NIST SRM 614 international glass standard. Standard data were used to correct data for samples of unknown trace element composition using the following formula:

$C_{samp} = (C_{std}/(Si_{std}*R_{std}))*R_{samp}*Si_{samp}$

Where C_{samp} is the concentration of the element of the element of interest in the sample, C_{std} is the known concentration of the element of interest in the standard, Si_{std} is the wt% concentration of silicon in the standard, R_{std} is the measured ratio of the element of interest over Si in the standard, R_{samp} is the measured ratio of the element of interest over Si in the sample, and Si_{samp} is the wt% concentration of silicon in the sample. This formula was used to correct all trace element analyses described below.

SIMS analysis of Al trace element concentrations was carried out on the same machine using an O^-, ~16nA primary beam and a -50 volt offset. SIMS analysis of Al trace element concentrations in 2009 quarry samples was carried out using an O^-, 10nA primary beam and no voltage offset. ^{27}Al and ^{29}Si were sequentially detected for 1 second each per analysis cycle using a Faraday cup. Each analysis consisted of 50 counting cycles. Prior to each analysis, samples were pre-sputtered for 1-3 minutes to remove the Au coat and any potential surface contamination. Three analyses were carried out on each sample to account for possible intrasample trace element variability. Al analysis was carried out on both 2007 and 2009 samples. Al data from the artifact and 2007 quarry materials was standardized using NIST 614 and is presented below as ppm concentration data. Al data from the 2009 quarry materials was collected as a rapid 'double check' of the feasibility of Al as a provenance indicator for quartz. As results of these analyses were not promising, no standardization was carried out.

Ti and Ge trace element analysis, and later analyses of Th and U were carried out using a 50nA O^- primary beam. ^{47}Ti, ^{74}Ge, ^{232}Th, ^{235}U were detected sequentially for 1s each by electron multiplier. Trace element yields were presented as ratios relative to ^{30}Si

yield which was held constant at a count rate of $1x10^6$ counts/second. A deadtime of 52s was applied to all analyses. Analyses comprised 30 counting cycles. Results were standardized using NIST SRM 614 to produce concentration data and an internal standard (HR-3) was run during each workday to monitor instrumental drift. A minimum of three analyses were placed on each sample to account for intra sample chemical variability. Results were averaged to produce mean concentration figures for each sample, and cumulative errors accounting for both intra sample variability and instrumental error were calculated.

SIMS measurements of $\delta^{18}O$ values were conducted using a 2.8nA Cs^+ primary ion beam. A +250 voltage offset was applied and counts of ^{18}O were held at 1x10ˆ6c/s. Secondary emissions of isotopes ^{18}O and ^{16}O were detected sequentially for 1s each using an electron multiplier and Faraday cup respectively. A deadtime of 52s was implemented during each counting cycle. Each analysis consisted of 130 cycles. $^{18}O/^{16}O$ ratios were standardized against a Brazilian quartz standard and converted into $\delta^{18}O$ values using the formula:

$$\delta^{18}O = (((^{18}O/^{16}O_{\text{measured sample}}/^{18}O/^{16}O_{\text{measured std}})/^{18}O/^{16}O_{\text{std}})-1)*1000$$

Pb isotope ratios were measured using a 200nA O^- primary beam – a high energy beam was used to maximize ionization of the Pb isotopes.^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb were detected sequentially using an electron multiplier. Analyses were run for 30 cycles, with a counting time of 10s for each isotope. At least three analyses were run on each sample to account for internal Pb isotopic heterogeneity. Results were averaged to produce mean ratios for each sample, and cumulative errors accounting for both intrasample variability and instrumental error were calculated. Standardization is not

required for Pb-Pb isotope analysis because instrumental mass fractionation has been shown to have no significant effect on Pb isotope ratios detected by SIMS. However, when a lengthy period of time had elapse between Pb isotope analysis sessions, a sample run during the previous session was rerun to ensure consistency of results.

6.3.3.2 Contamination issues, isobaric interferences and SIMS protocols.

During assay of low-concentration chemical constituents – like trace elements in quartz – special care must be taken to avoid contamination of samples either by environmental sources of the analyte, or by other environmental contaminants which may form isobaric interferences with each other or with other secondary ions emitted from the sample. Quartz sample prep for analysis of Pb – a common element in most environments that is usually found in low concentrations in quartz – must be carried out with great care and attention to cleanliness. During most of the research program described in this study, successive ultrasonic baths in distilled and deionized water, followed by 190 and 200 proof ethanol appeared to keep contamination to manageable levels during Pb isotope and trace element analyses. However, midway through SIMS analysis of artifact materials, Pb isotope and trace element results strongly indicative of sample contamination were recorded. To eliminate the contribution of contaminant ions to SIMS data, a -40 voltage offset was applied to subsequent analyses of Ti and Ge concentrations while a -25 voltage offset was applied to Pb isotope analyses. This resolved isobaric interferences into separate peaks. For Ti, the interference peak could be avoided during analysis. In addition to energy filtering, high mass resolution was also applied to further eliminate the contribution of the interference to recorded Ti values.

However, the interference peak associated with Ge was too large, and too close in mass to be avoided. Reliable Ge data for artifacts could not, therefore, be obtained.

6.3.3.3 Internal standard results

In addition to external standards (e.g. NIST glasses), an internal standard was run daily during trace element analysis. This was carried out to monitor internal drift and as a basis for correction factors in situations where instrument issues were encountered.

6.3.3.3.1 Internal standard (HR-3) Ti results

Daily Ti (ppm) result for internal standard HR-3 are recorded in Figure 6.3. Mean values range from 12.8ppm to 17.4ppm. However, as the relatively large standard deviations associated with each mean value indicate, much of this variation is a result of sample Ti heterogeneity, rather than serious instrumental issues. When these errors are accounted for, all mean Ti concentrations obtained from HR-3 fall within one standard deviation of the mean Ti value for the sample, with the exception of the mean value obtained on September 14th, 2012. Within error, the mean value measured on this day (17.4ppm) falls within the upper 1σ range of mean values from two other analysis days (February 3rd and October 26th), however, it falls above the 1σ range of the total mean Ti concentration of HR-3. It is possible the abnormally high mean Ti value recorded on September 14th is a result of sampling error rather than instrumental drift. This conclusion is supported by the fact that artifact HbMd-6/241 was analyzed on both September 13th, a normal analysis day in terms of Ti values obtained from HR-3, and on September 14th, returning similar results both days (Figure 6.4).

6.3.3.3.2 Internal standard (HR-3) Ge results

Daily Ge (ppm) results for HR-3 are shown in Figure 6.5. Daily results from January 29th – February 4th, 2012 are characterized by low error, indicating that HR-3 shows little internal Ge variability. Moreover, Ge results as a whole are internally consistent, falling within one standard deviation of the mean value for the sample, indicating good machine and sample consistency over the analysis period.

6.3.3.3.3 Internal standard (HR-3) Th/U results

Daily Th/U results for HR-3 are presented in Figure 6.6. Daily results are characterized by high standard deviations, which reflect the internal Th/U heterogeneity of sample HR-3. However, Th/U results from HR-3 are internally consistent, with all values falling within 1σ of the mean value for the sample. This is a strong indicator of consistent machine and sample behaviour during Th/U analysis.

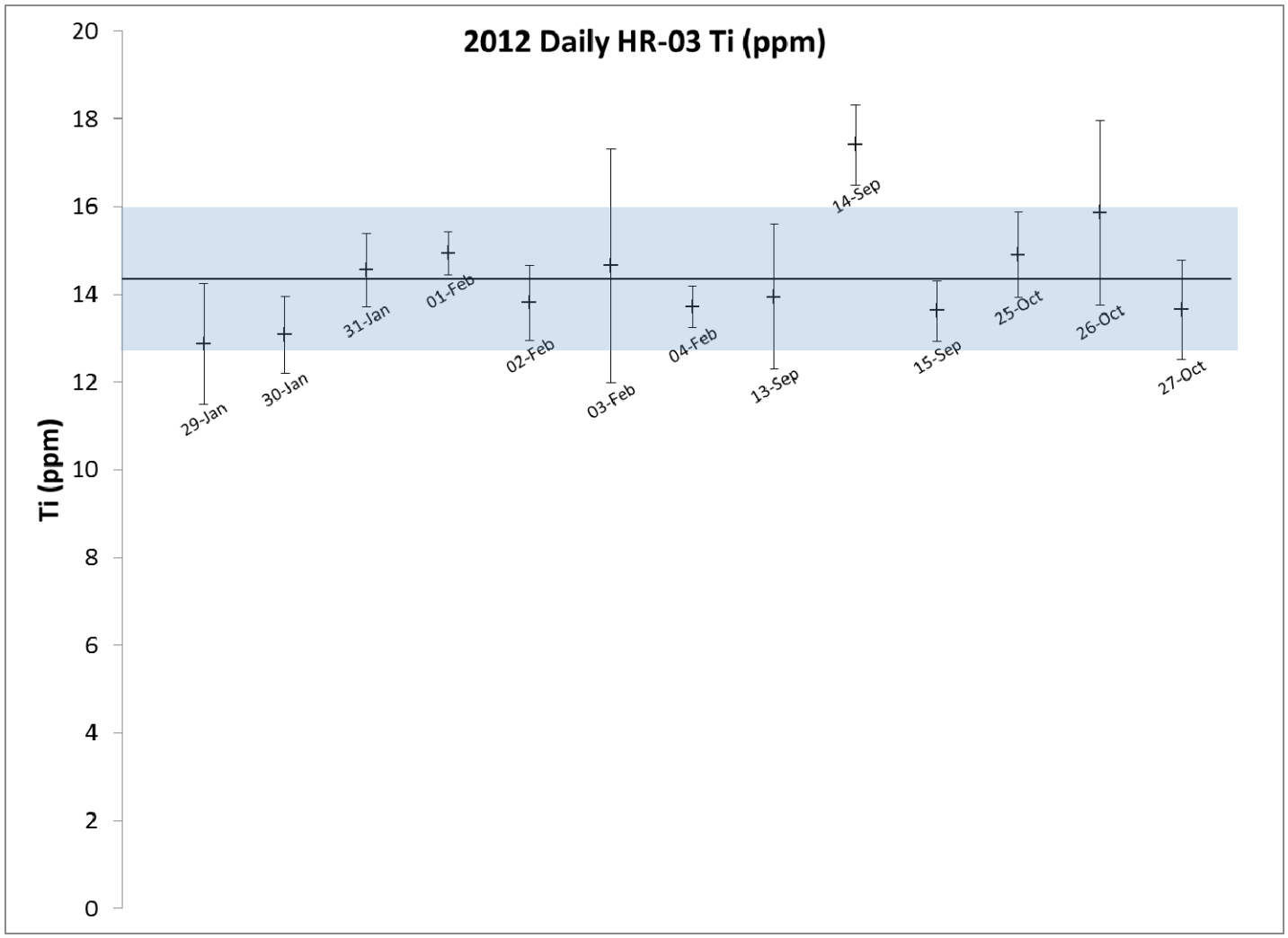


Figure 6.3 Plot of daily Ti (ppm) values obtained from HR-3 over the 2012 trace element analysis sessions

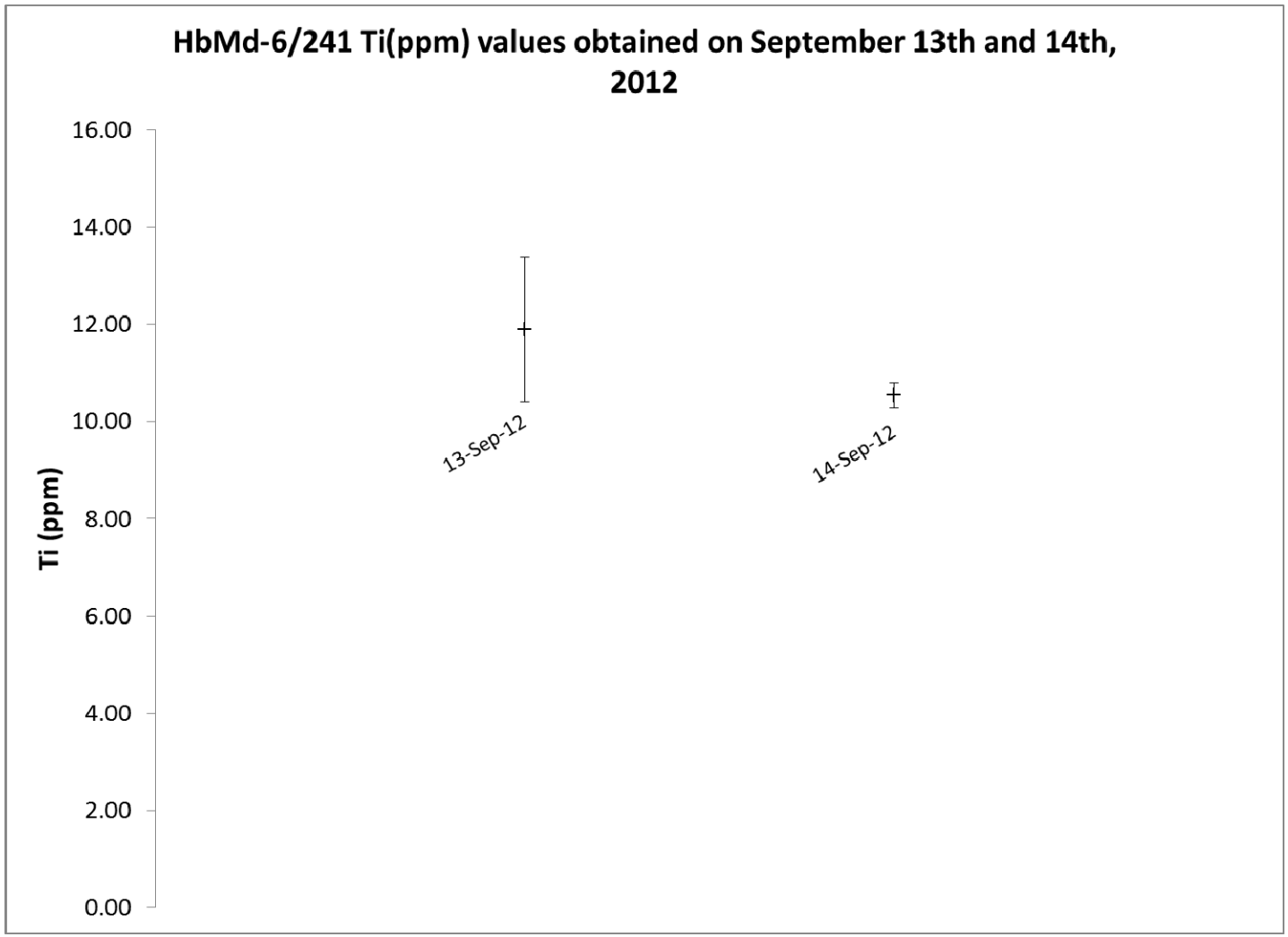


Figure 6.4 Plot of Ti (ppm) values obtained from HbMd-6/241 on September 13th and 14th, 2012. Note that the two values are statistically indistinguishable.

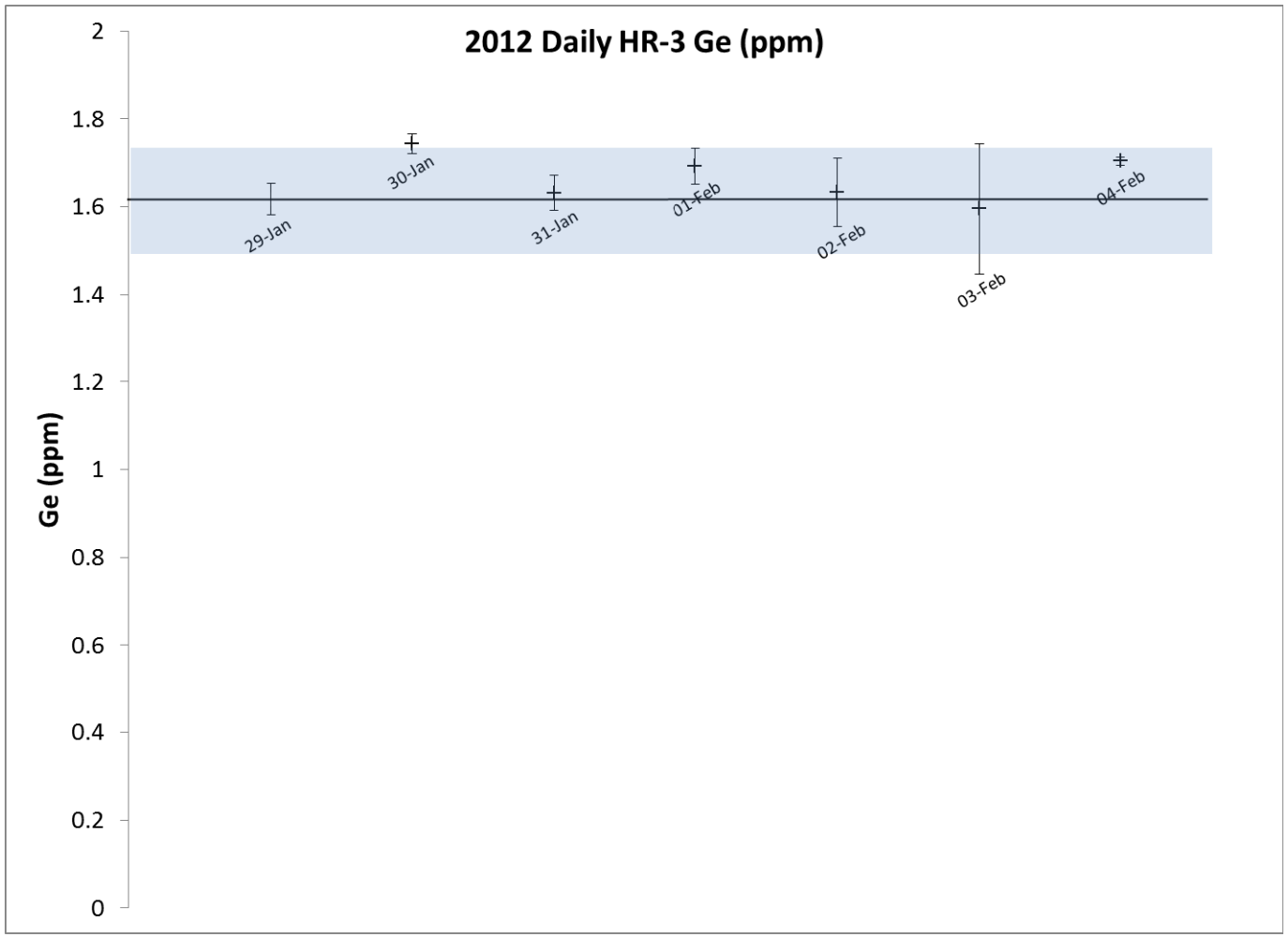


Figure 6.5 Plot of daily Ge (ppm) values obtained from HR-3 over the 2012 trace element analysis sessions

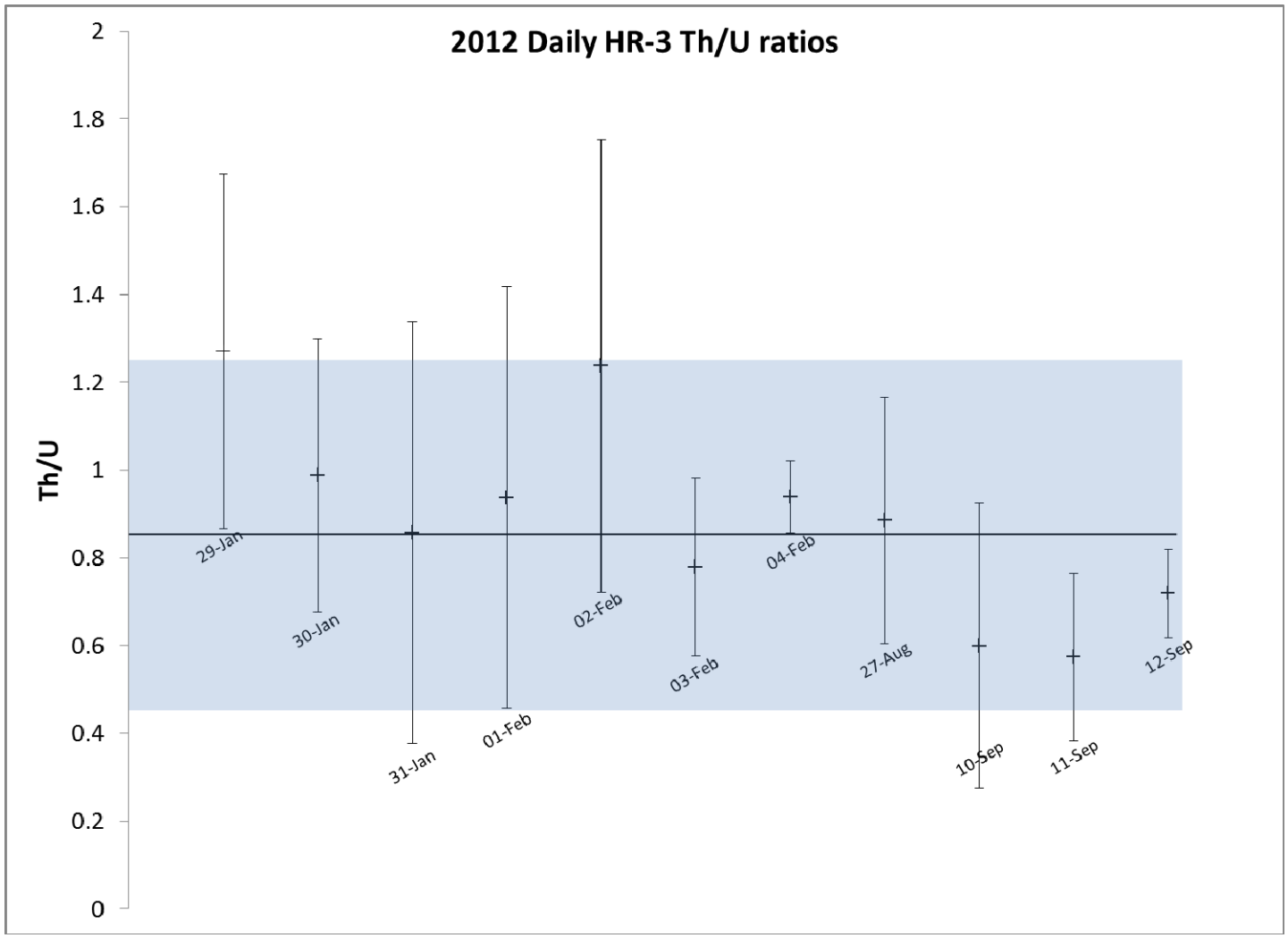


Figure 6.6 Plot of daily Th/U (ppm) values obtained from HR-3 over the 2012 trace element analysis session

6.4 Visual characterization

As a component of the final Pb-trace element characterization technique, quarry and artifact samples were classified according to their colour into one of three categories: rose, smoky, or white/clear. This was done to avoid comparing geochemical data from sources producing material that could be easily visually distinguished (e.g. Grandfather and *Mimikweapisk* quarries). This step could potentially inflate the number of identified 'sources' if cluster analysis of chemical data from artifacts of unknown provenance was to be carried out as a future avenue of research. However, at this stage of the study, colour categorization greatly simplifies the interpretation of geochemical results. Rose quartz samples correspond to Munsell colours 5R 7/4, 5R 6/6, and/or 5R 5/4. Smoky quartz samples correspond to Munsell colours 5Y 2/1, 5YR 2/1, or 10YR 2/1-2/1, and/or N5-N1. White/clear quartz samples are either completely colourless, or corresponded to Munsell colours N9-N6. Grandfather, *Mimikweapisk,* and Wheatcroft quarries all produced quartz that fell into more than one colour category (although the white quartz deposits at Mimikweapisk were not analyzed due to their very small overall contribution to quartz observed at the site), while the Smoky Quartz, Floating Island Bay, and Pickerel Bay quarries produced quartz that was visually homogeneous. It is not possible through visual analysis to distinguish between material in the same colour category taken from different quarries.

7.0 Outcomes and interpretation

The different possible outcomes of this provenance study will have distinct implications for the role that quartz played in the technological organization of the Churchill River basin and, specifically, the role of the Granville Lake and Pickerel Bay quarries. Presence/absence of material from analyzed quarries in sampled archaeological assemblages will be also informative with regard to the extent of procurement ranges in the Churchill River basin. Before drawing conclusions regarding technological organization from geochemical provenance data, however, care must be taken to avoid what Shackley (2008) terms the 'sourcing myth', or the idea that an artifact returning a chemical signature consistent with a known raw material procurement site can be attributed to that source with absolute certainty. Instead, the probability that artifact raw materials 'sourced' to a quarry were, in fact, procured at that source is contingent upon first, the quality of the data used to characterize sources, and second, the completeness of the source database to which artifact results are compared (Shackley, 2008). Honestly reporting the methodology of data collection and error associated with results, and explaining intersource chemical variation in terms of geological processes impacting the raw material in question allows readers to independently assess the quality of characterization data. However, the extent to which source data represent a comprehensive characterization of exploited materials within a region cannot be accurately assessed without carrying out thorough survey, sampling, and analysis of archaeologically utilized raw material sources in the region.

Very little of the Churchill River basin has been subjected to archaeological survey, making it unlikely that analysis of any sample of raw materials obtained from

currently documented extraction sites would result in a representative database of geochemical source signatures for the region. Because of this, rather than discussing artifacts in terms of being *sourced* to the Granville Lake or Pickerel Bay quarries, artifact raw material signatures will be discussed as either chemically consistent or chemically inconsistent with characterized sources. Artifacts with raw material signatures matching characterized sources will be discussed in terms of their provisional assignment to these sources, while artifacts with divergent chemical signatures will be tentatively discussed as being of unknown provenance.

The results of this study will be used to test several hypotheses. The most basic of these is that materials from the analyzed quarries were exploited, either through direct procurement or exchange, by toolmakers at represented sites. This hypothesis will be supported if raw materials chemically consistent with characterized Pickerel Bay and Granville Lake sources are identified in the artifact sample set. Support for this hypothesis carries further interpretive ramifications.

If the Granville Lake quarries were exploited by toolmakers at represented sites, lithic procurement ranges for toolmakers in the Churchill River basin likely ranged from 50-250 km. Use of Pickerel Bay quartz by toolmakers at represented sites would indicate procurement ranges in the order of 300-500km. Evidence for procurement ranges on this scale would support the hypothesis that the study area was inhabited by mobile hunter-gatherers (e.g. Seeman, 1994; Amick, 1996; Jones *et al.*, 2003). In some contexts, large procurement ranges may be the product of indirect procurement through trade or reciprocal exchange carried out by hunter-gatherers in the process of forming intergroup ties (Freund, 2012; Hertel and Tallavaara, 2011). Lithic exchange among hunter-

gatherers generally occurs in situations where populations are relatively dense, subsistence resources are distributed in patches that allow for reduced mobility and surplus production for trade, and sources of the traded lithic material are very scarce (Bettinger, 1982). The lithic landscape of the Churchill River basin is not well understood, as survey in the region has been minimal. Large, archaeologically exploited deposits of moderate to high quality pegmatite quartz appear to be rare, as the Granville Lake and Pickerel Bay quarries represent the only such recorded sources. This means that, at least in terms of lithic resource distribution, the Churchill River basin meets criteria expected of a context in which hunter-gatherer exchange could account for large procurement ranges. However, other expectations are not met. Other than large spring and fall fish runs, which occur at some sites around Granville and Southern Indian Lakes (Hanna, 1975), subsistence resources that would allow sedentary groups to participate in surplus production are absent in the Churchill River basin (Kroker, 1990). In addition to this, the use of bifacial technology by knappers at the Grandfather quarry (Beardsell, 2013), suggests that this source was exploited by residentially mobile groups (Shott, 1986; Kelly, 1988; Beck *et al.*, 2002). Moreover, as mentioned, low population density is indicated for much of the Churchill River basin's human history. If provenance data obtained through my dissertation research suggests large procurement ranges for toolmakers in the basin, mobility, rather than exchange, is implied.

Because the artifact sample selected for analysis is solely made up of formal artifacts – i.e. bifaces and scrapers - several other hypotheses regarding the relationship between technological strategies and environmental factors would be tentatively supported if positive matches between artifacts and characterized sources were

established. As Andrefsky (1994a, 1994b) demonstrates, formal artifacts are manufactured from relatively higher quality materials when they are available. Given this, the presence of formal artifacts manufactured from quartz chemically consistent with material from the Granville Lake and/or Pickerel bay quarries in the artifact sample set would indicate that quartz from these sources, despite its moderate quality for knapping, was incorporated into toolkits in the study area in a pattern consistent with better quality material. Such an outcome could be viewed supporting the hypothesis that toolmakers in the area were operating under a certain degree result of resource stress, i.e. the absence of other sources of raw material of higher quality than pegmatite quartz. Efficient use of raw materials, indicating expected lithic resource scarcity, is also implied by bifacial reduction strategies implemented at the Grandfather quarry (Beardsell, 2013), which lends additional support to this hypothesis. Further, archaeological survey of the basin, although restricted, has failed to identify lithic procurement sites exploiting raw materials of higher quality for tool manufacture than those produced at the large pegmatite quartz quarries described in this dissertation.

Given the distance between the Pickerel Bay and Granville Lake quarries, and the CRDAP study area around Southern Indian Lake, the identification of artifacts chemically consistent with analyzed quarries would imply that formal tools made from this material were carried over long distances, rather than discarded near to their site of initial procurement. Without assessing physical tool variables directly affected by curation, like scraper edge angle-to-thickness ratios (Kuhn, 1991) or degree of biface retouch (Clarkson, 2002; Andrefsky, 2006; 2008; 2009), it is difficult to say whether artifacts analyzed for this study were intensively curated. However, recovery of artifact

materials exhibiting chemical signatures consistent with the Granville Lake and/or Pickerel Bay quarries at sites several hundred kilometers away could be taken as an indication that these tools were not discarded soon after procurement and manufacture, but were curated to some degree. Again, this pattern would further support the hypothesis that toolmakers experienced some degree of lithic resource stress between material procurement and discard sites, as tool curation tends to be a response to raw material scarcity (Kelly, 1988; Blades, 2003; Andrefsky, 2008).

If raw material signatures that are inconsistent with the Pickerel Bay and/or Granville Lake quarries are exhibited by artifacts in my dissertation sample set, both the existence of other sources of pegmatite quartz and their use by toolmakers at these sites is implied. If all of the artifacts analyzed return geochemical results falling outside of the expected range of analyzed quarries, the null hypothesis, that material from these sources was not exploited by toolmakers at represented sites, will be supported. However, support for this hypothesis would not necessarily constitute confirmation that these sources did not contribute to formal toolkits in the Churchill River basin as a whole, especially considering evidence for biface production recovered from the Grandfather quarry (Beardsell, 2013). Instead, a lack of provisional artifact matches to characterized quarries would indicate that *if* formal tools were manufactured from quartz obtained from these sources, they were transported to areas other than those supplying artifacts for this dissertation.

Exploitation of raw materials distributed over the relatively large territories occupied by mobile hunter-gatherers can lead to the production of lithic assemblages where multiple quarry signatures are evident within geochemical data obtained from a

raw material type, while more sedentary groups may exploit relatively fewer sources, leading to the production of more homogenous lithic assemblages (e.g. Roth, 2000). The presence of multiple material signatures within a single site's quartz assemblage could be taken as weak support for a hypothesis in which site occupants were residentially mobile. However, the multicomponent nature and lack of temporal resolution due to collapsed stratigraphy and poor dating potential of many large boreal forest sites sampled for this dissertation means that it is often impossible to determine whether non-diagnostic artifact recoveries should be attributed to one group or many (Dickson, 1980: 107). It is possible that data patterns indicating exploitation of multiple sources by occupants of a single site is a reflection of use of that site by different groups, possibly separated by hundreds or thousands of years, with different procurement ranges. Also, without knowing where procurement sites producing artifacts of 'unknown' provenance are located, it is impossible to say how far apart uncharacterized quartz sources exploited by toolmakers at a single site might be.

In the same way, raw material homogeneity at sites represented by multiple analyzed artifacts cannot be taken as strong support for a hypothesis in which site occupants practiced reduced mobility. As lithic resource selection strategies have been tied to cultural affiliation (e.g. Evans *et al.*, 2010; Milne *et al.*, 2011), consistent exploitation of the same quartz sources by occupants at sites in the CRDAP study could be taken as evidence for cultural continuity. Lack of temporal control over assemblages, however, means that it would be impossible to establish whether consistent use, and thus, hypothesized continuity, spanned thousands of years, or a single visit.

8.0 Results

8.1 Acid digestion ICP-MS Results

Quartz samples collected during the 2007 field season were submitted to Actilabs for acid digestion ICP-MS, and returned results for 62 analytes between Li and U (Appendix 4). Significant separation of samples from Grandfather, *Mimikweapisk,* Wheatcroft, and Pickerel Bay quarries was observed when (Hf/Pb)+Th values were plotted against sample Nb concentrations (Appendix 4). There is also a strong, positive relationship between these two values. In general, quartz from Grandfather quarry is characterized by relatively high and variable (Hf/Pb)+Th values (5.9-21.3) and high Nb concentrations (2.7-7.6 ppm). In contrast, quartz samples from sources in the Pickerel Bay region have a relatively low and restricted range of (Hf/Pb)+Th values (0.5-1.3 ppm) and Nb concentrations (0.5-0.8 ppm). Samples from *Mimikweapisk* and Wheatcroft quarries exhibit (Hf/Pb)+Th values (*Mimikweapisk:* 2.5-8.43, Wheatcroft:1.27-1.69ppm) and Nb concentrations (*Mimikweapisk*: 1.3-2.9 ppm, Wheatcroft: 0.8-1.2ppm) that fall between these two extremes.

Quartz samples collected during the 2009 field season were submitted to Actilabs for acid digestion ICP-MS, and returned results for 62 analytes between Li and U (Appendix 5). In contrast to ICP-MS results from the 2007 sample set, 32 of the 62 analytes measured (including Mg, P, Ca, Ti, V, Ge, As, Sc, Pr, Gd, Ho, Er, Tm, Nb, Cd, In, Sb, Te, La, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Re, Au, Tl, Bi, Th, U) were below the detection limits of ICP-MS in most or all of the 2009 samples. The 30 analytes that were found in detectable amounts in the 2009 quartz samples (Li, Be, B, Na, Al, S, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Dy, Mo, Ag, Sn, Cs, Ba, Ce, Nd, W, Pb) do not

vary between material from the different sources in such a way that they could be used to distinguish between samples from Grandfather, *Mimikweapisk*, Wheatcroft and Pickerel Bay quarries

8.2 LA-ICP-MS Results

LA-ICP-MS analyses were set up as line scans across the surface of quartz samples. Calibrated LA-ICP-MS data show spatially resolved Nb, Hf, Pb, and Th concentrations over the course of the line scans carried out on each sample (Figures 8.2-8.5, Appendix 6). All samples exhibit internal spatial variability in Nb, Hf, Pb, and Th concentrations. For some elements, especially Th, drastic intrasample variation is universal. In all cases, the chemical variability detected during transect analysis of the Churchill river basin quartz samples is too pronounced to be attributed to instrumental error alone and instead, likely reflects tightly resolved chemical zoning within the quartz samples, or possibly the presence of micro-mineral inclusions.

For each sample, mean trace element concentrations in ppm were calculated by taking an average of concentration data produced by each analysis over the course of the line scan (Table 8.1). Mean concentrations of Nb, Hf, and Pb detected by LA-ICP-MS were lower than those detected by acid digestion ICP-MS on the corresponding split of each sample. Concentrations of Th, on the other hand, are either comparable or higher than those obtained through solution ICP-MS (Table 8.1). Nb, Hf, Pb, and Th mean concentration data obtained by LA-ICP-MS do not vary significantly between samples from the three different quarries considered during analysis (Table 8.1).

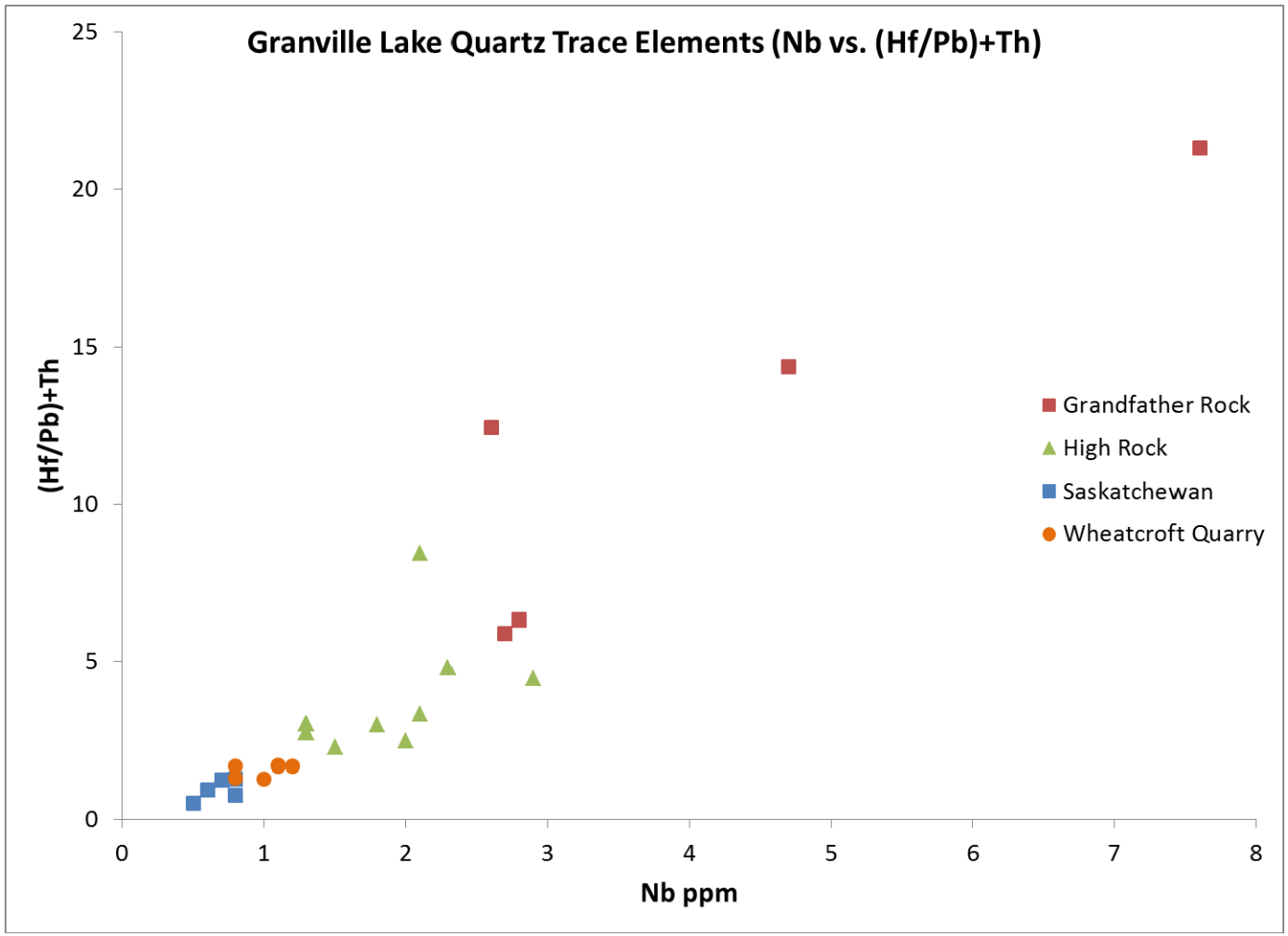


Figure 8.1 Biplot of 2007 quarry quartz sample Nb against (Hf/Pb)+Th detected by acid digestion ICP-MS

Table 8.1: Average trace element concentrations obtained through LA-ICP-MS transect analysis of Churchill river basin quartz samples given in parts per million (ppm). Error given as 1σ value of calculated mean concentrations.

Sample	**No. Data Points**	**Nb (ppm)**	**±**	**Hf (ppm)**	**±**	**Pb (ppm)**	**±**	**Th (ppm)**	**±**
GF 1-03	1059	0.03	0.12	0.01	0.03	0.19	0.17	9.29	17.09
HR -CM1	968	0.06	0.13	0.06	0.15	0.30	0.92	7.34	12.38
HR -CM1-B1	646	0.34	4.96	0.02	0.18	4.39	37.20	0.75	6.20
HR -CM2	1217	0.02	0.07	0.01	0.02	0.12	0.30	8.01	14.15
SW1-01	1199	0.01	0.03	0.01	0.05	0.09	0.19	6.64	11.90
SW 2-02	1118	0.02	0.08	0.00	0.05	0.01	0.21	32.41	56.19

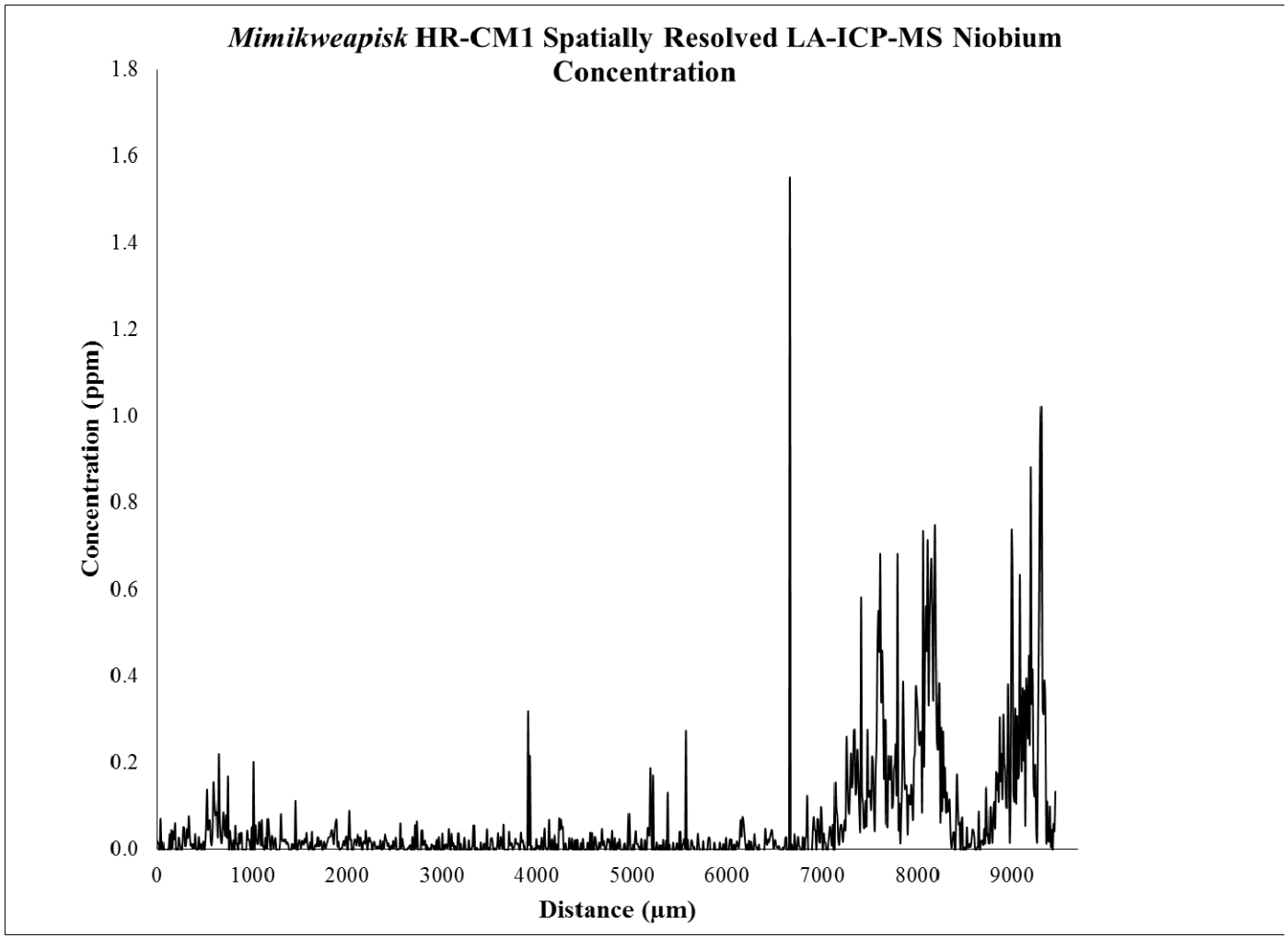


Figure 8.2 Spatially resolved Nb (ppm) data from line scan of *Mimikweapisk* quarry sample HR-CM1

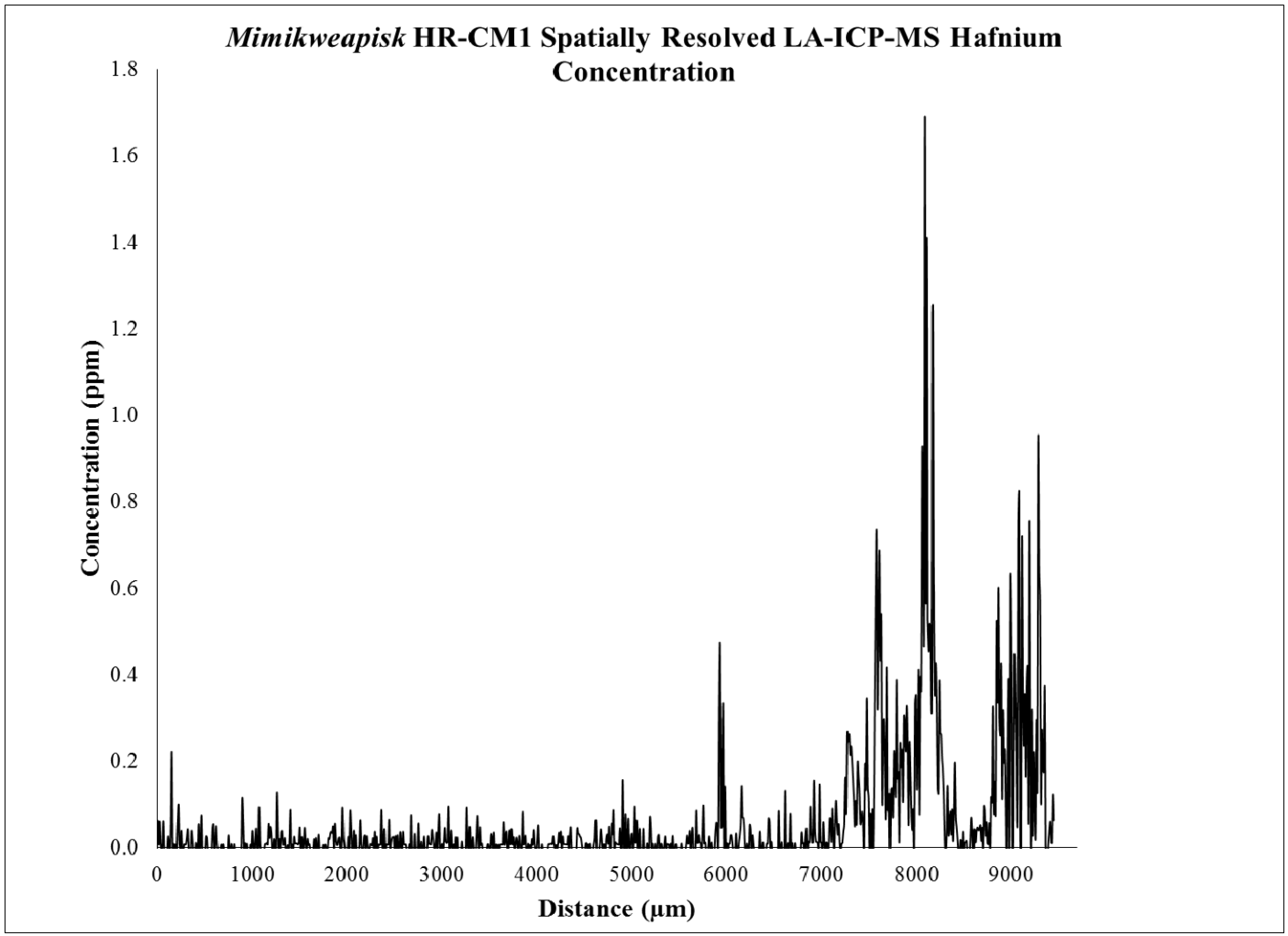


Figure 8.3 Spatially resolved Hf (ppm) data from line scan of *Mimikweapisk* quarry sample HR-CM1

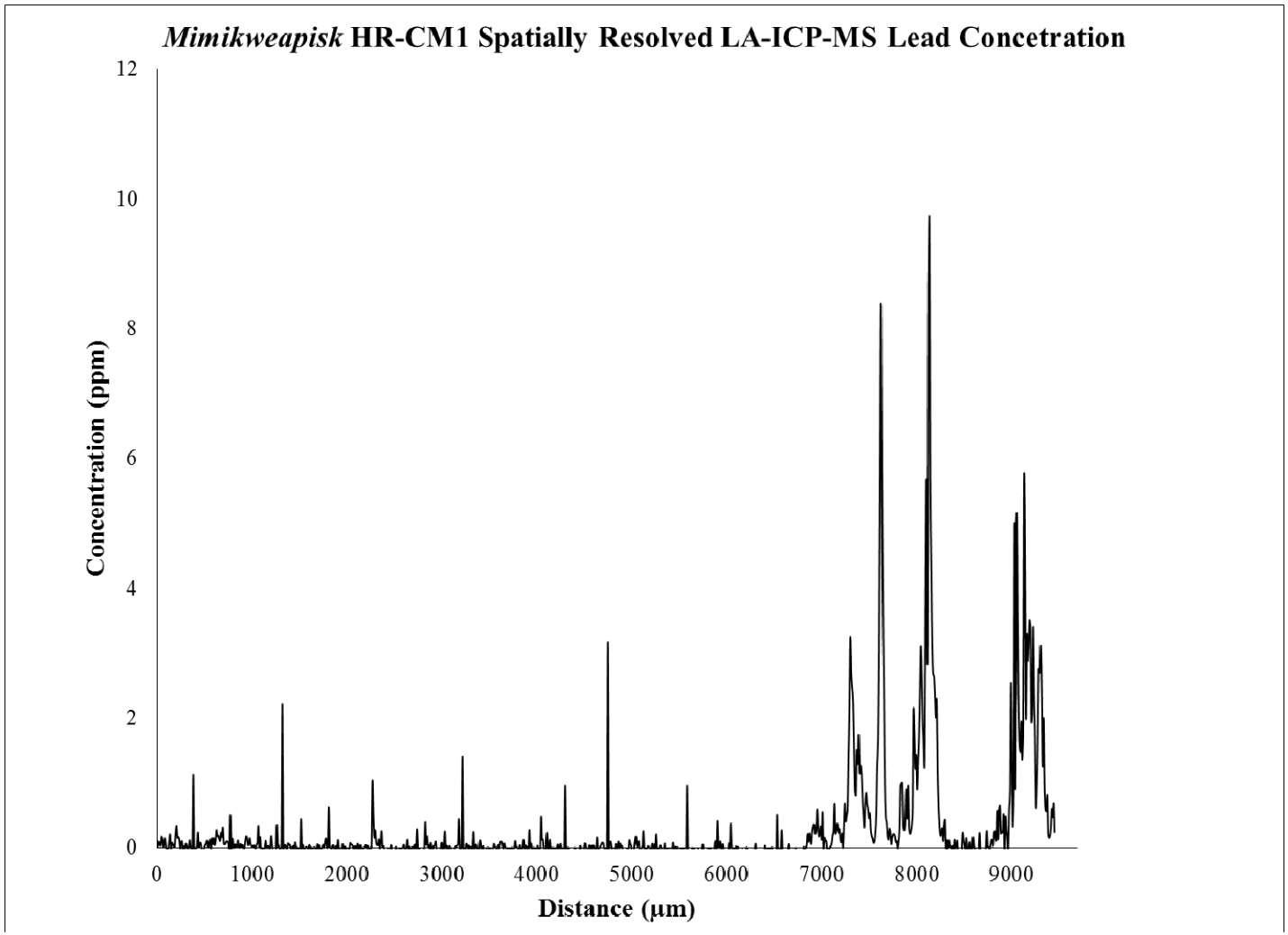


Figure 8.4 Spatially resolved Pb (ppm) data from line scan of *Mimikweapisk* quarry sample HR-CM1

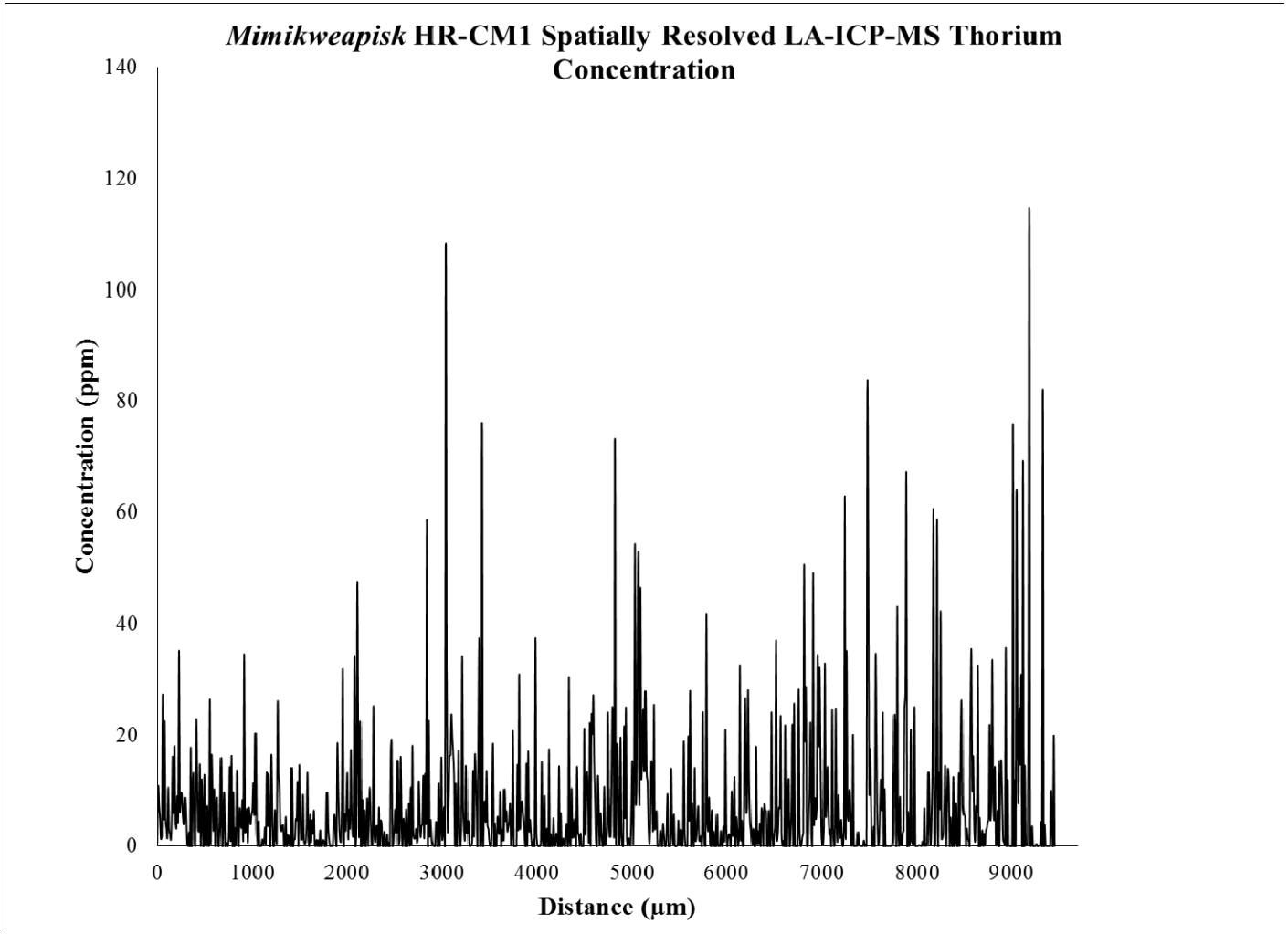


Figure 8.5 Spatially resolved Th (ppm) data from line scan of *Mimikweapisk* quarry sample HR-CM1

8.3 Cathodoluminescence Results

The quartz matrix of samples taken from the Churchill River basin quarries generally luminesces a dark grey-blue. This colour was shifted in most CL photomicrographs of quarry materials to a dull brown-red, which is likely a result of prolonged electron bombardment during the lengthy exposure time required to collect suitable images using the set-up described in section 6.3.2 (Müller, 2000:3) (Figure 8.6). Areas of chemical variability are apparent as either amorphous streaks of lighter grey-blue (or red in photo), indicating chemical variability within the quartz matrix itself, or as discrete, small points of bright green, yellow, blue, orange, or red indicating the presence of solid or fluid inclusions, or point defects in the structure of the quartz itself (Muller, 2000:61) (Figure 8.6). Overall, quartz samples obtained from the Pickerel Bay quarry appear to exhibit the highest degree of matrix based chemical variability (Figure 8.7), while fluid and solid inclusions are present to a roughly equal degree in samples from all three sources.

8.4 SIMS Results

8.4.1. SIMS Nb, Hf, Pb, and Th results

In contrast to trace element results obtained through acid digestion ICP-MS, SIMS analysis shows average concentrations of Nb, Th, and Hf to be at sub-ppb levels (Table 8.2). Pb is the only element detected in concentrations that approach those obtained by solution-based ICP-MS. Concentrations of Nb, Th, Hf and Pb detected by SIMS do not vary consistently based on raw material provenance. However, at such low concentrations, the total variability exhibited SIMS data obtained from the Churchill River basin quarry sample set falls within instrumental error and therefore, SIMS Nb, Hf, Th, and Pb data are inconclusive.

8.4.2 SIMS Al results

Aluminum concentrations from seven 2007 quarry samples and three artifacts are plotted in Figure 8.8, while $^{27}Al/^{30}Si$ results for eight 2009 quarry samples are plotted in Figure 8.9. Because one dataset constitutes standardized concentration data, while the other is made up of uncalibrated ratios, the two datasets cannot be merged into a single figure or directly compared. Overall, 2007 quarry samples exhibit a relatively restricted range of Al concentrations (225-726ppm), while Al values obtained from the artifact sample are more variable (649-2326ppm) (Table 8.3). Within the quarry sample, *Mimikweapisk* (345-726ppm) quarry exhibits appreciable intra-source variability. Quartz from Grandfather quarry (466-499ppm), while on average more homogenous than the *Mimikweapisk* sample set, shows more intrasample Al variability than material from other sources, observable in the large errors associated with each sample mean. In contrast to these two sources, Al values from Pickerel Bay quarry samples are less variable, both on the inter- and intrasample scale, and generally lower (225-309ppm).

Mean sample $^{27}Al/^{30}Si$ ratios from 2009 quarry materials are distributed between 0.011-0.035. Material from Grandfather quarry exhibits a relatively high degree of Al variability, with results from that quarry making up the upper and lower limits for this sample set. Al variability in Grandfather materials appears to be linked to colour in this sample set; the two samples exhibiting lower Al/Si ratios, GF-12 (0.018) and GF-13 (0.011), are both white quartz samples, while higher-Al/Si samples GF-27 (0.035) and

Table 8.2: Results of SIMS trace element oxide analysis of Churchill river basin quartz given in parts per million (ppm). Error given as 1σ values for calculated mean concentrations

Sample	**Nb O (ppm)**	**±**	**Hf O (ppm)**	**±**	**Th O (ppm)**	**±**	**Pb O (ppm)**	**±**
GF1-02	1.36×10^{-03}	8.00×10^{-04}	4.85×10^{-04}	3.58×10^{-04}	7.52×10^{-05}	3.63×10^{-05}	3.41×10^{-01}	1.59×10^{-01}
GF1-03	1.51×10^{-03}	1.27×10^{-03}	4.71×10^{-04}	4.32×10^{-04}	6.99×10^{-05}	4.64×10^{-05}	2.05×10^{-01}	3.03×10^{-01}
HR-CM1	1.08×10^{-03}	1.03×10^{-03}	4.42×10^{-04}	3.59×10^{-04}	7.38×10^{-05}	4.98×10^{-05}	3.09×10^{-01}	2.19×10^{-01}
HR-CM1-B1	1.84×10^{-03}	1.79×10^{-03}	6.63×10^{-04}	6.30×10^{-04}	1.68×10^{-04}	1.24×10^{-05}	3.19×10^{-01}	2.90×10^{-01}
HR-CM2	1.39×10^{-03}	1.23×10^{-03}	5.42×10^{-04}	5.35×10^{-04}	1.11×10^{-04}	9.23×10^{-05}	2.36×10^{-01}	1.78×10^{-01}
SW1-01	1.27×10^{-03}	1.34×10^{-03}	5.31×10^{-04}	3.49×10^{-04}	9.34×10^{-05}	4.75×10^{-05}	3.24×10^{-01}	2.11×10^{-01}
SW2-02	1.34×10^{-03}	1.21×10^{-03}	5.35×10^{-04}	3.86×10^{-04}	9.39×10^{-05}	4.04×10^{-05}	2.06×10^{-01}	1.46×10^{-01}

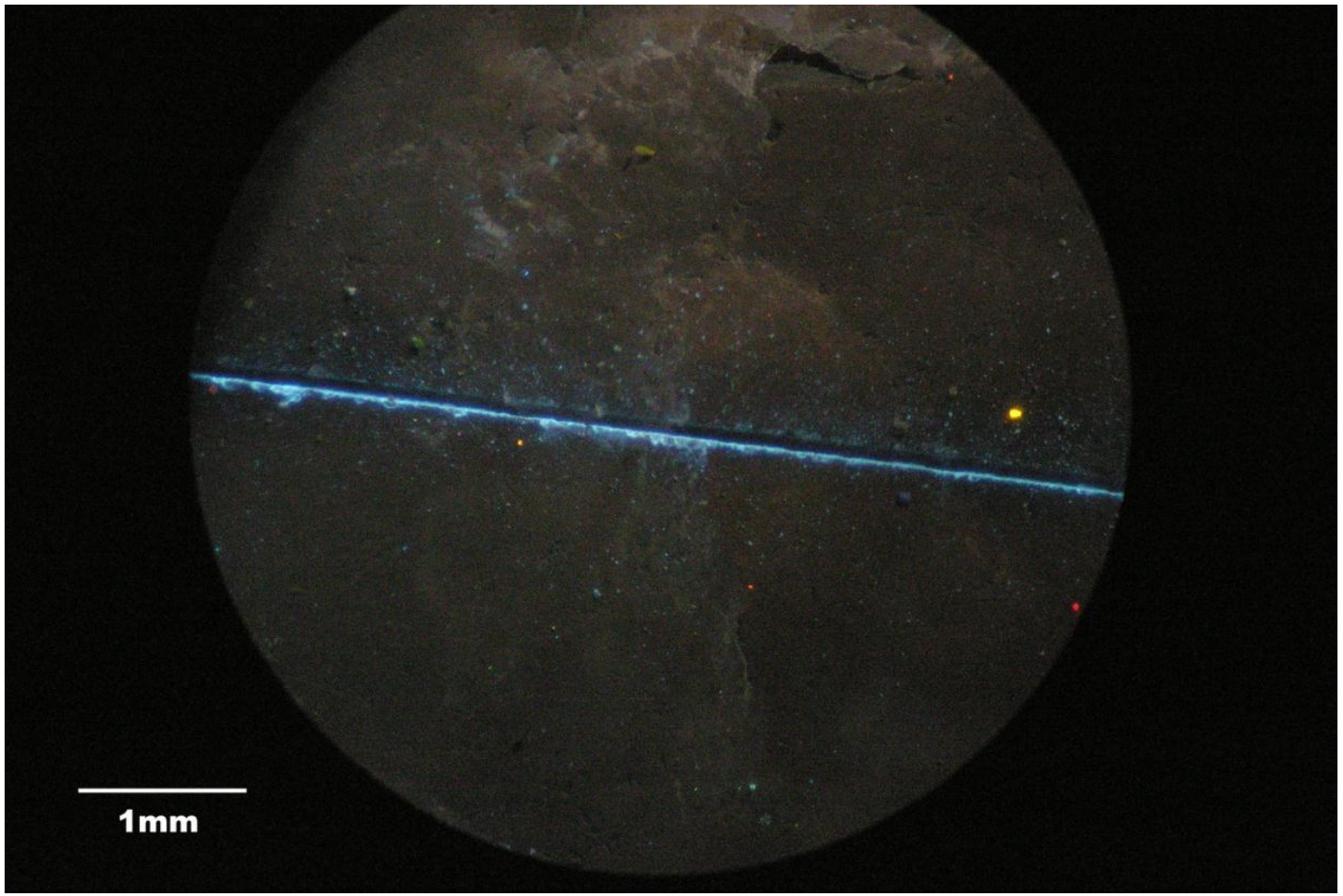


Figure 8.6 Cathodoluminescence micrograph of Grandfather quarry sample GF1-3. Blue line is a result of LA-ICP-MS raster scan of sample. Note mottling in quartz matrix and bright orange, red, and green inclusions and/or defects

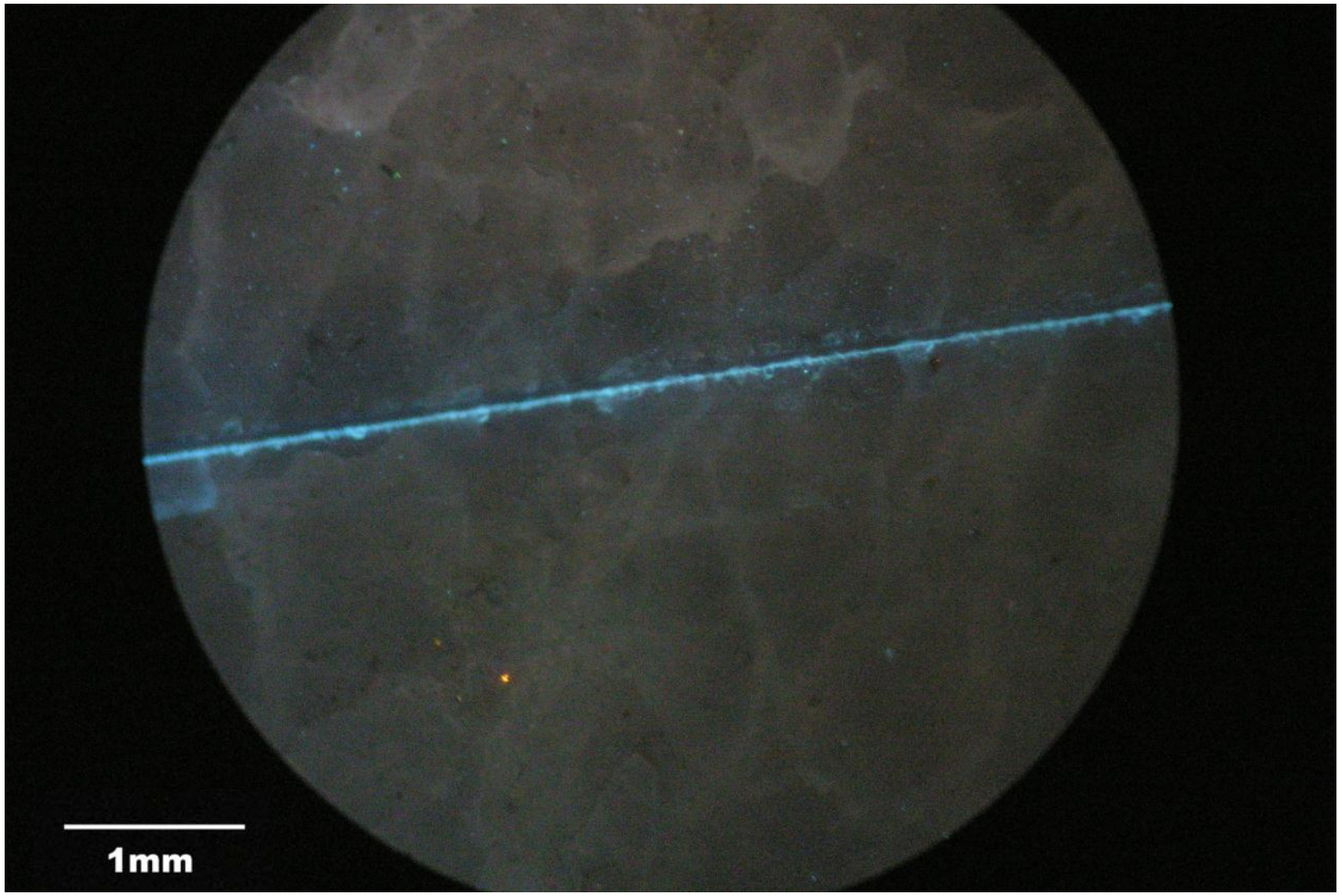


Figure 8.7 Cathodoluminescence micrograph of Pickerel Bay quarry sample SW1-1. Note relatively high degree of mottling in quartz matrix coloration.

GF-45 (0.022) are both smoky quartz. 2009 *Mimikweapisk* quartz samples exhibit a relatively restricted Al/Si distribution (0.025-0.028).

Table 8.3: SIMS Al concentrations for artifact and 2007 quarry samples

Sample	**Al (ppm)**	±
GF1-03	466.23	181.00
HR-CM1	726.57	87.13
HR-CM1-B1	345.42	60.81
HR-CM2	383.88	7.95
SW1-1	308.68	27.51
SW2-2	224.60	44.51
HgLt-7/M50	2325.59	511.58
GlLr-28/11	1273.34	289.93
GkLs-16/152	648.86	299.71

Similarly, 2009 quartz samples from Wheatcroft quarry show comparatively little Al variation (0.028-0.035). No statistically significant inter-quarry Al/Si variability is observable in this data set.

8.4.3 SIMS Oxygen Stable Isotope Results

$\delta^{18}O$ values were obtained from six Churchill River basin quarry samples and three artifact samples (Figure 8.10, Table 8.4). Error ranges of ~2‰ are associated with most samples and are largely the product of high intrasample $\delta^{18}O$ variation, rather than instrumental error. Mean $\delta^{18}O$ values for quarry materials are distributed from 7.9-13.8‰, while artifact $\delta^{18}O$ values fall within a relatively tight range from 9.8-10.2‰. Mean values from within each quarry show an appreciable degree of variation. The difference between Grandfather sample $\delta^{18}O$ values from GF1-2 (13.8‰) and GF1-3 (11.8‰) is not significant, due to the high error – resulting from intrasample variability –

associated with GF1-2. However, variation between *Mimikweapisk* samples HR-CM1 (14.2‰), and HR-CM1-B1 (12.7‰) and HR-CM2 (12.6‰) is significant, as is variation between Pickerel Bay samples SW1-1 (11.8‰) and SW2-2 (7.9‰). With the exception of SW2-2, mean values for all of these samples fall within the expected range for quartz from granitoid pegmatites (e.g. Longstaffe, 1981: 201). It is interesting to note that mean $\delta^{18}O$ values obtained from the three artifacts are lower than those obtained from the Granville Lake district quarries and one of the Pickerel Bay samples (SW1-1), and higher than those obtained from the remaining Pickerel Bay sample (SW2-2).

8.4.4 SIMS Pb isotope and trace element (Ti, Ge, Th/U) results.

Detection of Pb by acid digestion ICP-MS, LA-ICP-MS, and SIMS in nearly all analyzed samples, along with the promising results of trace element analysis of pegmatite quartz by Larsen *et al.* (2004) and the TitaniQ geothermometry of Wark and Watson (2006), led to the formulation of a quartz characterization technique based on qualitative colour categorization, and SIMS Pb isotope and Ti, Ge, and Th/U quantification. The best geochemical discriminators for Churchill River basin pegmatite quartz sources vary between colour categories. Results for white/clear, smoky, and rose quartz will be discussed separately below. These results will be discussed using biplots of individual sample data points and errors, rather than 95% confidence intervals plotted around mean quarry data. The former more accurately reflects the true geochemical variability of each source; however, 95% confidence plots are included in quarry figures below to illustrate the degree of variability lost when mean quarry data alone are considered (Figured 8.11b, 8.12b, 8.21b and c, 8.22b, 8.23b).

Table 8.4: SIMS $\delta^{18}O$ values for artifact and 2007 quarry samples		
Sample	**$\delta^{18}O$**	**±**
GF1-02	13.8	2.24
GF1-03	11.8	0.89
HR-CM1	14.2	0.33
HR-CM1-B1	12.7	0.86
HR-CM2	12.6	0.34
SW1-1	11.8	1.16
SW2-2	7.9	1.15
HgLt-7/50	9.8	0.64
GlLr-28/11	10.2	0.81
GkLs-16/152	9.8	0.98

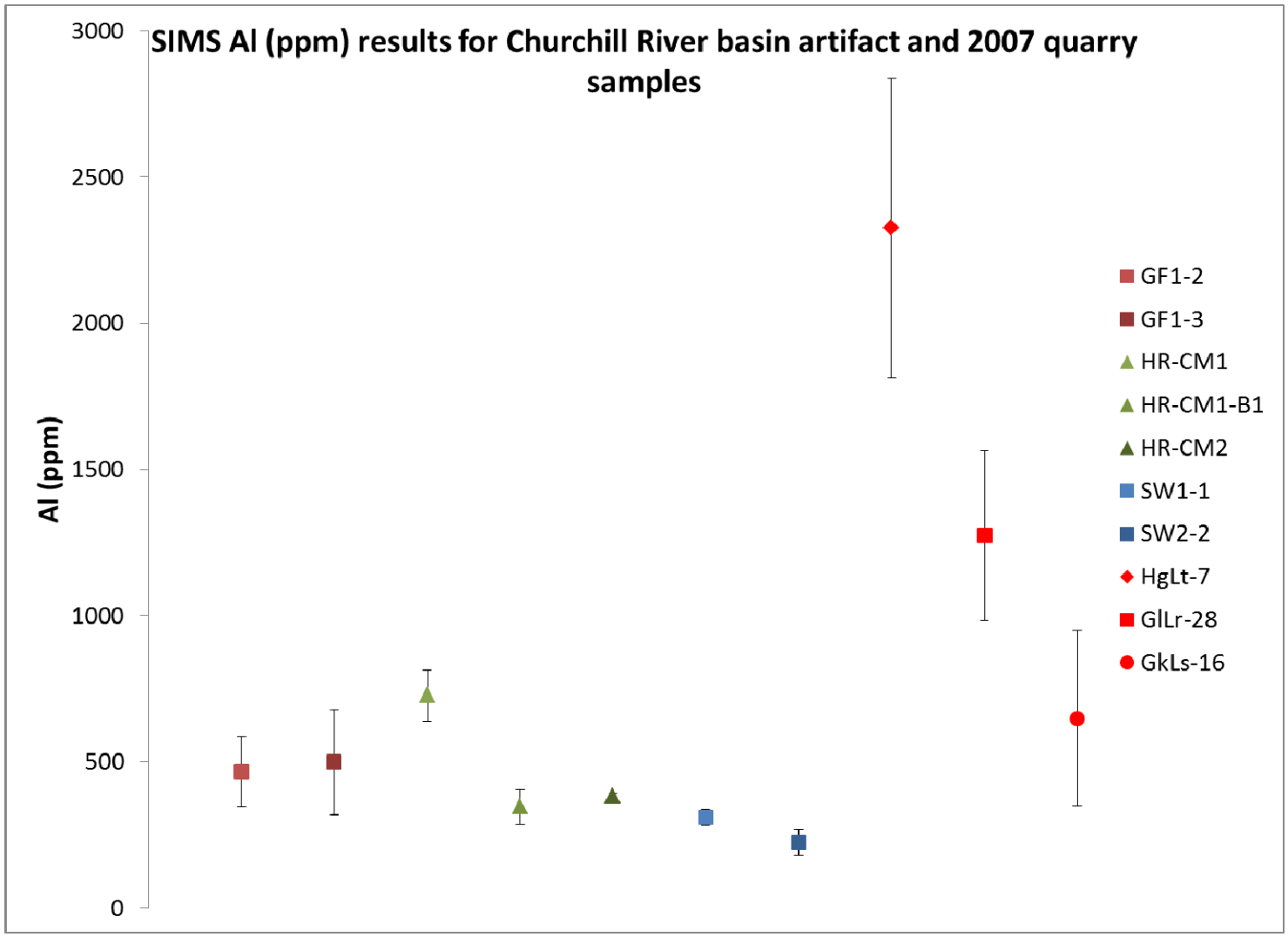


Figure 8.8 SIMS Al(ppm) data for 2007 Churchill River basin quartz quarry and artifact samples

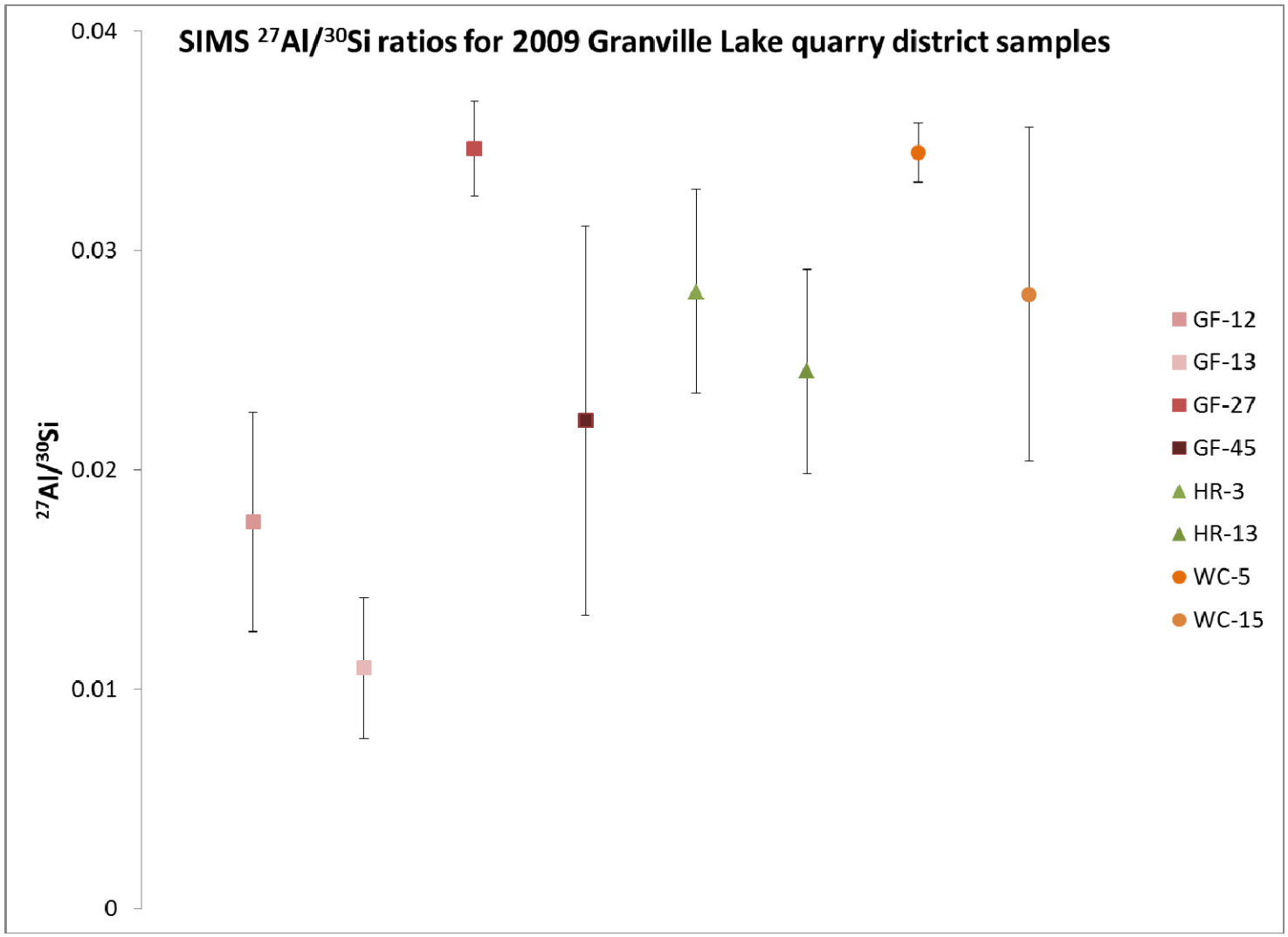


Figure 8.9 SIMS $^{27}Al/^{30}Si$ ratios for 2009 Granville Lake quarry district quartz quarry samples

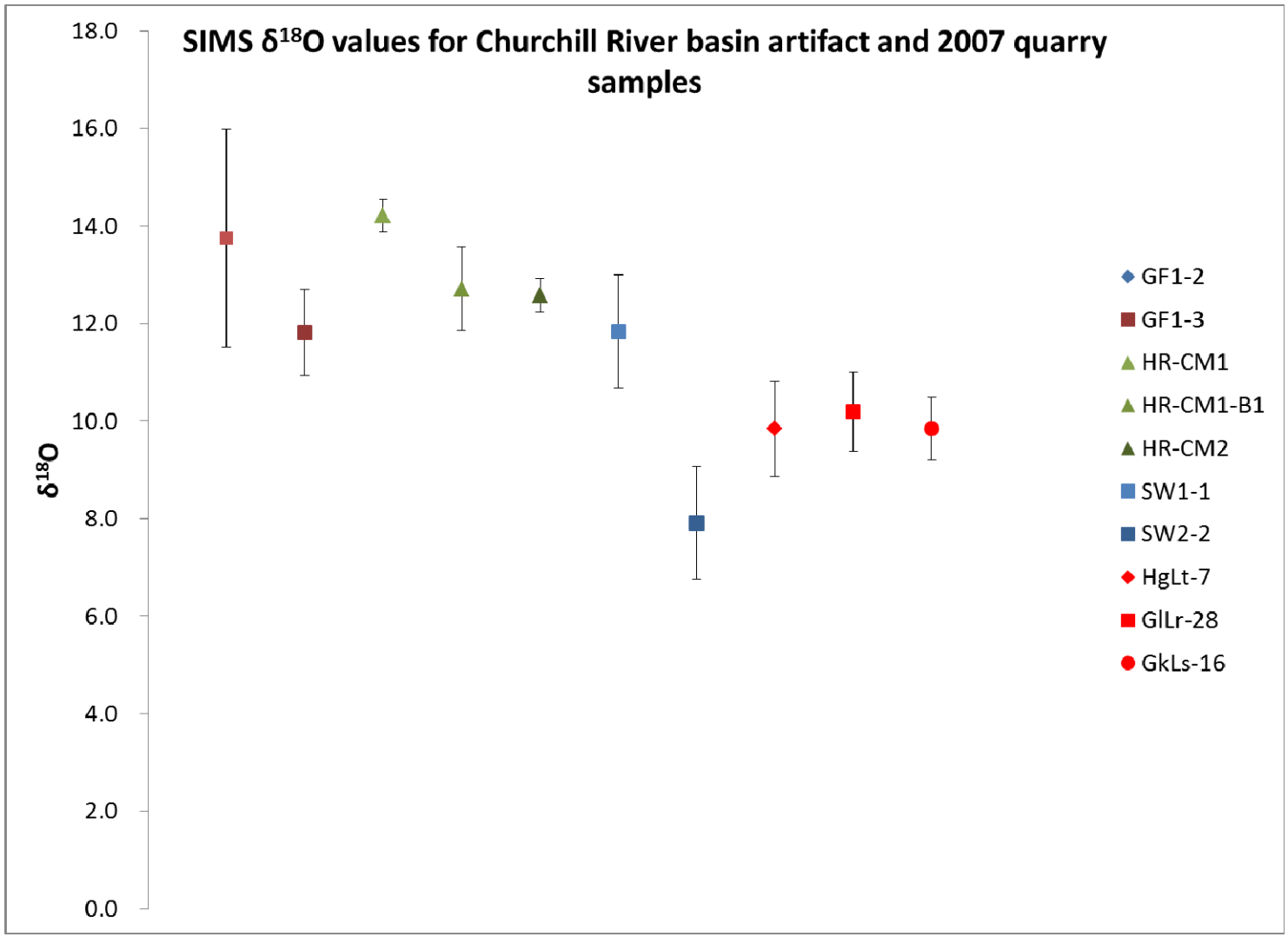


Figure 8.10 SIMS $\delta^{18}O$ values for Churchill River basin artifacts and 2007 quarry samples

8.4.4.1 White/clear quartz SIMS $^{208}Pb/^{204}Pb$ ratio and trace element (Ti, Ge) results

8.4.4.1.1 Quarry results

White or clear quarry samples are best differentiated using a combination of $^{208}Pb/^{204}Pb$ and Ti concentrations (Figure 8.11, Appendix 1, Table 8.5). White quartz from Grandfather is enriched in ^{208}Pb relative to other quarries (33.2-35.7) and falls within the middle of the Ti distribution exhibited by the white quartz sample set (9.5-12.3ppm). White quartz samples from Little Grandfather, despite being obtained in such close proximity to the larger Grandfather quarry, exhibit significantly different Pb isotope and Ti concentration (9.2ppm) data. White quartz from this source is also chemically homogenous; the two samples analyzed are indistinguishable from each other in terms of $^{208}Pb/^{204}Pb$ and Ti chemistry. The Little Grandfather samples are, on average, less enriched in Ti (9.2ppm) than material from Grandfather quarry and exhibit lower $^{208}Pb/^{204}Pb$ ratios (31.9). Pickerel Bay white quartz Pb isotope ratios and Ti concentrations are distinct from those of Granville Lake district white quartz. Compared to Granville Lake quarry materials, Pickerel Bay quartz is depleted in ^{208}Pb relative to ^{204}Pb (28.5, 20.4). Ti concentrations in the two Pickerel Bay white quartz samples analyzed are variable, comprising the upper and lower limits of the data set (6.4ppm, 18.4ppm). $^{208}Pb/^{204}Pb$ ratios and Ti values are not sufficient to distinguish white quartz samples from the Grandfather and Wheatcroft quarries. However, its higher mean Ge concentration (1.7ppm) in combination with lower $^{208}Pb/^{204}Pb$ ratio (33.1) place the single white quartz sample obtained from the quarry pit exploiting this material at Wheatcroft outside of the expected chemical distribution of Grandfather white quartz samples (Figure 8.12a).

Table 8.5: White quartz sample mean $^{208}Pb/^{204}Pb$ and trace element concentrations			
Sample no.[1]	$^{208}Pb/^{204}Pb$	Ti (ppm)	Ge (ppm)
GF07	34.39	9.53	1.42
GF12	33.70	12.30	1.46
GF13	34.77	10.93	1.45
GF19	35.66	11.14	1.29
GF23	33.23	10.95	1.58
GFNW11	31.94	9.21	1.54
GFNW13	31.88	9.16	1.52
WC15	33.11	11.79	1.40
SW1	30.39	18.37	1.58
SW2	28.52	6.33	1.48
HbMd-6/241	34.36	11.90	NA
HcLx-1/241	30.02	15.65	NA
HcLx-1/381	33.69	14.66	NA
HcLx-1/622	33.93	1.52	NA
HcLx-1/624	30.16	6.81	NA
HdLw-1/254	32.44	14.04	NA
HdLw-2/80	34.18	17.68	NA
HdLw-6/28	31.65	8.80	NA
HdLw-7/43	32.96	13.15	NA
HdLx-23/14	32.24	10.66	NA
HdLx-7/5	33.18	12.96	NA
HeLs-16/4	27.60	9.08	NA
HeLw-1/20	34.06	3.43	NA
HeLw-1/229	34.04	13.72	NA
HeLw-2/18	33.92	7.93	NA
HeLw-2/19	35.05	15.78	NA
HeLw-2/240	33.79	8.60	NA
HeLw-20/455	27.44	9.01	NA
HgLt-7/27	34.01	24.96	NA
HhLp-16/24	31.78	27.35	NA
HhLp-16/31	28.17	18.51	NA
HhLp-7/12	29.09	14.08	NA
HhLp-7/8	31.04	N/A	NA
HhLt06/15	34.00	17.85	NA
HiLp-1/12132	33.39	13.30	NA
HiLp-1/12322	33.28	5.31	NA

HiLp-1/12485	28.30	6.69	NA
HiLp-1/4976	31.32	2.92	NA
HiLp-1/6498	33.86	0.86	NA
HiLp-1/7421	34.41	6.53	NA
HiLp-1/7456	32.37	13.37	NA
HiLp-1/8715	30.85	9.11	NA
HiLp-1-2980	33.39	12.55	NA
HiLp-15/67	26.97	17.66	NA
HjLp-15/58	33.54	20.75	NA
HjLp-15/61	33.53	12.76	NA
HjLp-6/5	35.64	20.34	NA

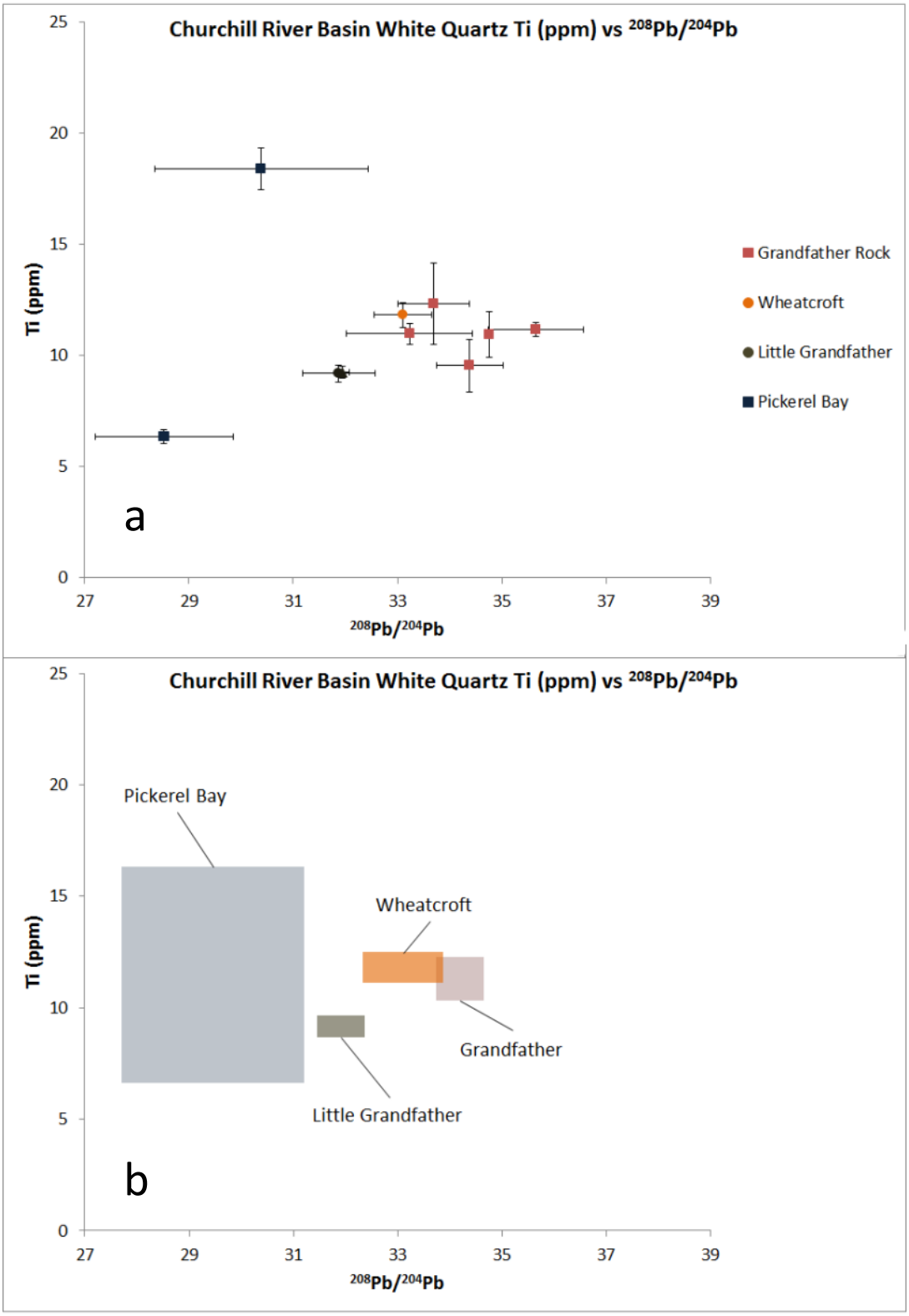


Figure 8.11 (a) Bivariate plot of Churchill River basin white quartz Ti concentrations (ppm) against 208Pb/204Pb values. (b) Bivariate plot of 95% confidence polygons for white quartz quarry Ti concentrations (ppm) and $^{208}Pb/^{204}Pb$ values.

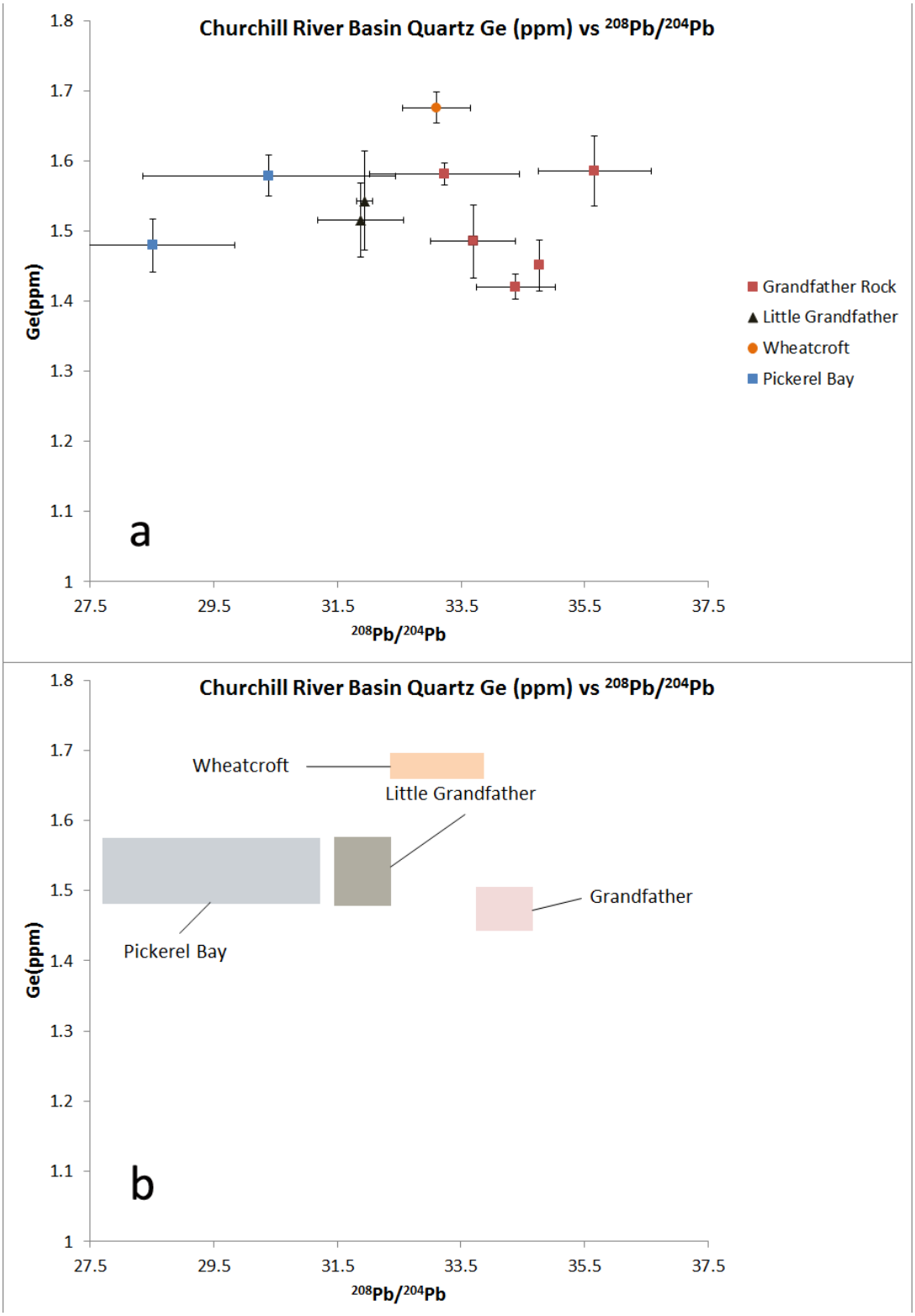


Figure 8.12 (a) Bivariate plot of Churchill River basin white quartz Ge concentration (ppm) against $^{208}Pb/^{204}Pb$ values. (b) Bivariate plot of 95% confidence polygons for white quartz quarry Ge concentrations (ppm) and $^{208}Pb/^{204}Pb$ values

8.4.4.1.2 Artifact results

Of the 36 white/clear quartz artifacts analyzed, 22 yielded valid Ti concentration and $^{208}Pb/^{204}Pb$ data (Figure 8.12, Table 8.5). Ti concentration data were obtained from the remaining 14 artifacts, but poor ionization of Pb meant that accurate Pb isotope data could not be collected from these samples. Eleven of the artifacts yielding both Pb and Ti data plot within the expected chemical distribution of one or more of the analysed Churchill River basin white quartz samples (Figure 8.14). The 11 remaining artifacts are chemically distinct from analyzed quarry materials. Of the artifacts with Ti and Pb chemistry similar to known Churchill River basin quarries, eight plot exclusively within the chemical distribution expected for white quartz from Grandfather quarry. The remaining three are chemically similar to material from more than one source. Two samples are similar to both Grandfather and Wheatcroft white quartz (HiLp-1/12132, HdLw-7/43), but only fall within the expected chemical distribution of the latter at the extreme low end of their Ti errors, and have mean values more characteristic of Grandfather quarry material. Due to an unresolvable isobaric interference affecting artifact Ge data, this discriminator cannot be applied to resolve this overlap.

One artifact is chemically similar to quartz from both Grandfather and Little Grandfather quarries (HdLw-6/28), but exhibits mean $^{208}Pb/^{204}Pb$ and Ti concentration values that are more similar to those from Little Grandfather, falling within the expected chemical distribution of Grandfather white/clear quartz at the extreme lower end of the $^{208}Pb/^{204}Pb$ range of this source.

The eleven artifacts plotting outside the expected chemical range for white/clear quartz from analyzed quarries are distinct due to their Ti contents, rather than their

$^{208}Pb/^{204}Pb$ values, which all fall within the range exhibited by Granville Lake quarry district sources (Figure 8.33). Five of these artifacts (HcLx-1/622, HiLp-1/6498, HiLp-1/7425, HiLp-1/12322, HeLw-1/20) have lower Ti concentrations than Granville Lake quarry material, while six (HcLx-1/381, HeLw-2/19, HdLw-2/80, HgLt-7-27, HhLp-16/24, HjLp-15/58) have higher Ti concentrations than Granville Lake quarry material. None of the samples show chemistry consistent with samples from the Pickerel Bay sources.

Sites represented by multiple white quartz samples with associated $^{208}Pb/^{204}Pb$ ratio and Ti concentration data show different degrees of chemical variability (Figures 8.15-8.19). Neither of the two artifacts from HcLx-1(HcLx1/381,622) fall within the chemical range of material from the Churchill River basin quarries (Figure 8.15). Both artifacts have similar Pb chemistry, but are unlike in terms of Ti concentration. HcLx-1/622 produced one of the lowest Ti concentrations of the entire artifact sample (1.5ppm), while HcLx-1/381 (14.7ppm) falls just above the Ti range of Granville Lake quarry district materials.

One of the artifacts from HjLp-15 (HjLp-15/61, $^{208}Pb/^{204}Pb = 33.5$, Ti = 12.8ppm) falls within the chemical range of white quartz from Grandfather quarry (Figure 8.16), while the other (HjLp-15/58), has higher Ti levels than white quartz from any of the Churchill River Basin quarries (20.8ppm) and a higher $^{208}Pb/^{204}Pb$ ratio (33.5) than samples from the Pickerel Bay quarries.

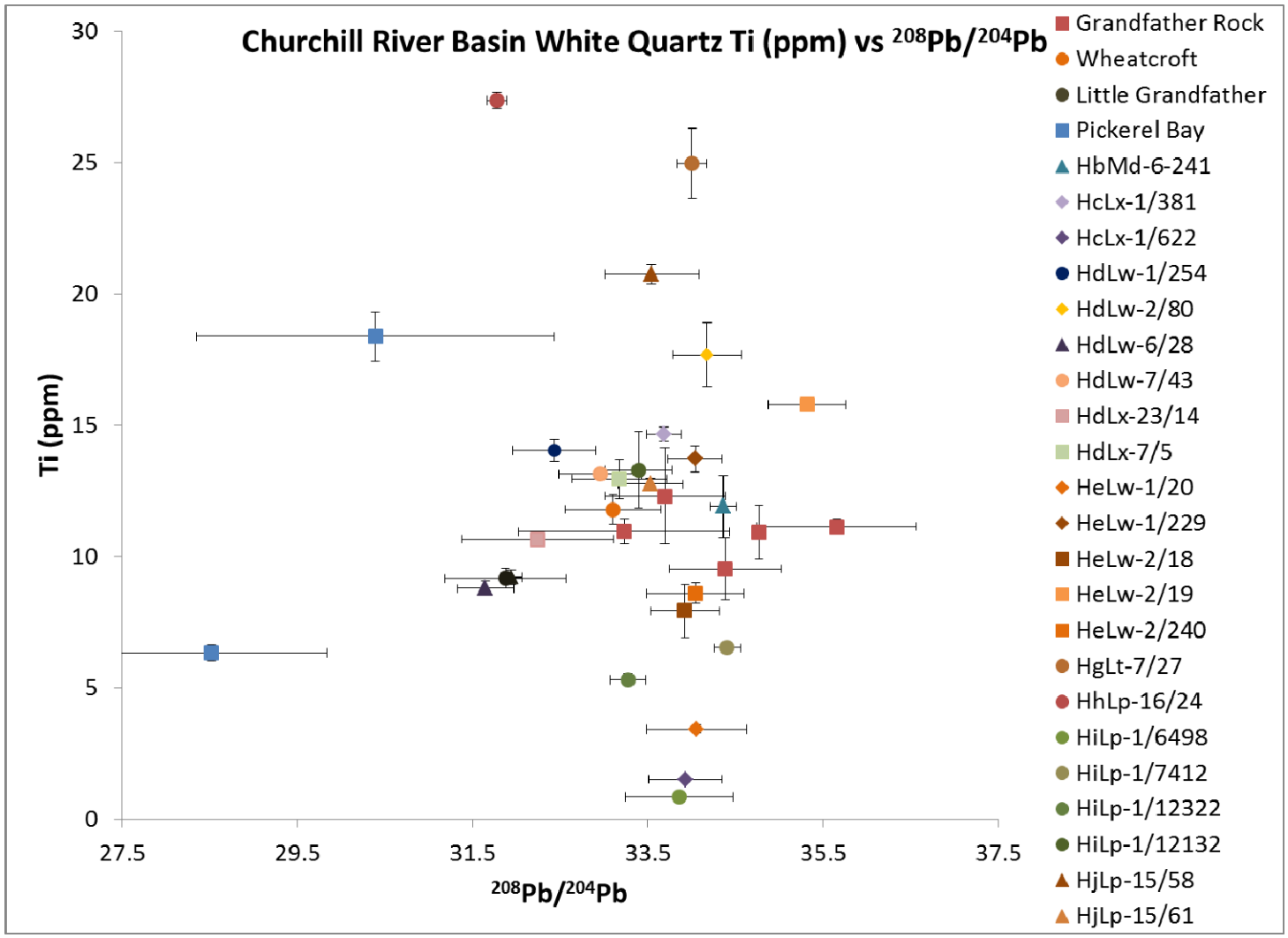


Figure 8.13: Biplot of white/clear quartz artifact and Churchill River basin quarry sample $^{208}Pb/^{204}Pb$ against Ti (ppm)

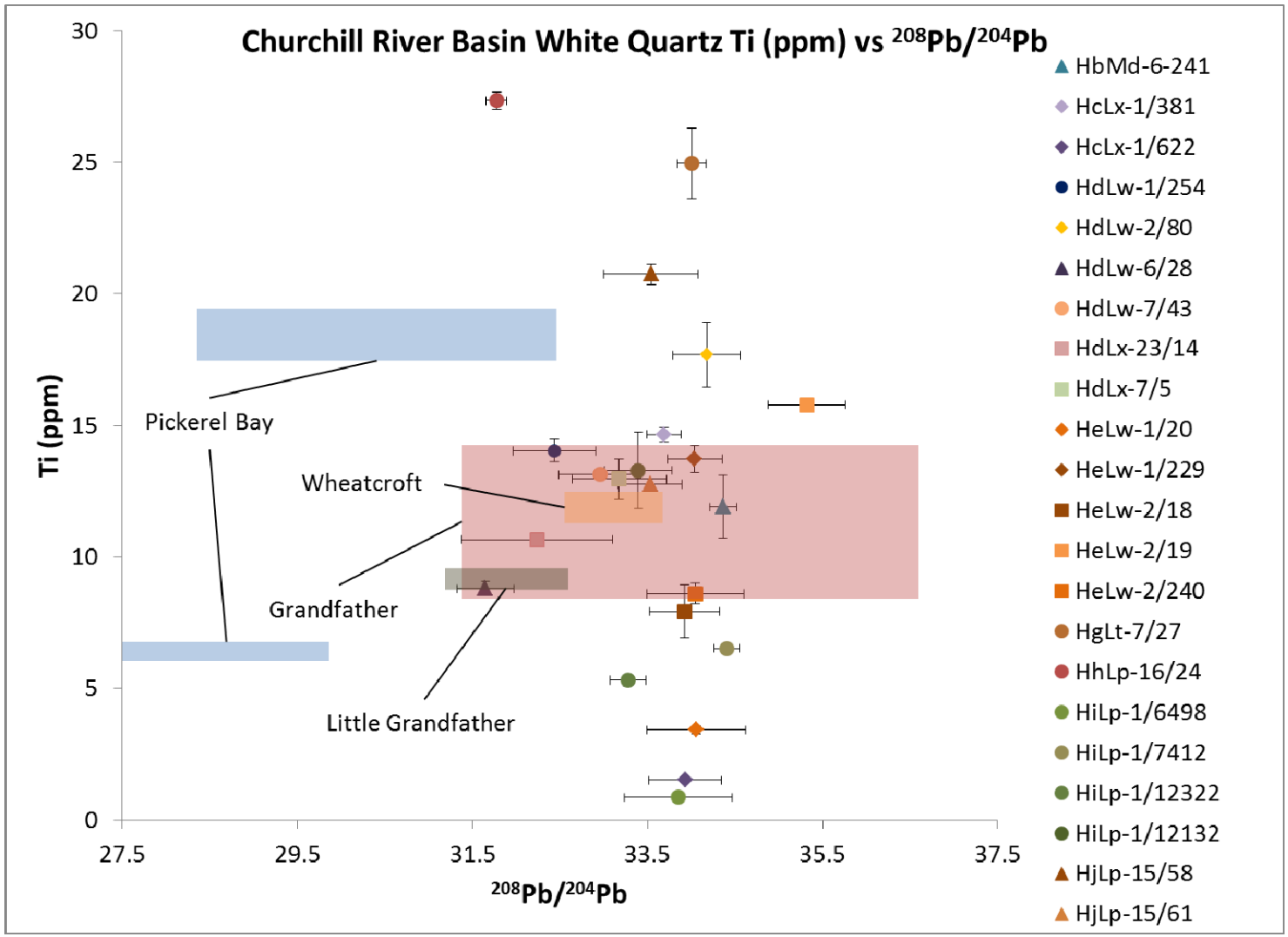
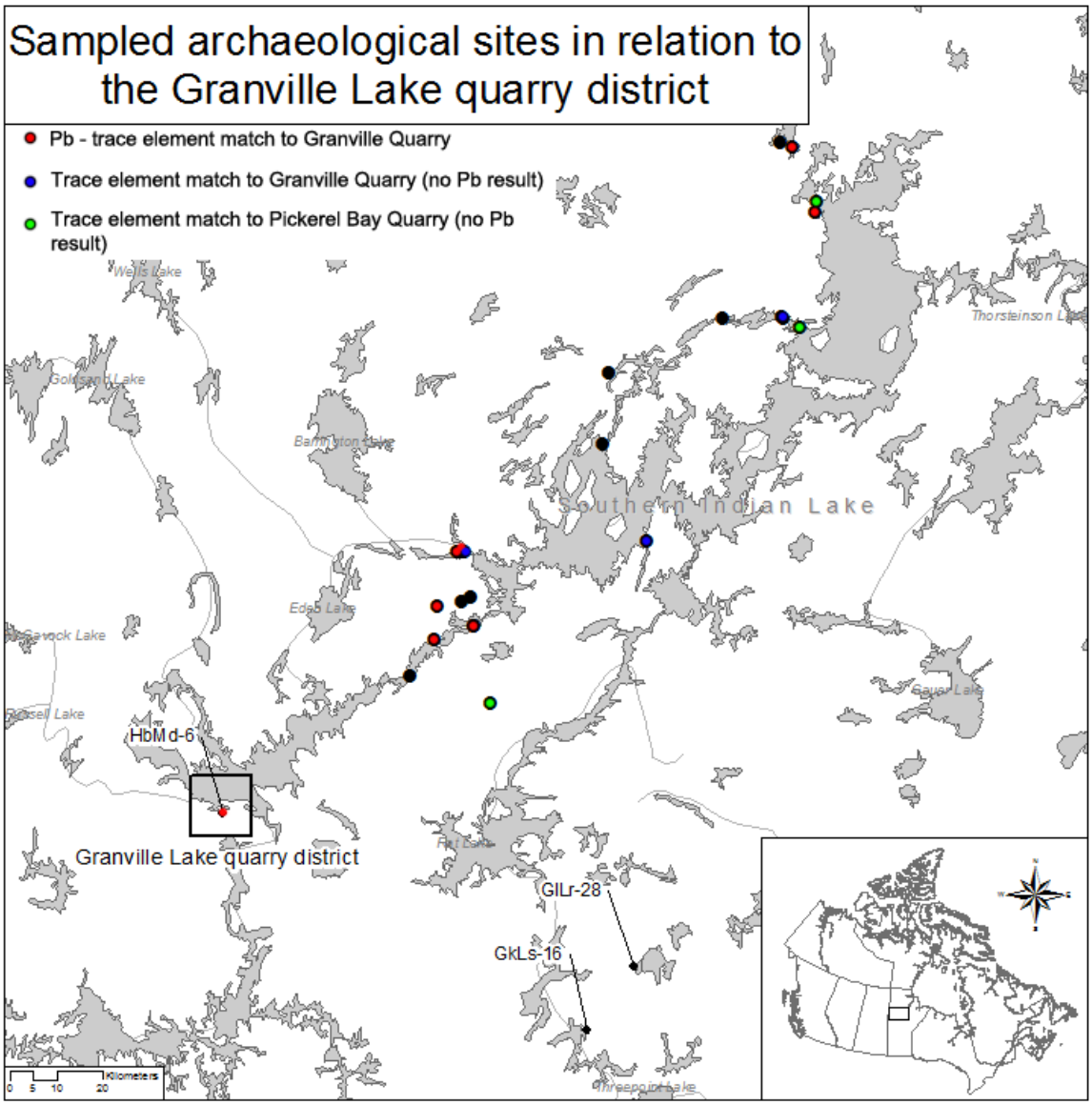


Figure 8.14 Biplot of white/clear quartz artifact $^{208}Pb/^{204}Pb$ against Ti (ppm) with polygons representing quarry chemical ranges

Three artifacts from HeLw-2 analyzed for this study produced both Pb isotope and Ti concentration data (Figure 8.17). Of these, two fall within the chemical range of white quartz from Grandfather quarry (HeLw-2/18, $^{208}Pb/^{204}Pb = 33.9$, Ti = 7.9ppm; HeLw-2/240, $^{208}Pb/^{204}Pb = 34.1$, Ti = 8.6ppm). The fourth artifact, HeLw-2/19 has significantly higher Ti levels than the Granville Lake quarry material (15.8ppm) and a higher $^{208}Pb/^{204}Pb$ ratio (33.3) than material from the Pickerel Bay sources.



Map 1 Sampled archaeological sites with provenance affiliations

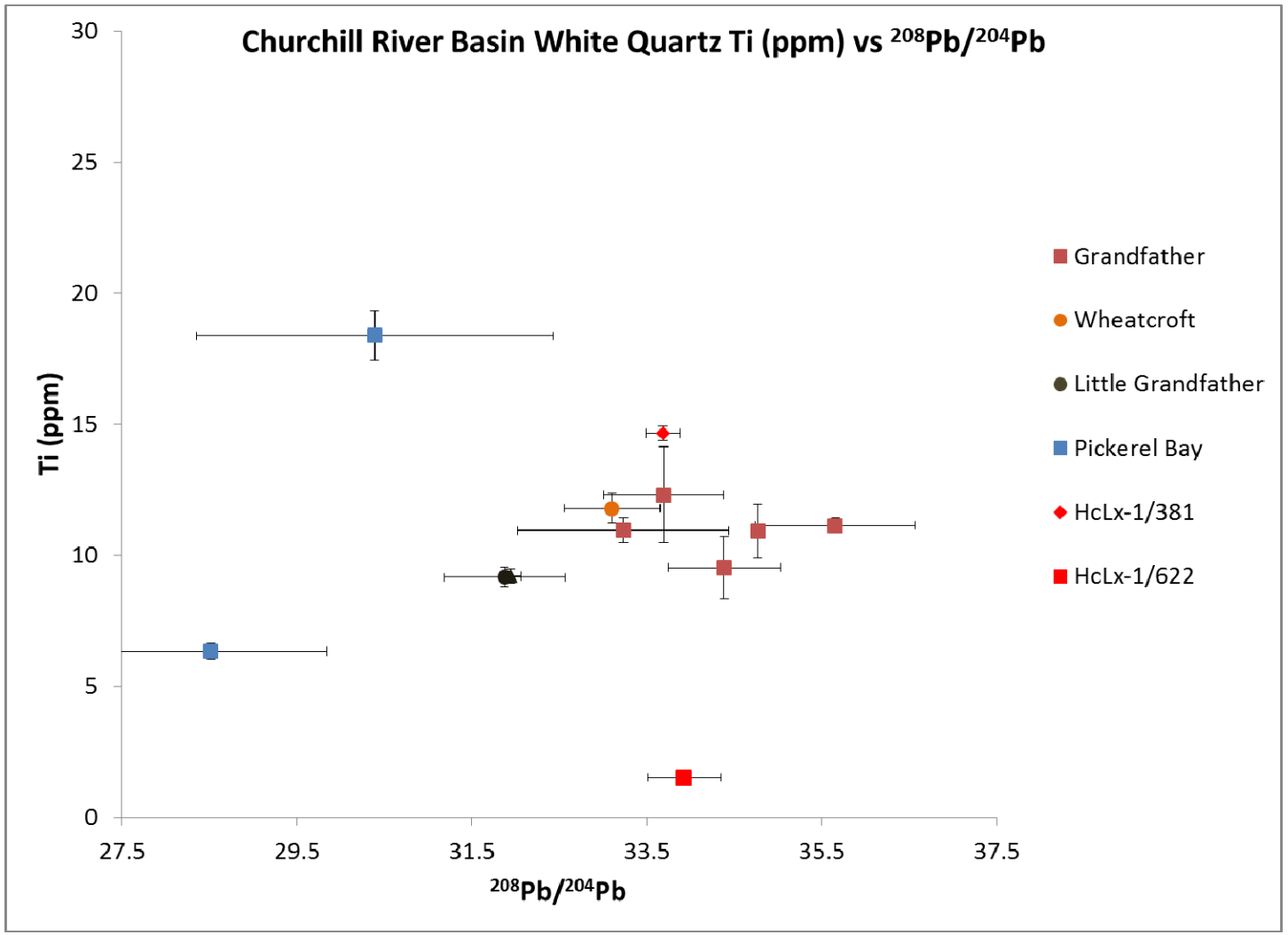


Figure 8.15 Biplot of HcLx-1 artifact and Churchill River basin quarry white/clear quartz $^{208}Pb/^{204}Pb$ against Ti (ppm)

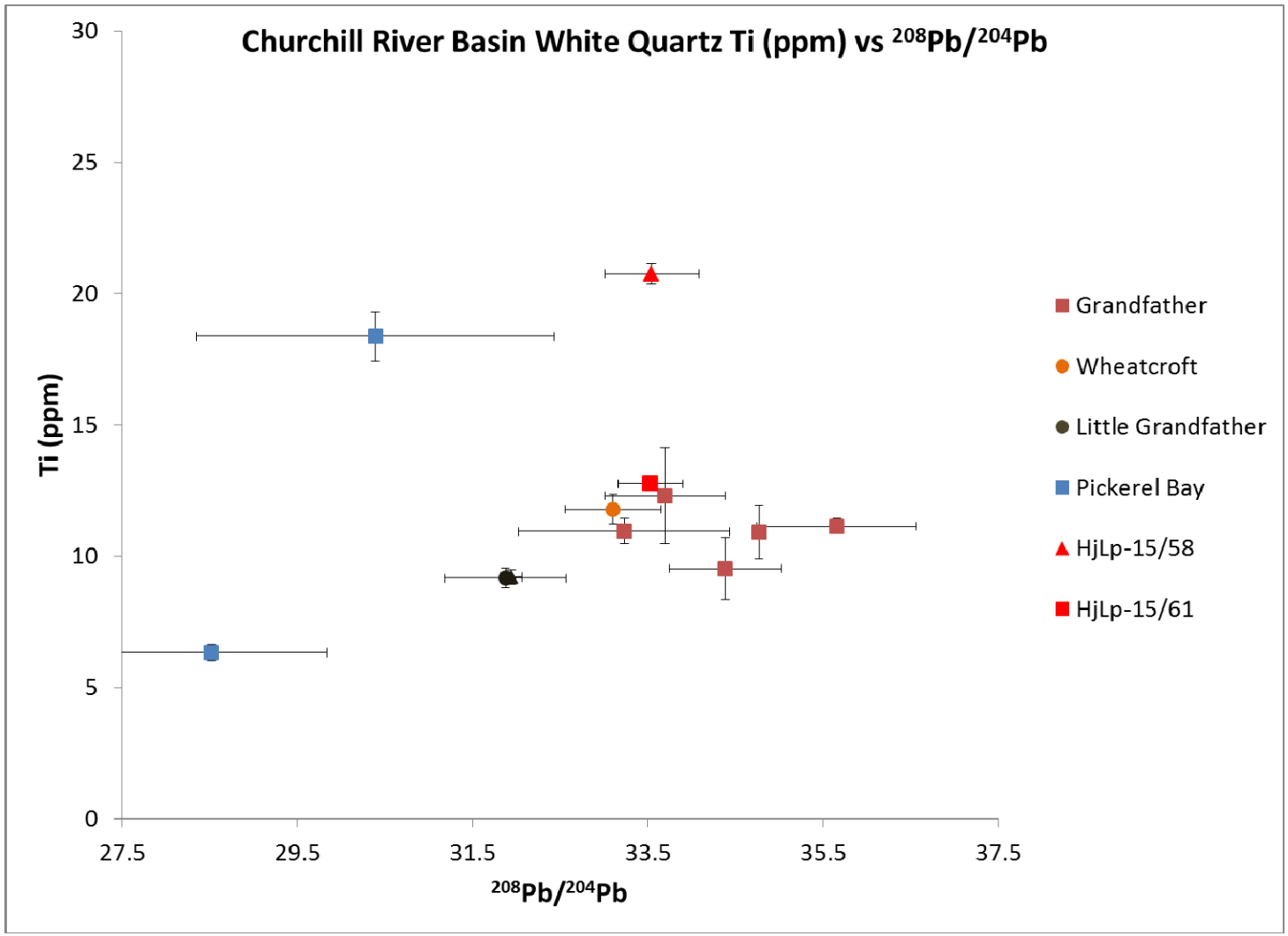


Figure 8.16 Biplot of HjLp-15 artifact and Churchill River basin quarry white/clear quartz $^{208}Pb/^{204}Pb$ against Ti (ppm)

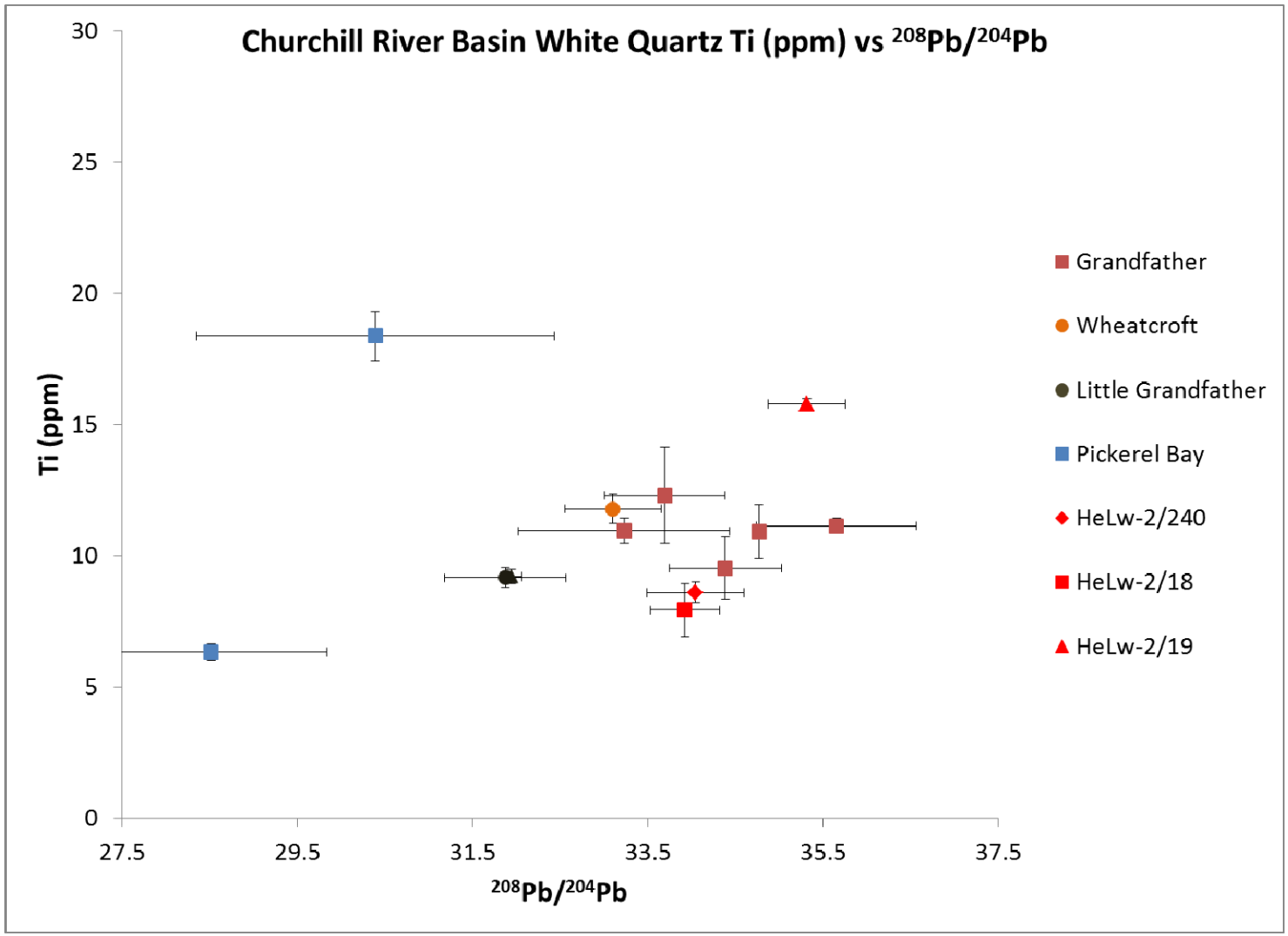


Figure 8.17 Biplot of HeLw-2 artifact and Churchill River basin quarry white/clear quartz $^{208}Pb/^{204}Pb$ against Ti (ppm)

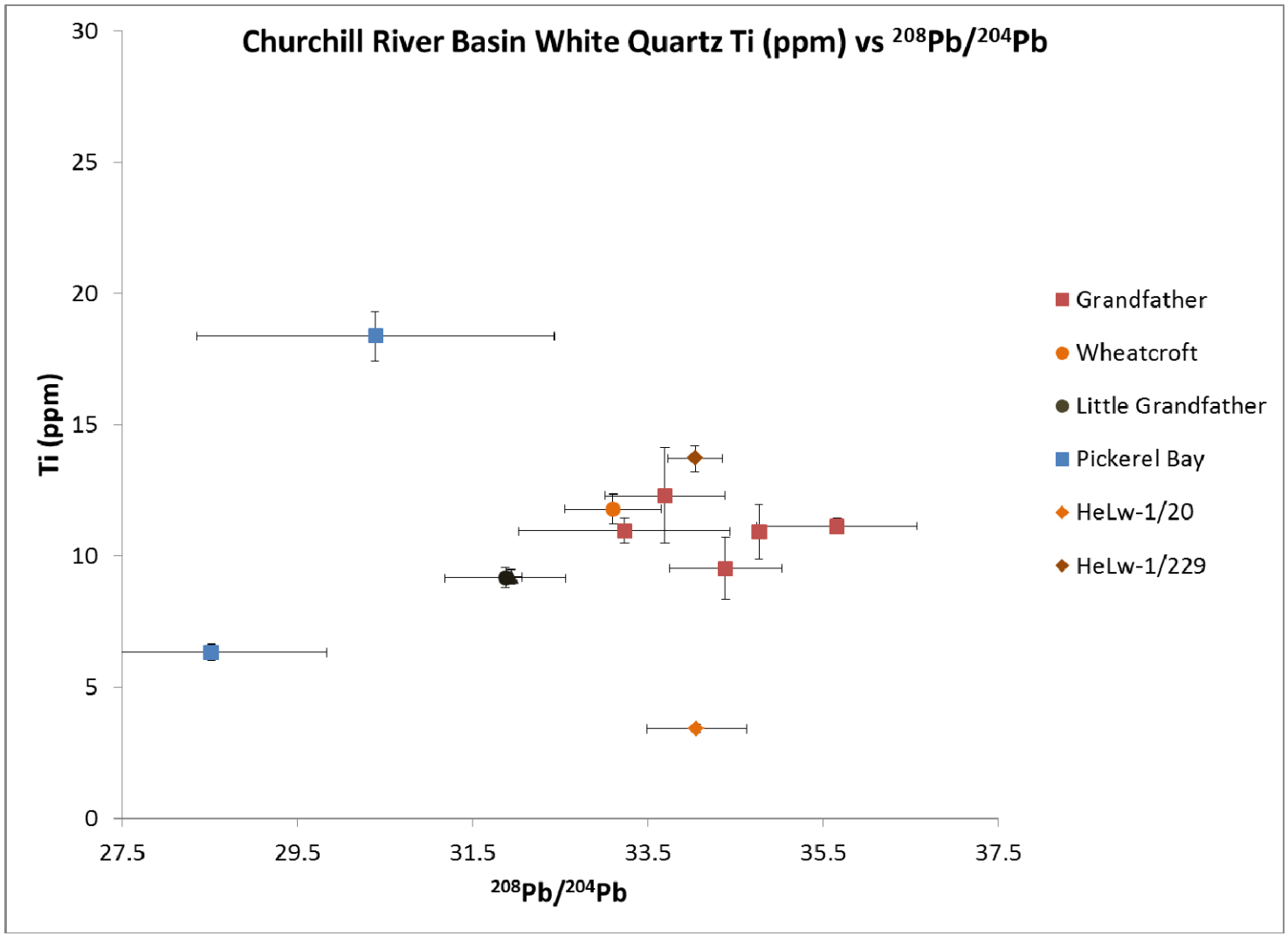


Figure 8.18 Biplot of HeLw-2 artifact and Churchill River basin quarry white/clear quartz 208Pb/204Pb against Ti (ppm)

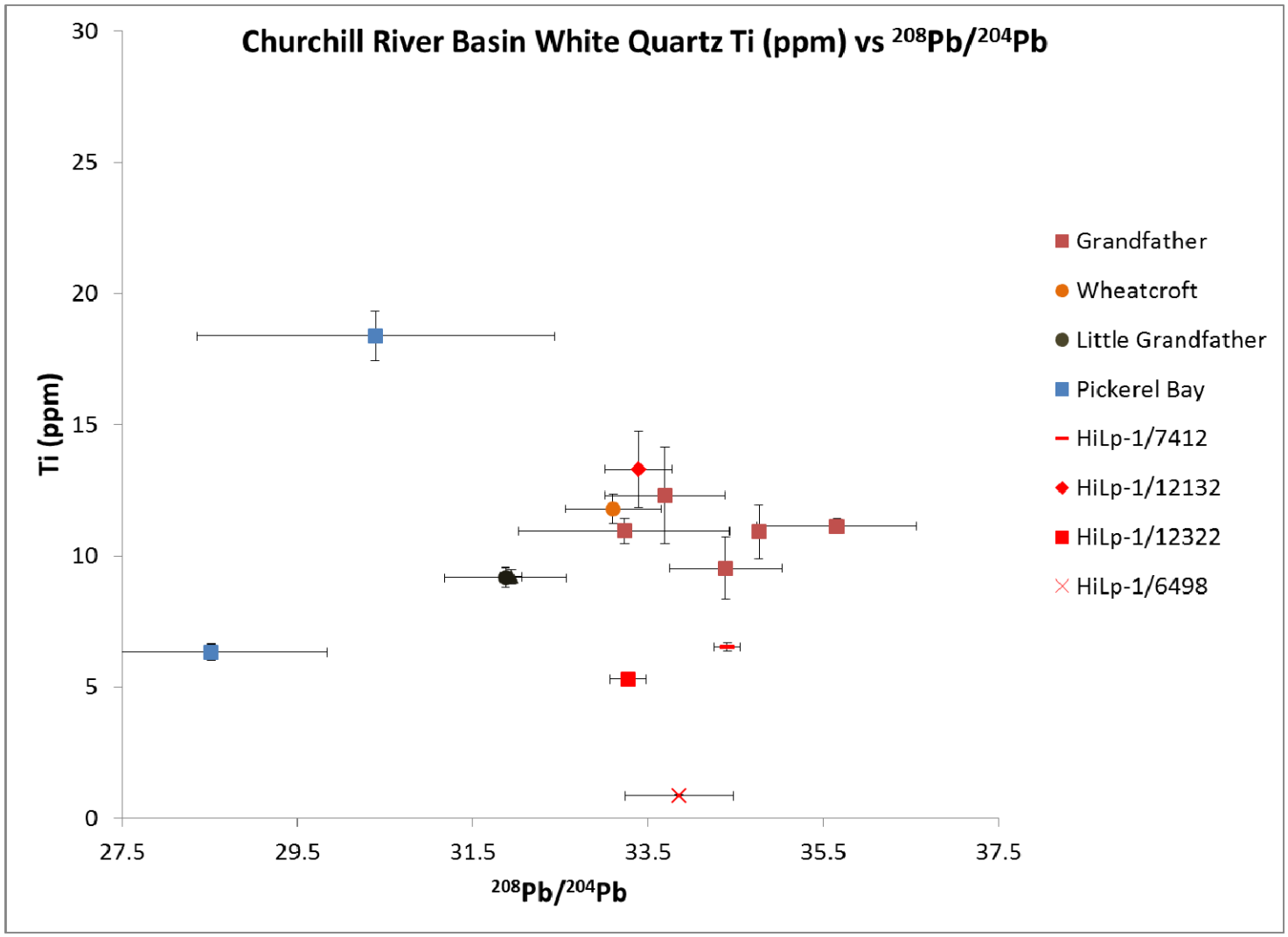


Figure 8.19 Biplot of HiLp-1 and Churchill River basin quarry white/clear quartz 208Pb/204Pb against Ti (ppm)

Two white quartz artifacts from HeLw-1 were analyzed (Figure 8.18). One, HeLw-1/229 ($^{208}Pb/^{204}Pb$ = 34.0, Ti = 13.7ppm) falls within the chemical range of white/clear quartz from Grandfather quarry. The other, HeLw-1/20, has a Ti concentration that is significantly lower than white/clear quartz from any of the Granville Lake quarry sources (Ti = 3.4), and a $^{208}Pb/^{204}Pb$ ratio that is too high for the Pickerel Bay sources ($^{208}Pb/^{204}Pb$ = 34.1)

Out of four artifacts from HiLp-1 that produced Ti concentration and Pb isotope data, only one (HiLp-1/12132, $^{208}Pb/^{204}Pb$ = 33.4, Ti = 13.3ppm) falls within the chemical range of white quartz from the Granville Lake quarries (Figure 8.19). Within error, this artifact is chemically similar to white quartz samples from both Grandfather and Wheatcroft sources. The other three artifacts from HiLp-1 have significantly lower Ti concentrations than white quartz from the Granville Lake quarries (HiLp-1/6498 = 0.9ppm; HiLp-1/7412 = 6.5ppm; HiLp-1/12322 = 5.3ppm) and higher $^{208}Pb/^{204}Pb$ ratios (HiLp-1/6498 = 33.9; HiLp-1/7412 = 34.4; HiLp-1/12322 = 33.3) than samples from the Pickerel Bay sources.

Ti concentration data for the 14 artifacts for which Pb isotope data are not available are presented in Figure 8.20. Six of these artifacts fall within the Ti range of Granville Lake quarry district white quartz, while eight fall outside of this range. Of the latter, five exhibit higher Ti concentrations than Granville Lake white/clear quartz, while three contain Ti in concentrations lower than Granville Lake white/clear quartz (Table 8.6). Four artifacts (HjLp-6/5, Ti = 20.3ppm; HhLt-6/15, Ti = 17.9ppm; HiLp-15/67, Ti = 17.7ppm; HhLp-16/31, Ti = 18.5ppm) are chemically indistinguishable from Pickerel Bay sample SW1-1 on the basis of Ti data alone, while two (HiLp-1/12485, Ti = 6.7ppm;

HcLx-1/624, Ti = 6.8ppm) are similarly indistinguishable from sample SW2-2. In the absence of reliable $^{208}Pb/^{204}Pb$ data, petrographic analysis could be implemented as part of an attempt to distinguish the latter samples from the Pickerel Bay material, as Pickerel Bay quartz is made up of relatively small, strained crystals of quartz. Presence of these in artifacts with Ti values similar to Pickerel Bay samples would support assigning them to the same source, while their absence would indicate they were procured elsewhere. Unfortunately, Ge data that might support or challenge assigning artifacts with Ti values similar to Grandfather white quartz are unavailable due to an unresolvable isobaric interference affecting Ge data obtained from artifact samples.

8.4.4.2 Smoky quartz SIMS $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ and trace element (Ti) results

8.4.4.2.1 Quarry results

Distinguishing between material from different smoky quartz quarries in the Granville Lake district is relatively straightforward. A trivariate plot of Ti concentration, $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ ratios differentiate between the Smoky Quartz, Floating Island Bay, and Grandfather quarries (Figure 8.21). The Floating Island Bay and Smoky Quartz quarries exhibit low $^{207}Pb/^{206}Pb$ ratios relative to the Grandfather and Little Grandfather quarries (Table 8.6). Samples from the Smoky Quartz quarry can be differentiated from Floating Island Bay quartz by their relatively high mean $^{208}Pb/^{204}Pb$ ratios (Smoky Quartz: 32.7, 34.0, Floating Island Bay: 29.7, 30.5). Smoky quartz from Smoky Quartz and Floating Island Bay quarries can be distinguished from Grandfather smoky quartz

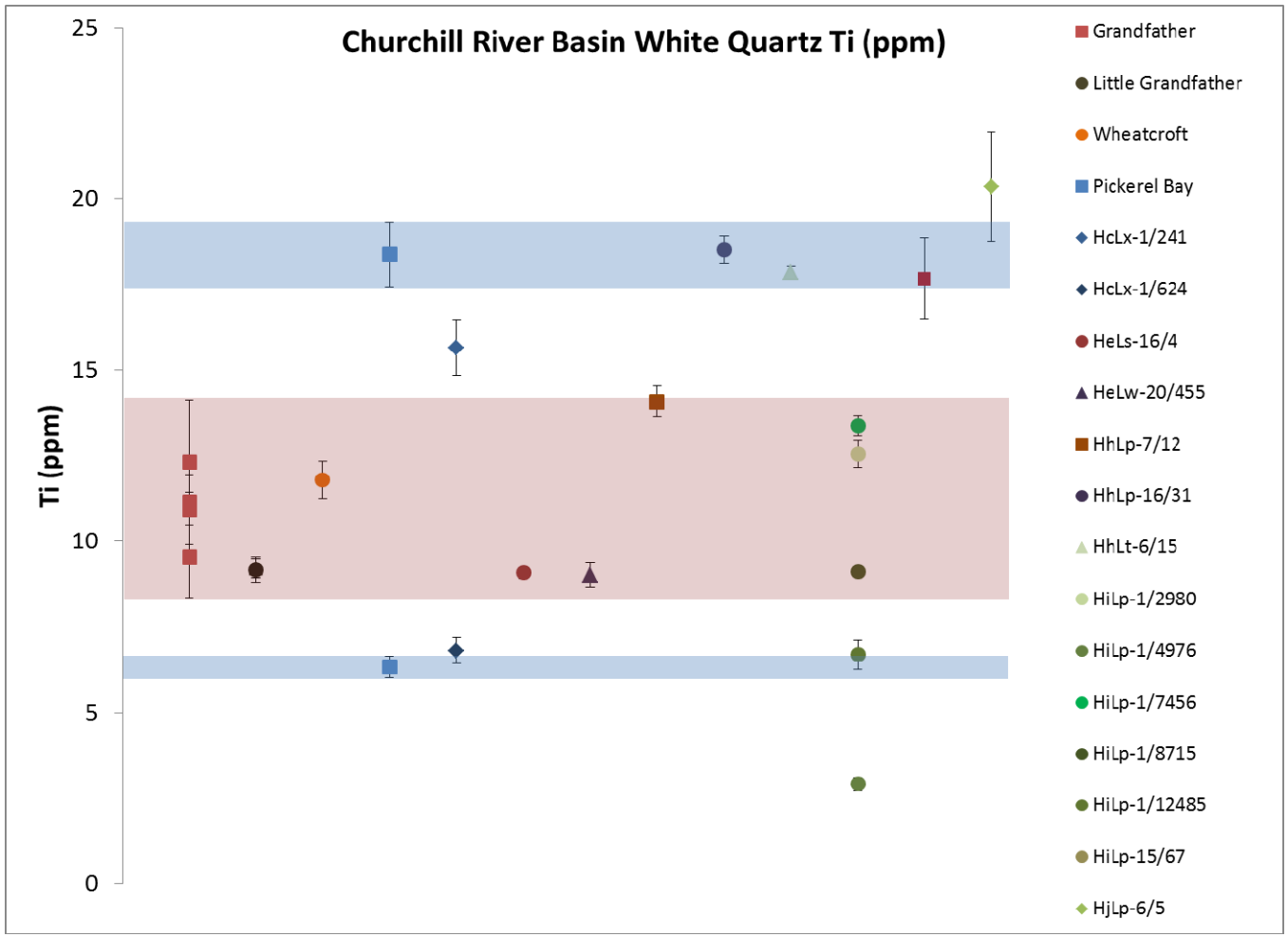


Figure 8.20 Plot of Ti (ppm) values of Churchill River basin white/clear quartz samples and artifact samples for which no Pb isotope data is available. Ti range of Granville Lake quarries shown in red, range of Pickerel Bay sources shown in blue.

based on their relatively high $^{207}Pb/^{206}Pb$ ratios (Smoky Quartz: 9.1, 9.1, Floating Island Bay: 0.88, 0.91, Grandfather: 0.83-0.85). There is significant chemical convergence between smoky quartz from Grandfather and Little Grandfather quarries, although, on average, samples from Little Grandfather exhibit lower Ti concentrations (9.3-9.7ppm) than those from Grandfather (9.7-16.5). Given their close proximity to one another, this is not surprising. Unlike white quartz extracted from these quarries, smoky quartz deposits at these sites likely formed from the same parent magma under similar evolutionary conditions.

7.4.4.2.2 Artifact results

Five smoky quartz artifacts were analyzed for this study (Table 8.6). $^{208}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, and Ti concentration data were obtained from four of these. All four of these artifacts fall outside of the chemical range of Granville Lake smoky quartz (Figure 8.22). HjLp-1/21 is the most easily distinguished from the Granville Lake sources, exhibiting high Ti (24.9ppm) relative to the Granville Lake sources. High Ti (19.4ppm) coupled with relatively a low $^{208}Pb/^{204}Pb$ (29.4) places GkLs-16/152 outside of the chemical range of any of the analyzed Granville Lake smoky quartz sources, while intermediate $^{207}Pb/^{206}Pb$ ratios place HiLp-1/7929 (0.88) and HiLp-1/8243 (0.88) outside of the distribution for analyzed smoky quartz sources.

Lead isotope data could not be obtained from one smoky quartz artifact, HiLp-1/7425 (Figure 8.23). This artifact exhibits Ti levels that are significantly lower than Granville Lake district smoky quartz (7.7ppm).

8.4.4.3 Rose quartz SIMS $^{208}Pb/^{204}Pb$ and trace element (Ti, Th/U) results

8.4.4.3.1 Quarry results

Differentiation between pegmatitic rose quartz samples requires measurement of chemical parameters other than those used for smoky or white/clear quartz source. Ti concentrations combined with $^{208}Pb/^{204}Pb$ ratios do not completely distinguish between the two major rose quartz quarries in the Granville Lake district (Figure 8.24). Material from the Wheatcroft quarry generally exhibits lower $^{208}Pb/^{204}Pb$ ratios (25.4-32.5) than rose quartz from the *Mimikweapisk* quarry (28.9-34.0) (Table 8.7), however, there is significant Pb isotopic overlap between the two sources. There is also significant overlap in Ti concentration data from *Mimikweapisk* (6.4-13.9ppm) and Wheatcroft (7.4-10.3ppm) quarries.

To differentiate between rose quartz from Wheatcroft and *Mimikweapisk* quarries, Th and U concentrations were quantified (Table 8.7). Mean Th/U values obtained from Granville Lake rose quartz samples show both intra- and inter-source variability (Figure 7.25). On average, rose quartz from *Mimikweapisk* quarry exhibits lower Th/U (0.9-2.1) ratios relative to Wheatcroft quarry rose quartz (1.8-2.1). However, one sample from the Wheatcroft quarry exhibits uncharacteristically low Th/U and high $^{208}Pb/^{204}Pb$ ratios (WC-5: Th/U = 0.6, $^{208}Pb/^{204}Pb$ = 32.5).

8.4.4.3.2 Artifact results

Eight rose quartz artifacts were analyzed for this study. Both Pb isotope and trace element data were obtained from seven of these artifacts (Figures 8.26-8.27, Table 8.7).

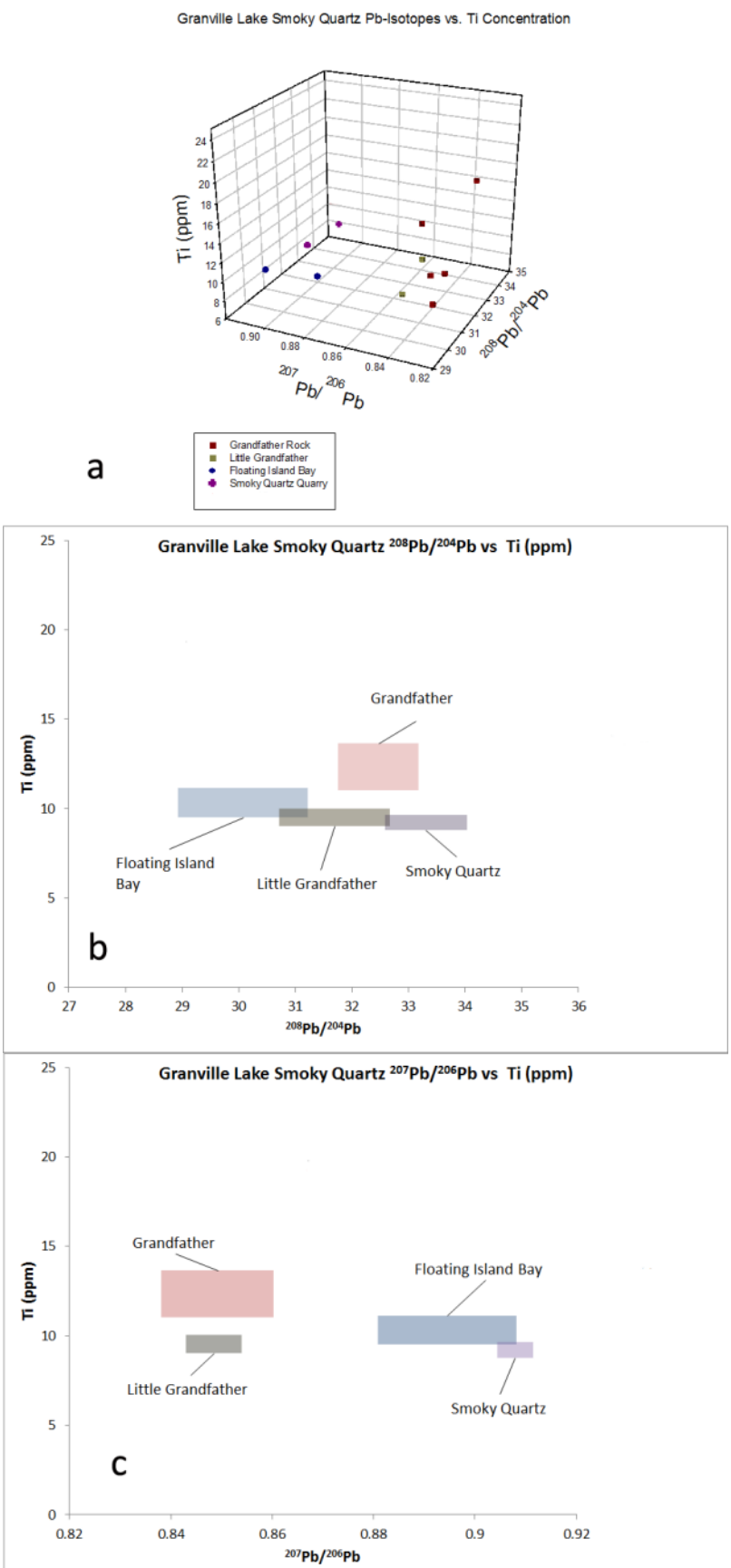


Figure 8.21 (a) Plot of Granville Lake smoky quartz Ti concentration (ppm) against $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$. (b) Bivariate plot of 95% confidence polygons for smoky quartz quarry Ti concentrations (ppm) and $^{208}Pb/^{204}Pb$ values. (c) Bivariate plot of 95% confidence polygons for white quartz quarry Ti concentrations (ppm) and $^{207}Pb/^{206}Pb$ values

Table 8.6: Smoky quartz artifact and Granville Lake quarry sample mean Pb isotope ratios and Ti concentrations

Sample no. [1]	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	Ti (ppm)
GF25	31.01	0.84	11.23
GF27	32.78	0.85	13.36
GF29	31.05	0.83	11.67
GF45	34.35	0.84	16.47
GFNW10	30.68	0.85	9.34
GFNW12	32.68	0.85	9.67
FIB02	30.46	0.91	9.30
FIB03	29.68	0.88	11.34
SQ05	32.65	0.91	8.77
SQ06	33.95	0.90	9.57
GkLs-16/152	29.38	0.87	19.44
HiLp-1/7425	NA	NA	7.74
HiLp-1/8243-1	33.22	0.88	11.09
HiLp-1/7929-1	33.23	0.88	14.33
HjLp-1/21-1	34.45	0.87	24.86

Three of these artifacts, HhLp-11/45 ($^{208}Pb/^{204}Pb$ = 34.0, Th/U = 0.42), HhLp-11/45 ($^{208}Pb/^{204}Pb$ = 34.0, Th/U = 0.31) and HgLt-7/28 ($^{208}Pb/^{204}Pb$ = 33.5, Th/U = 1.85) fit the Pb-Th-U profile of rose quartz from *Mimikweapisk* quarry, while the other artifacts fall outside of the chemical range of rose quartz from the Granville Lake quarries (Figure

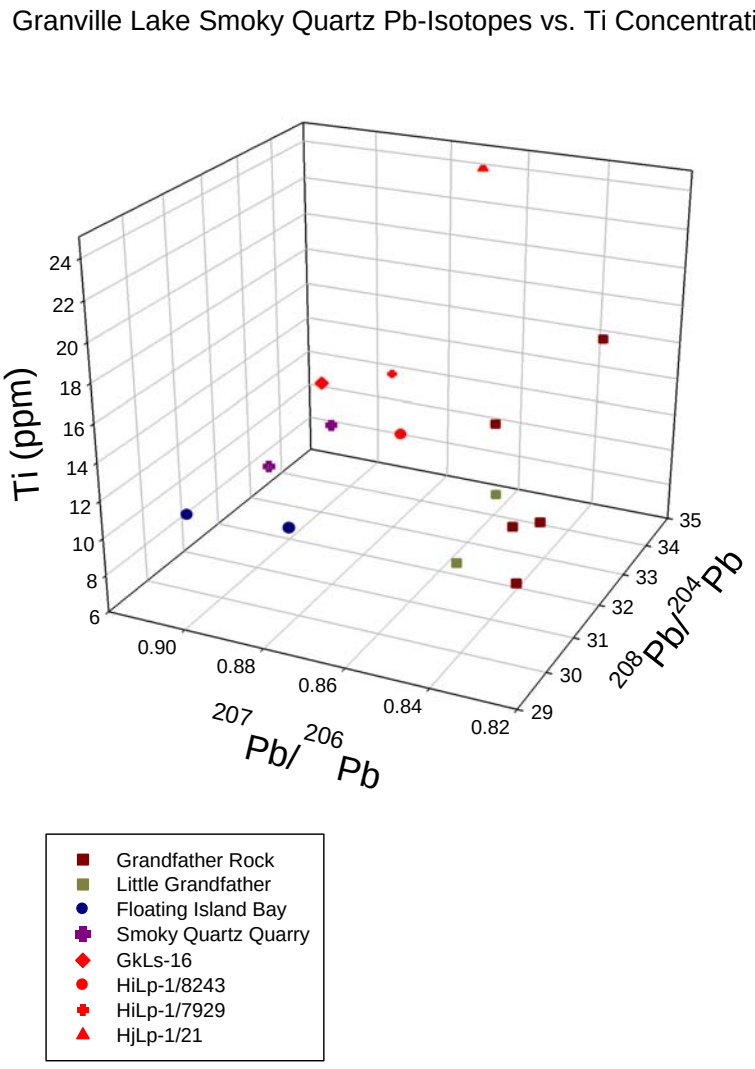


Figure 8.22 Triplot of smoky quartz artifact and Granville Lake quarry sample $^{208}Pb/^{204}Pb$ against $^{207}Pb/^{206}Pb$ against Ti (ppm)

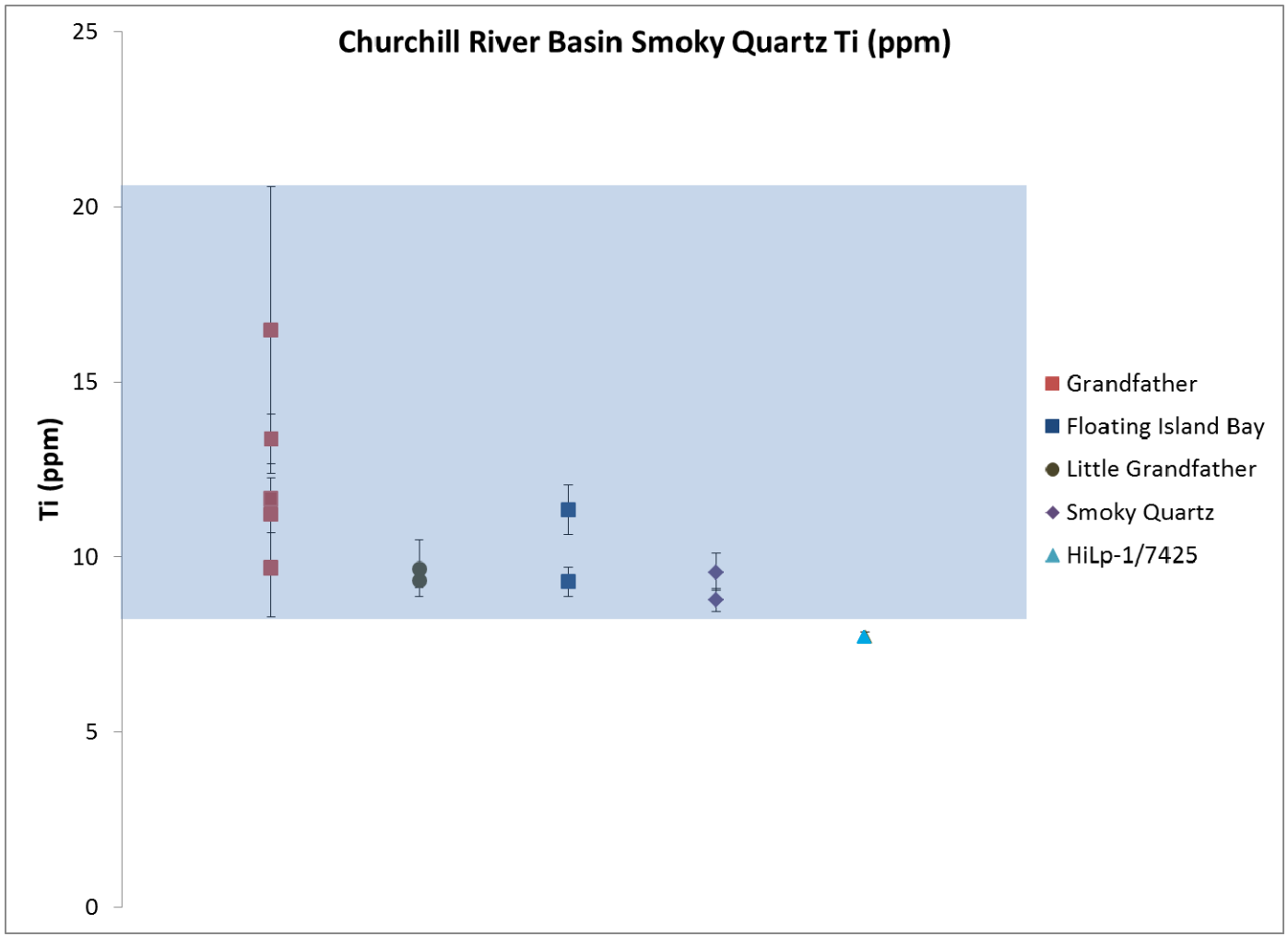


Figure 8.23 Plot of Ti (ppm) values of smoky quartz from Granville Lake quarries and artifacts for which no Pb isotope data is available

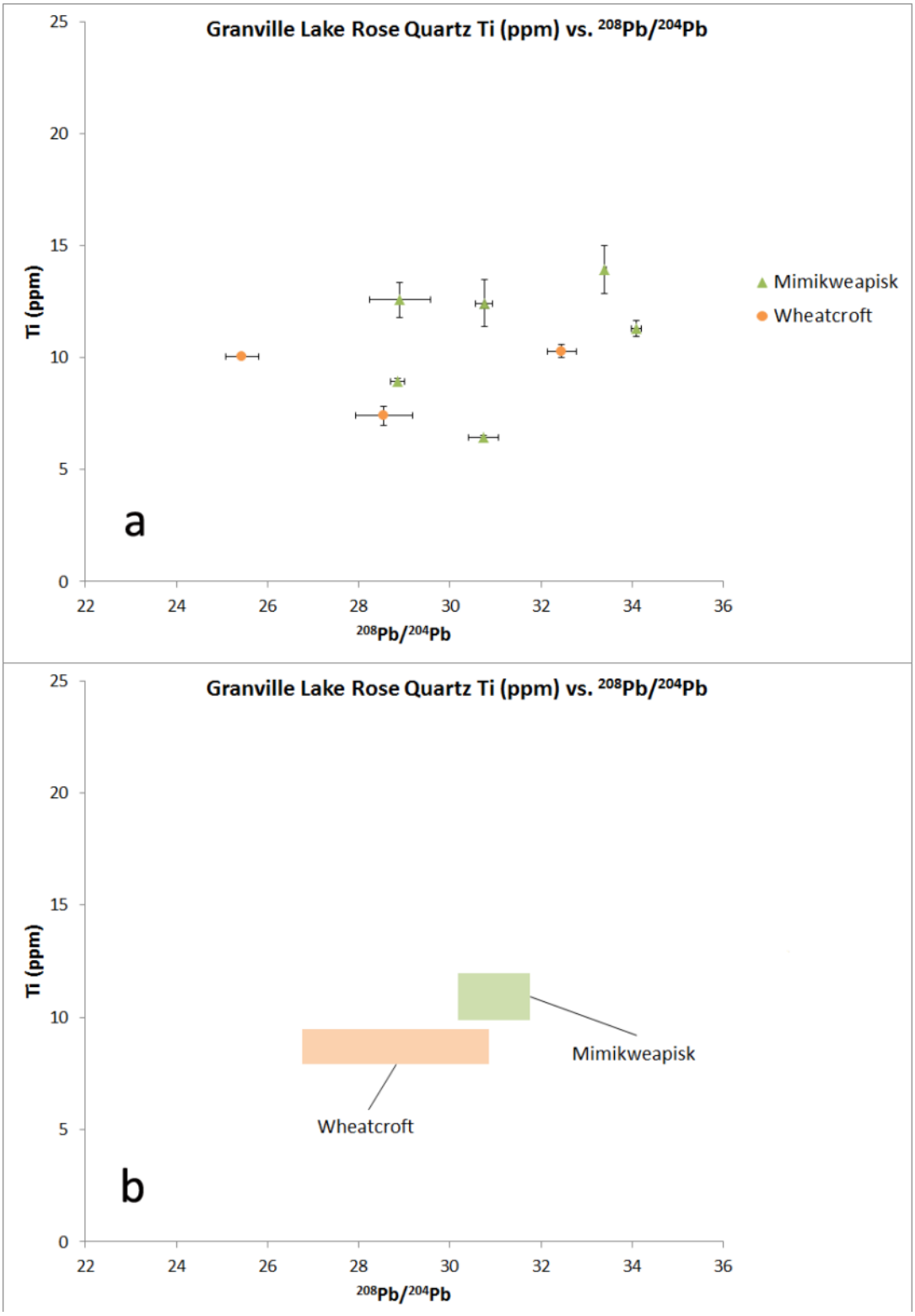


Figure 8.24: (a) Plot of Granville Lake rose quartz and rose quartz quarry Ti concentration (ppm) against $^{208}Pb/^{204}Pb$. (b) Bivariate plot of 95% confidence polygons for rose quartz quarry Ti concentrations (ppm) and $^{208}Pb/^{204}Pb$ values.

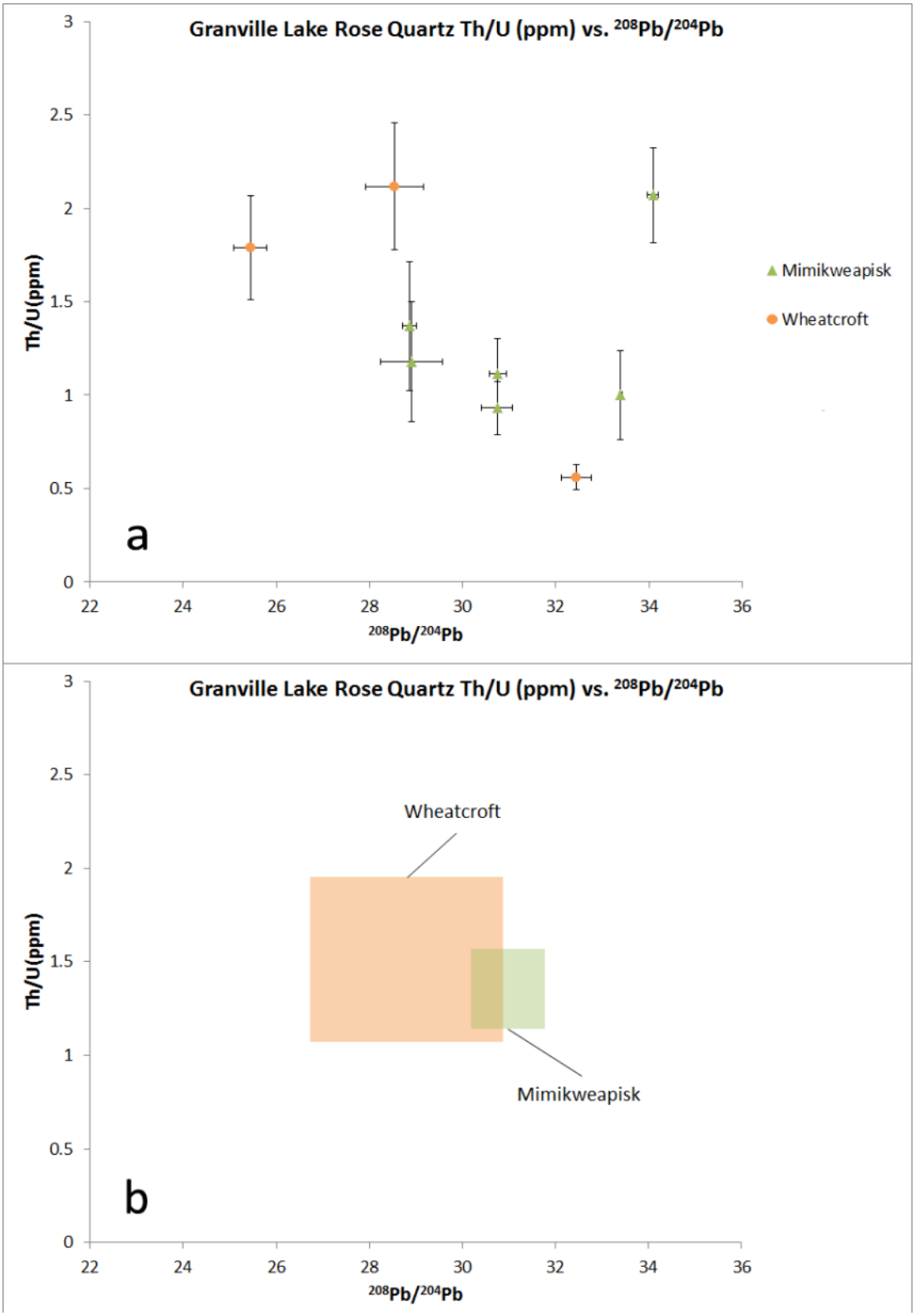


Figure 8.25 (a) Plot of Granville Lake rose quartz and rose quartz quarry Th/U values against $^{208}Pb/^{204}Pb$ values. (b) Bivariate plot of 95% confidence polygons for rose quartz quarry Th/U values and $^{208}Pb/^{204}Pb$ values.

8.26). Only one of the artifacts analyzed for this study falls within the Ti concentration/Pb isotope range of Granville Lake rose quartz (Figure 8.27). GlLr-28/11 and HgLt-7/50 are distinguished from Granville Lake material by their combined low $^{208}Pb/^{204}Pb$ ratios (GlLr-28/11 = 26.2; HgLt-7/50 = 23.4) and relatively high Ti concentrations (GlLr-28/11 = 14.5ppm; HgLt-7/50 =21.9ppm). Combined low $^{208}Pb/^{204}Pb$ and low Th/U (GlLr-28/11 = 1.10; HgLt-7/50 =0.76) exclude GlLr-28/11 and HgLt-7/50 from attribution to Granville Lake rose quartz sources. Three artifacts have relatively high Th/U values that fall outside of the range of rose quartz from Granville Lake sources (HhLr-4/5, Th/U = 16.0; HeLw-2/229, Th/U = 9.7; HdLx-20/9, Th/U = 5.6). Two of these artifacts also have significantly higher Ti concentrations relative to Granville Lake rose quartz samples (HhLr-4/5, Ti = 35.6ppm; HdLx-20/9, Ti = 18.3ppm), while one has Ti in concentration consistent within the range of the Granville Lake sources (HeLw-2/229, Ti = 6.6ppm). HhLp-11/45 contains Ti in concentrations significantly lower than Granville Lake rose quartz (5.2ppm), while HgLt-7/28 is characterized by significantly higher Ti levels (23.6ppm). Pb data could not be obtained from one rose quartz artifact (HiLp-1/4703). This artifact falls within both the Ti and Th/U range of Granville Lake rose quartz sources (Figures 8.28-8.29)

Table 8.7: Rose quartz artifact and Granville Lake quarry mean $^{208}Pb/^{204}Pb$ ratios and trace element concentrations

Sample no.	$^{208}Pb/^{204}Pb$	Ti(ppm)	Th(ppm)/U(ppm)
HR-3	33.39	13.91	1.00
HR-6	30.75	12.41	1.11
HR-13	34.09	11.29	2.07
HR-CM2	28.90	12.58	1.18
HR-CM3	28.85	8.92	1.37
HR-BM9	30.42	14.04	1.48
WC-3	28.55	7.41	2.12
WC-5	32.45	10.28	0.56
HgLt-7/50	23.40	21.87	0.76
GlLr-28/11	26.15	14.00	1.10
HhLr-4/5	33.21	35.62	5.34
HgLt-7/28	33.54	23.6	0.42
HhLp-11/45	34.02	5.16	0.31
HdLx-20/9	33.33	18.29	1.85
HeLw-2/229	32.14	6.59	3.24
HiLp-1/4703	34.35	7.58	0.72

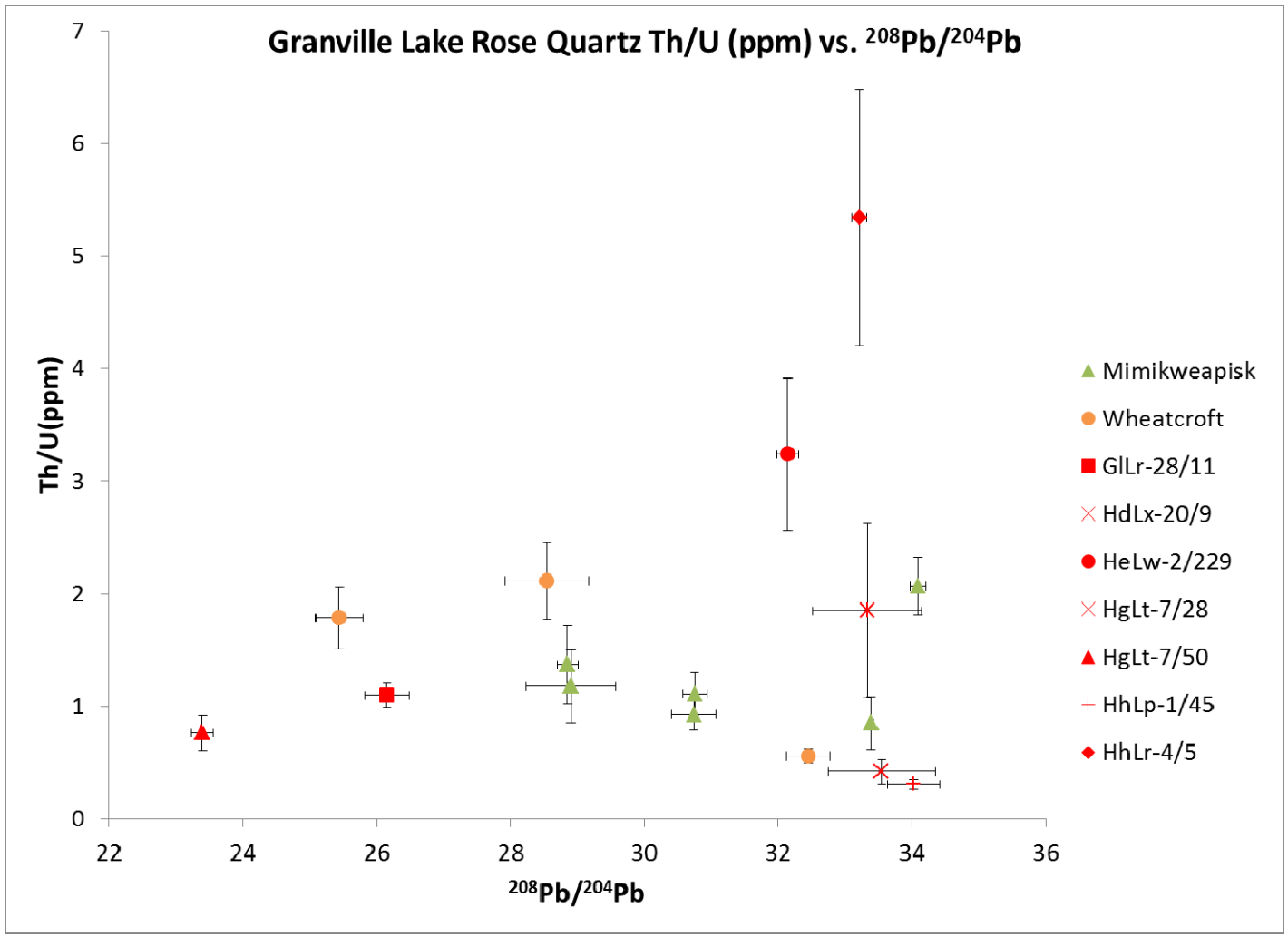


Figure 8.26 Biplot of rose quartz artifacts and Granville Lake quarry sample 208Pb/204Pb against Th/U

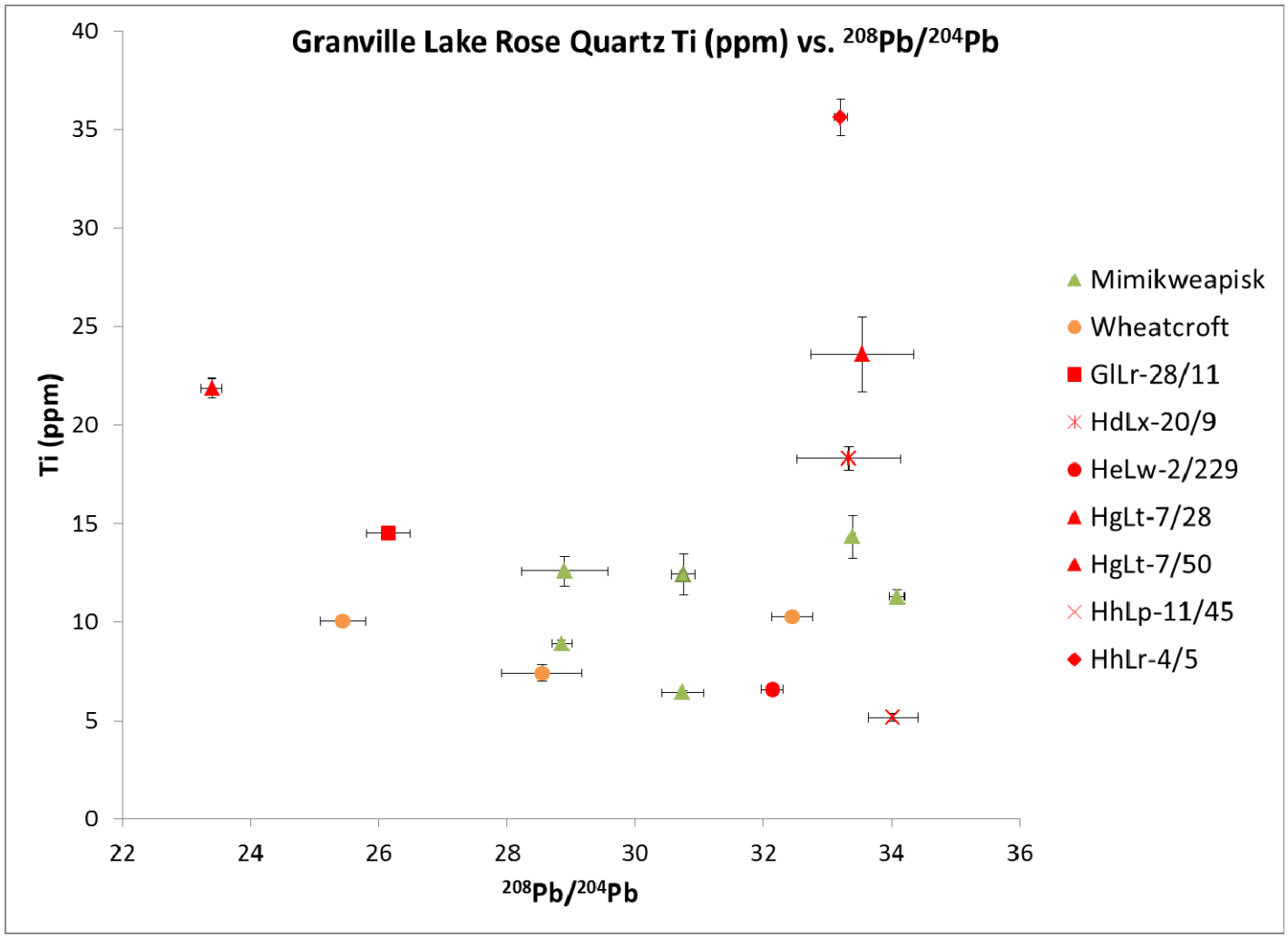


Figure 8.27 Biplot of rose quartz artifact and Granville Lake quarry sample 208Pb/204Pb against Ti (ppm)

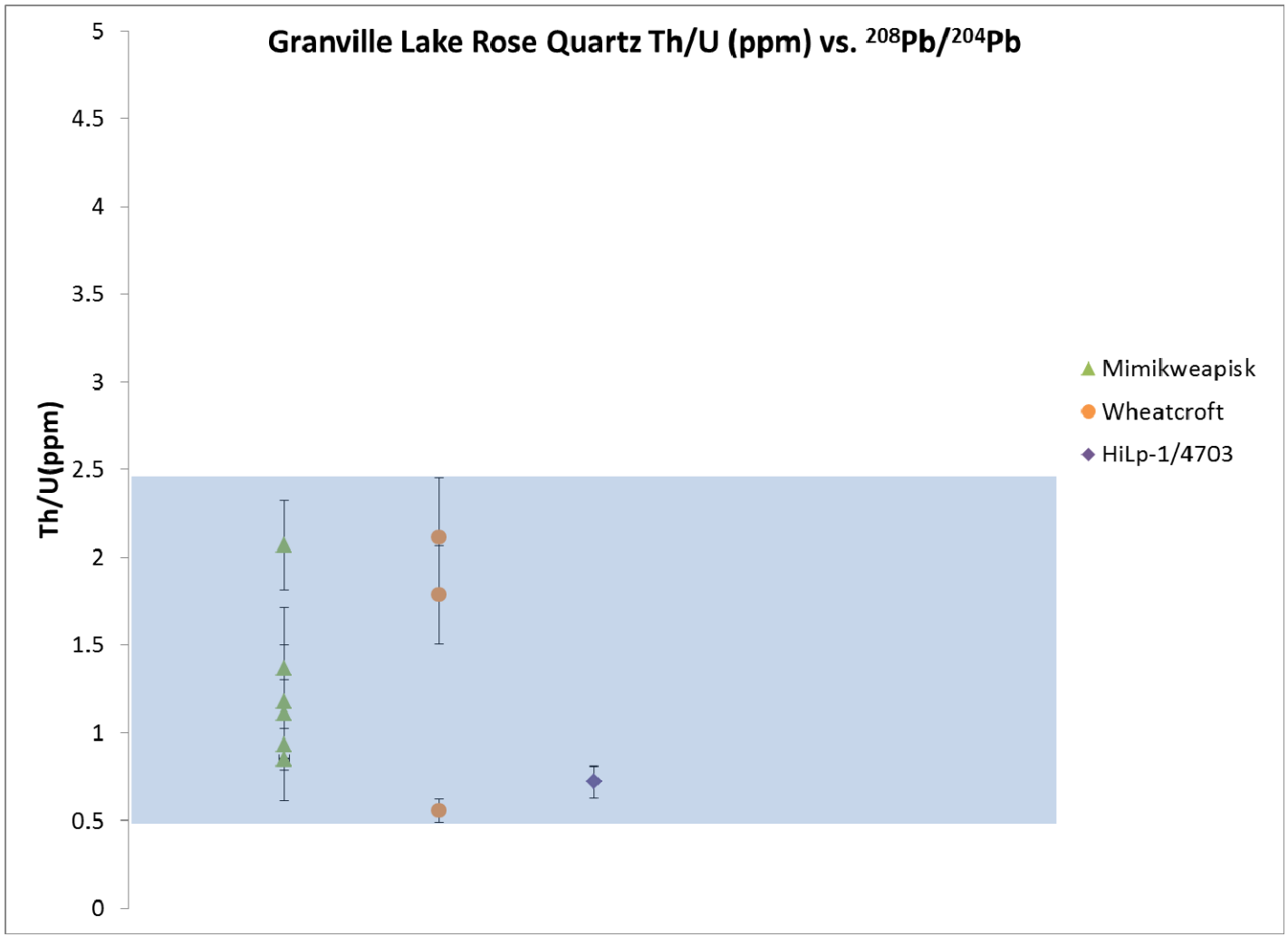


Figure 8.28 Plot of Th/U ratios for rose quartz from Granville Lake quarries and HiLp-1/4703, which produced no Pb isotope data

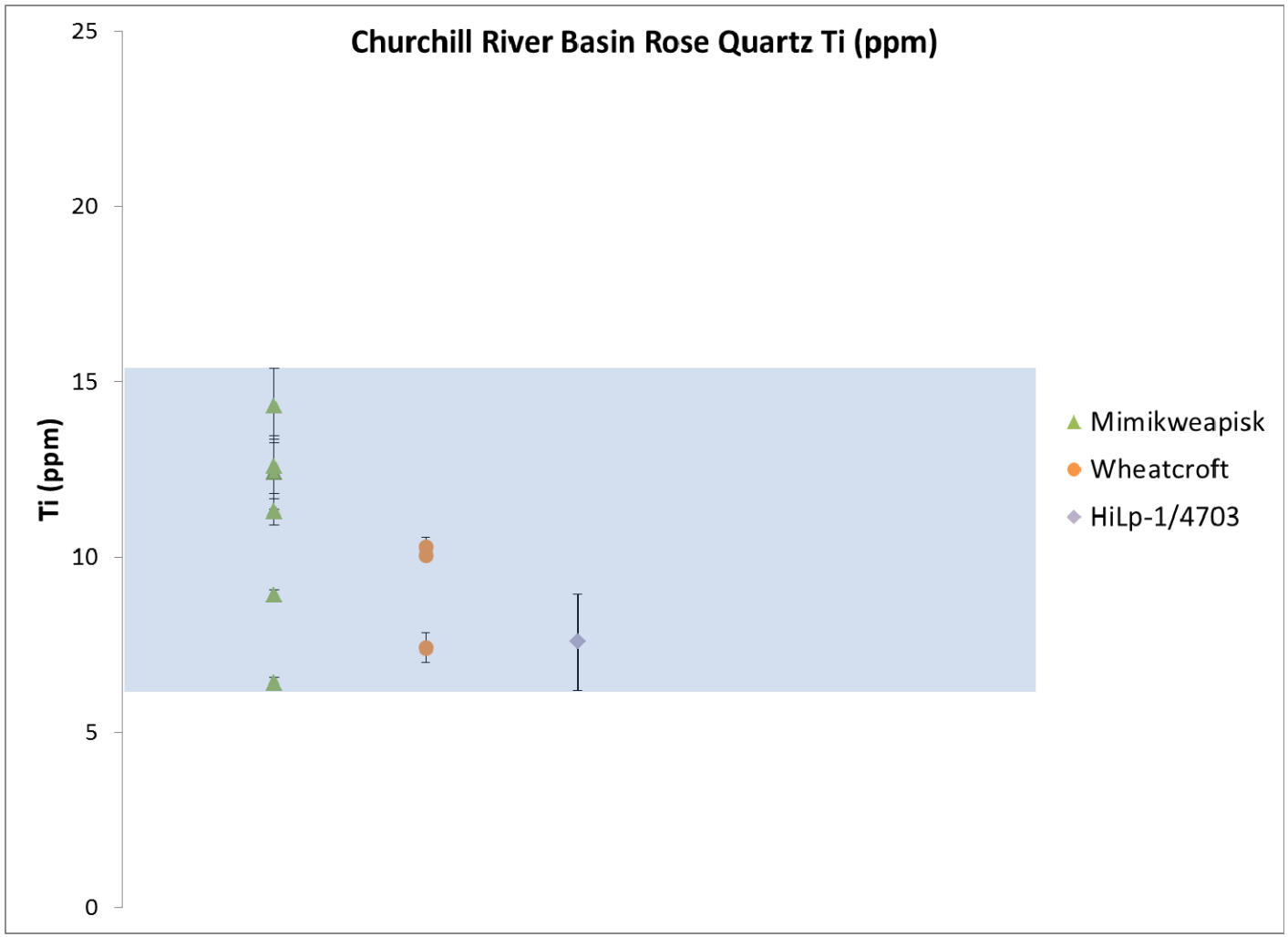


Figure 8.29 Plot of Ti (ppm) values for rose quartz from Granville Lake quarries and HiLp-1/4307, which produced no Pb isotope data

9.0 Discussion

9.1 Technique development

9.1.1 ICP-MS and SIMS Nb, Hf, Pb, and Th results

The success of (Hf/Pb)+Th and Nb results obtained by acid digestion ICP-MS analysis in discriminating between 2007 Churchill River basin quarry sample sources could be ascribed to these incompatible elements' behaviour in the igneous system in which pegmatite quartz is formed. Deposits of pegmatite quartz, derived from granitic magmas of variable composition, undergoing different degrees of fractional crystallization and crustal assimilation, would be expected to contain incompatible elements in different concentrations. However, this interpretation is challenged by SIMS, LA-ICP-MS, and acid digestion ICP-MS results, which indicate that Nb, Hf, Pb, and Th are not found in detectable, characteristic concentrations in quartz from the Churchill River basin.

Petrographic analysis of slides made from splits of 2007 acid digestion ICP-MS samples offers a possible explanation for the conflict between the 2007 ICP-MS results and the other datasets. It appears from these photographs that contaminants, in the form large inclusions of micas and feldspars – a major component of most pegmatites – were not removed from 2007 quartz samples prior to ICP-MS analysis (Figures 9.1 and 9.2). These inclusions would have been crushed and digested along with the quartz and introduced into the ICP-MS. Due to the chemical purity of quartz relative to these contaminant minerals, the 2007 data set could more accurately be said to represent trace element analysis of feldspars and micas from the Churchill River basin sources, rather than quartz chemistry.

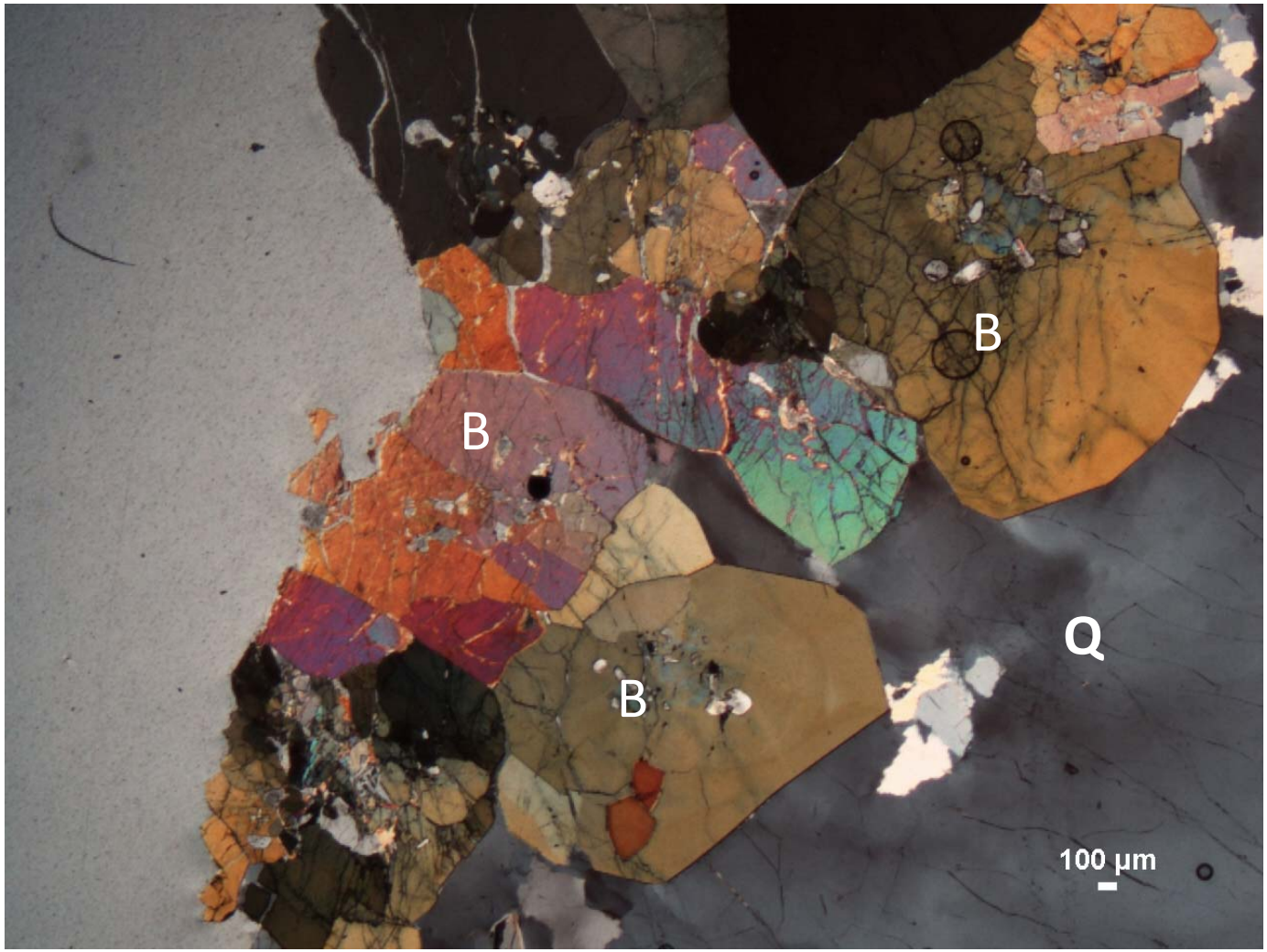


Figure 9.1 Crossed polarized light micrograph of sample HR-BM9. B=Biotite, Q=Quartz

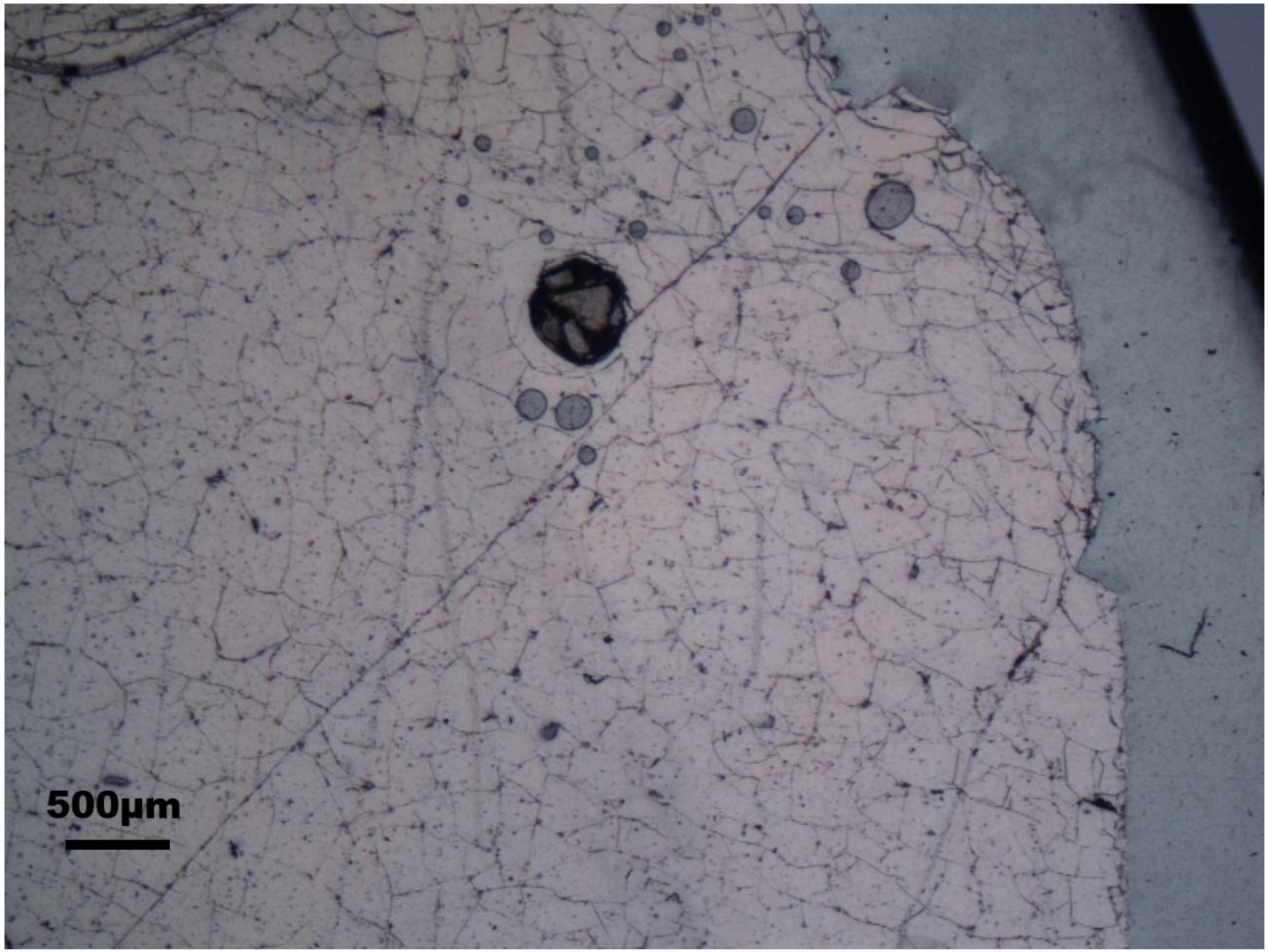


Figure 9.2 Plane polarized light micrograph of sample GF1-3. Note large mineral inclusion in centre of image.

In light of the potential contribution of trace-element rich feldspars and micas to the results of bulk ICP-MS analysis of the 2007 Churchill River basin quarry samples, the results of other analyses carried out during my dissertation research, which show low to undetectable concentrations of Nb, Hf, Th, and Pb, make more sense. If these elements are present in the quartz samples, their relatively large ionic radii mean that they would likely be present either as a component of micro-mineral inclusions, or as interstitial defects, rather than more evenly distributed substitutions for Si. Low concentration, spatially dispersed distribution of Nb, Hf, Th, and Pb in the 2007 quartz samples is in accordance with the results of cathodoluminescence imaging, which shows microscale, highly luminescent inclusions in these samples. This hypothesis is also supported, to some degree, by the results of LA-ICP-MS. Though not significant within error, distinct peaks for Nb, Hf, Th, and Pb detected over rastered line scans of the 2007 samples indicate that, if present, these elements are distributed with a high degree of spatial resolution. The low mean trace element concentrations detected by LA-ICP-MS relative to solution based ICP-MS can be explained as a result of the absence of feldspar or mica contaminants in areas selected for ablation, as visible mineral inclusions were purposefully avoided during laser analysis. SIMS data do not contradict this model of Nb, Hf, Th, and Pb distribution in quartz. Detecting elements distributed in a highly spatially restricted manner with SIMS, which only samples a nanometer thick layer of 2-200μm of a sample surface, would be exceedingly improbable.

The absence of Nb, Hf, and Th, and relatively reduced Pb concentrations in the acid digestion ICP-MS results obtained from 2009 quarry sample, however, contradicts a model in which these elements are present in small micromineral or fluid inclusions. If

2009 ICP-MS results are taken at face value, these incompatible trace elements are either not present in the quarry material – or not present in source specific concentrations, in the case of Pb. However, in this case, low trace element signals may be the result of the acid digestion used dissolve to the quartz samples prior to introduction into the ICP-MS. As mentioned in section 5.3.1.1, digestion methods must be selected based on the mineral or material of interest and the desired element package. Selection of an aqua regia digestion for quartz was likely not appropriate; as a silicate mineral, quartz is resistant to digestion by aqua regia. Much of the 2009 – and quartz component of the 2007 – samples were likely not dissolved into liquid introduced to the ICP-MS, and were therefore not analyzed. Given this, it is unlikely that elements incorporated as rare micromineral or interstitial impurities would be detected. To determine if this phenomenon is behind the divergence between the 2009 ICP-MS results, and the presence of discrete trace-element impurities indicated by LA-ICP-MS and cathodoluminescence, ICP-MS analysis of quartz samples free of visible mineral contaminants dissolved in a four-acid or pure HF digestion should be undertaken. As there is enough leftover material from 2009 quarry sampling to pursue this kind of analysis without further field sampling, this forms a potential promising avenue of future research for this project.

9.1.2 SIMS Al results

Al is the most common trace element impurity in quartz (Dennen, 1964; Götze, 2009). Al impurities in quartz generally occur as substitutions for Si associated with interstitial cations as charge compensators (Müller, 2005). As Al concentrations in quartz have been linked to temperature during quartz crystallization (Dennen and Blackburn,

1970), which can vary between different pegmatite deposits, it was thought that a successful characterization technique could be based on SIMS quantification of this analyte. There is some inter-quarry variability in SIMS Al results from the 2007 quarry and artifact samples, with quartz from Grandfather and Pickerel Bay sources, for example, appearing significantly different, even given large error ranges associated with sample means. However, uncalibrated Al/Si data from the 2009 samples is less encouraging. There is significant overlap between all three analyzed sources in this data set.

It should be noted that differences in achieved characterization between the two data sets may be related to different sample preparation protocols executed on the two sample sets. The 2007 quarry material was prepared as thin section slides, while 2009 samples were prepared as thick sections mounted in drilled aluminum slugs. It is possible that Al contamination from the slugs contributed to data obtained from 2009 quarry samples. This could also explain the variation between standardized Al(ppm) values from 2007 quarry samples and the three artifact samples, which were also mounted in aluminum slugs. Al results from ICP-MS analysis of four-acid or HF digested quarry samples would be helpful in determining whether further Al analysis could be of aid in characterizing these materials.

9.1.3 SIMS $\delta^{18}O$ results

$\delta^{18}O$ values of pegmatite quartz deposits are related to O isotope chemistry of the parental granitic magmas from which the pegmatites formed, which is influenced by temperature conditions and assimilation and, to a lesser extent, fractional crystallization

events occurring during magmatic evolution (Taylor, 1968:65; 1983). These factors may vary between pegmatites on a small geographic scale, such that related pegmatites in the US and Canada have shown $\delta^{18}O$ variability of up to 2‰ (Taylor, 1983). Additionally, $\delta^{18}O$ values of detrital quartz grains in ochre are used as a source discriminator by Smith and Pell (1997), while Meighan *et al* (2003) measure $\delta^{18}O$ in hydrothermal vein quartz deposits – albeit with limited success – to determine the provenance of quartz artifacts from Newgrange Tomb in Ireland. Given these results, it was thought that $\delta^{18}O$ values could be useful for discriminating between pegmatite quartz sources in the Churchill River basin.

Unfortunately, this does not appear to be the case. Sample $\delta^{18}O$ values for Churchill River basin quartz quarries fall within a normal range for pegmatite quartz (e.g. Longstaffe *et al.*, 1981), with the exception of sample SW2-2 which was taken from a highly metamorphosed source. $\delta^{18}O$ values from Grandfather, *Mimikweapisk*, and Pickerel Bay all overlap within error due to high intra-sample variability, indicating that microbeam oxygen stable isotope assay is an unsuitable characterization technique for these materials. Interestingly, mean $\delta^{18}O$ values from the three artifact samples are significantly lower than Granville Lake quarry values, possibly indicating that, while $\delta^{18}O$ values may not be suitable for discriminating between sources, they may have some utility for ruling out analyzed quarries as potential sources for artifacts of unknown provenance.

9.1.4 SIMS Pb isotope and Ti, Ge, Th, and U data

The use of trace element and Pb isotope data by geologists to establish geographically broad provenance signatures for quartz is not a new practice (see: Dennen, 1964, 1967; Hemming et al., 1994; Larsen et al., 2004). My dissertation results demonstrate that these techniques can also be applied to reconstruct the provenance of pegmatite quartz on a much finer scale. In addition, this technique shows significant potential for investigating and reconstructing regional-scale patterns of quartz procurement for stone tool-using populations.

Like Al, Ti impurities are incorporated into quartz as substitutions for Si, rather than interstitial impurities (Thomas *et al.*, 2010: 743). The rate at which Ti is incorporated into quartz is dependent upon temperature, Ti activity (Cherniak et al., 2007; Ghent and Stout, 1984; Wark and Watson, 2006), and pressure conditions during crystallization (Thomas *et al.*, 2010). All of these factors have the potential to vary between different deposits of pegmatite quartz, making Ti concentration an excellent potential characterization parameter for quartz. For example, Ti is one of the analytes found by Larsen and colleagues (2004) to vary significantly between deposits of pegmatite quartz, within and between the Evje and Froland pegmatite fields in southern Norway.

Ti was not detected by acid digestion ICP-MS in either the 2007 or 2009 quarry sample sets. This is likely a result of incomplete dissolution of quartz by the aqua regia digestion. Even under optimal circumstances, however, the low detection limits, high spatial resolution, and relatively non-destructive nature of SIMS analysis make it one of the better options for analyzing Ti in samples where it is concentrated below ~10ppm, as

it is in many of the Churchill River basin artifact and quarry samples (Behr *et al.*, 2011). SIMS results, rather than the acid digestion ICP-MS results, are likely an accurate reflection of Ti levels in these quartz samples.

Mean Ti concentration in quartz samples from the Granville Lake quarry district ranges from ~6-17ppm. Within this range, samples from some quarries – such as the Smoky Quartz and Little Grandfather quarries – exhibit a restricted range of Ti concentrations, indicating relatively stable conditions of temperature and Ti activity during quartz formation. Ti variability in material from other quarries – such as the geologically complex Grandfather quarry and the metamorphosed Pickerel Bay sources – approaches the entire range of Ti concentrations within the sample set, indicating fluctuating temperature, pressure, and/or Ti activity during quartz formation.

Ti concentration in the artifact sample set shows even more variety than the quarry sample set, ranging between 0.9 and 35.6 ppm. This strongly indicates that multiple sources, formed under variable conditions of temperature, pressure, and Ti activity were exploited by populations in the study area. Some of these artifacts plot within the Ti range of Churchill River basin quarries – indicating exploitation of these sources, or sources formed under similar conditions, while others plot outside this range – indicating exploitation of other, unknown sources.

Ge, like Ti, occurs as a substitutional defect in quartz crystal lattices. There has been less investigation into Ge concentration in quartz as a function of geological processes. Larsen *et al*. (2004), claim that Ge is relatively incompatible and tends to be found in higher concentrations in quartz formed at lower temperatures from highly evolved granitic melts. Other authors have suggested that Ge incorporation into quartz

lattices is related to Cl and Br uptake and the salinity of included fluids (Gerler, 1990). Variation in Ge concentration in granitic pegmatite quartz samples analyzed by Larsen *et al.* (2004) occurs within a restricted range, between 0.5 and 2.5 ppm. Ge results from the Churchill River basin pegmatite quartz sources show even less variability, falling between 1.4 and 1.7ppm. Within this dataset, Ge is mainly useful for distinguishing between quartz from the Grandfather quarry and white quartz quarry pit at Wheatcroft. This analyte's utility for resolving multi-source attributions based on Ti and Pb isotope chemistry is currently untestable due to the effects of interferences on Ge data obtained from artifact samples.

Variable rose quartz Th/U ratios – which range between 0.6 and 2.1 in the quarry sample and 0.3 and 5.3 in the artifact sample - can be explained as a result of variation in parental melt and host rock Th and U chemistry. Additionally, as U and Th are incompatible trace elements, their concentration in pegmatite quartz should be affected by the frequency and extent of fractional crystallization and crustal assimilation events occurring during the evolution of their host magma. The bimodal patterning of Pb isotope and Th/U ratios exhibited by rose quartz samples from the Wheatcroft and *Mimikweapisk* quarries likely represents the deposition of two generations of rose quartz at these sites, rather than Pb, Th and U variability within a single generation of quartz. The latter scenario would result in a range of values, rather than the bimodal clustering in Figure 7.44. There is a higher degree of Th/U variability in the artifact samples analyzed for this research than in materials from *Mimikweapisk* and Wheatcroft quarries combined. Like artifact Ti data, this strongly indicates that multiple sources were utilized by toolmakers in the study area.

Pb isotope ratios, in combination with trace element data, can be used to differentiate between quartz from the Churchill River basin quarries sampled in this study. Pegmatite quartz Pb isotope ratios primarily reflect the Pb chemistry of the pegmatite's parental magma, the Pb chemistry of the host rock surrounding the pegmatite, and – because ^{206}Pb, ^{207}Pb and ^{208}Pb are the final daughter products of the radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively– the age of the deposit. Variation in these parameters between sampled pegmatite quartz deposits is a likely cause for the variability in Pb isotope chemistry described above, although this variation is not consistent enough to allow Pb isotope chemistry alone to act as a source discriminator – except between Pickerel Bay and Granville Lake quartz samples.

Unlike other chemical parameters discussed in this section, Pb isotopic variability in the CRDAP artifact sample ($^{208}Pb/^{204}Pb$ = 23.4-35.3, $^{207}Pb/^{206}Pb$ = 0.82-0.89) is comparable to variability exhibited by the quarry sample ($^{208}Pb/^{204}Pb$ =28.5-35.7, $^{207}Pb/^{206}Pb$ = 0.83-0.91). Within the white/clear colour category, for example, all artifacts fall within the $^{208}Pb/^{204}Pb$ range exhibited by the Granville Lake quarry sources. In fact, there is almost as much $^{208}Pb/^{204}Pb$ variability between samples separated by the 70m between Grandfather and Little Grandfather quarries than there is in the entire CRDAP white/clear artifact sample. Compared to Ti concentration, which distinguishes many of the artifacts analyzed from the Granville Lake quarries, $^{208}Pb/^{204}Pb$ does not act as robust parameter for assigning provenance to artifacts of unknown origin, and, like Ge is primarily useful for distinguishing between samples from the analyzed quarry set. Within other colour categories, however, artifacts show greater isotopic variability. The reason why different colour categories of pegmatite quartz would exhibit differing

degrees of Pb isotopic variability is currently unclear. It is possible that this phenomenon is the product of Pb contamination – a serious issue when analyzing such low concentration isotopes in samples prepared in an environment where Pb has not been reduced through special measures to minimal levels. The artifacts contributing most to Pb-isotopic variability in the smoky and rose colour categories (GlLr-28/11, GkLs-16/152, and HgLt-7/50) were all mounted together in a single aluminum slug several years prior to other artifact samples. It is possible that higher relative ^{204}Pb signals obtained from artifacts mounted on this slug are the result of exposure to some environmental Pb source that other artifacts were not subjected to. Conversely, it is possible that the relatively similar ^{208}Pb/^{204}Pb and ^{207}Pb/^{206}Pb values exhibited by the other artifacts relative to these three outliers and Churchill River basin quarry samples is a product of contamination during artifact sample prep. During SIMS artifact analysis, non-Pb contaminants in the form of interference peaks not observed during quarry material analysis were noted, lending additional credence to this latter hypothesis. Future Pb-isotope analysis on archaeological quartz materials would be best carried out on samples prepared in a clean lab using Pb-free tools and consumables.

Reliable Pb isotope data could not be collected from 18 of the 48 quartz samples prepared for analysis, due to poor ionization of all four Pb isotopes assayed. Efforts were made to resolve this issue: artifact mounts were subjected to additional cleaning, fresh gold coats were applied to affected mounts, and one mount was entirely recreated from fresh artifact samples, all to no avail. Affected artifacts were confined to four mounts, and all artifacts on each mount were affected, indicating that the issue affecting Pb ionization lay somewhere in the sample preparation phase of analysis. As a duplicate of

one of these mounts created with new artifact chips with utmost attention paid to cleanliness and surface smoothness failed to produce better results, the problem likely lies with an unknown change in mounting or polishing supplies used to create the affected mounts, and the quarry and unaffected artifact mounts. In the future, care should be taken to obtain and use consumables known to be free of potential interferences in sample preparation.

9.2 Technique application: interpretation of artifact provenance results

Some basic, tentative interpretations regarding technological organization, and mobility and/or exchange patterns can be drawn using the results of provenance analysis of quartz formal artifacts recovered from sites in the Churchill River basin.

Quartz artifacts recovered from sites throughout the CRDAP study area exhibit trace element-Pb isotope signatures consistent with Granville Lake quarry material. At several other sites, artifacts without valid Pb results exhibit Ti signatures consistent with either the Granville Lake or Pickerel Bay quarry areas. Keeping in mind the provisional nature of source assignments based on the limited quarry data set described above, these results have several implications for quartz utilization by toolmakers in the Churchill River basin.

First, these results support the conclusion that the Granville Lake quarries contributed to formal toolkits utilized not only in the immediate surrounding area, but in parts of the Churchill River basin up to 200km away. At its most basic level, this means that quartz procurement ranges in the basin were substantial, extending between the study areas of the Granville Lake quarries project and the CRDAP. While identification of

Pickerel Bay quartz in the artifact sample is extremely tentative, given that these identifications are restricted to tools for which there is no reliable Pb-isotope data, these results could indicate a quartz procurement range for toolmakers in the CRDAP extending as far as north-central Saskatchewan. These results strongly imply that quartz from these sources was being exploited by residentially mobile toolmakers with territories covering 200-500km of the Churchill River basin. Interestingly, the two artifacts from sites outside the basin analyzed during my dissertation research do not fall within the chemical range of either quarry area. This could be taken as exceedingly tenuous evidence for lack of interaction between the Churchill and Nelson River basins, however, the low sample size of artifacts from outside of the basin analyzed during this research prevents this hypothesis from being stated here with confidence. Analysis of more artifacts from outside the Churchill River basin to test whether residential mobility followed the course of river basins in northern Manitoba and Saskatchewan is a potentially fruitful avenue of future research.

The fact that toolmakers likely incorporated quartz from the Granville Lake, and potentially Pickerel Bay source areas into formal toolkits discarded at sites around Southern Indian Lake indicates scarcity of high-quality raw materials in the study area. This is consistent with other evidence, including the results of field surveys of the Churchill River basin, which have failed to uncover procurement sites other than quartz quarries in the region (Beardsell, 2013). Recovery of formal quartz tools 60-200km away from their source of origin also strongly indicates that, at least in some cases, these tools were not used expediently. Implied curation of formal tools manufactured from quartz also indicates that sources of higher quality material were scarce in the study area.

Recovery of a scraper made from raw materials chemically consistent with Grandfather quartz from a site (HbMd-6) located between two major quarries is not unexpected. It is possible that recovery of this artifact close to its probable site of procurement represents decreased curation in an area where raw materials are relatively accessible.

At all of the sites providing multiple artifacts for this analysis, artifact results exhibit greater trace element/Pb variability than any of the analyzed sources. This could be taken as evidence for exploitation of multiple sources by groups using these sites. In the absence of a more complete characterization of sources within the Churchill River basin, this evidence is tentative, at best. Lack of chronologic or cultural control over artifact assemblages prevents me from saying with certainty whether exploitation of multiple sources is related to mobility of a single group using the site or organizational discontinuity between multiple groups using the site at different times. Both mobility (e.g. Roth, 2000; Freund, 2012) and cultural discontinuity (e.g. Hood, 1994; Odess, 1998) can be invoked to explain exploitation of different raw material sources by groups at the same site, as indicated by multiple source signatures.

Finally, the presence of quartz manufactured from raw materials that are chemically inconsistent with materials from characterized quarries strongly indicates that pegmatite quartz deposits as yet unrecorded contributed to formal quartz toolkits in the Churchill River basin. Further survey aimed at procurement site identification and characterization should be carried out as a further step in this research.

10.0 Conclusions

Several conclusions, conditional on the results of future survey and material analysis, can be drawn from the results of my dissertation research. At the most basic level, the first of these conclusions is that SIMS analysis of Ti, Ge, Th, and U concentrations and Pb-isotope ratios form a feasible protocol for distinguishing between exploited pegmatite quartz sources and assigning provenance to pegmatite quartz artifacts within the Churchill River basin. Trace element and Pb-isotope data differentiate between seven analyzed sources of pegmatite quartz, and show definite signs of utility for assigning quartz artifact provenance to these sources, or ruling it out.

Provenance data gathered through my dissertation research supports the hypothesis that strategies of quartz lithic technology in the Churchill River basin were selected, at least partially, as a response to lithic material scarcity within the basin as a whole. Incorporation of raw material from Granville Lake, and possibly Pickerel Bay quartz sources into formal lithic toolkits is a strong indicator that higher quality raw materials were simply not available to toolmakers in the region. Further, transport of this material over hundreds of kilometers, likely through curation over the course of group movements, indicates that sources of material suitable for replacing these tools were scarce within the study area. This model of quartz technological organization is consistent with other work carried out in the region, including attribute and mass analyses showing implementation of high-efficiency reduction strategies at Grandfather quarry, as well as surveys indicating that quartz was the highest quality locally available toolstone. Artifacts manufactured from raw materials falling outside of the chemical range of characterized quartz sources were also detected during my dissertation research. First,

this demonstrates that other, as yet unknown sources of pegmatite quartz were exploited by toolmakers in the Churchill River basin. Additionally, assemblages from which multiple artifacts were drawn for analysis show signs of variable source exploitation. At most sites, at least one artifact falls within the chemical range of the Granville Lake quarries, while others fall outside; at other sites, exploitation of multiple pegmatite quartz sources is indicated by variability in Pb isotope ratios and/or trace element concentrations greater than that exhibited by large, complex characterized sources, like Grandfather or *Mimikweapisk*. Interpretation of this phenomenon is difficult, given issues assigning temporal or cultural context to artifacts analyzed for this dissertation. However, this result could either be taken as tentative evidence for residential mobility practiced by hunter-gatherers in the Churchill River basin, or variability or discontinuity in procurement behaviour between multiple related or unrelated groups using the same site.

Several courses of future research should be undertaken to either make the results of this dissertation more robust, or explore other facets of quartz technological organization in the Churchill River basin and surrounding regions. First, in terms of methodological improvement, ICP-MS analysis should be undertaken on quarry samples subjected to a four acid, rather than aqua regia, digestion. This analysis would allow me to make more definitive statements regarding the concentration and distribution of a wider range of potentially helpful trace elements in quarry materials. It is possible, for instance, that incompatible trace elements incorporated as fluid or mineral microinclusions in pegmatite quartz may serve to characterize sources more accurately than the present technique. Additionally, if this course of analysis was expanded to the artifact sample, it is possible that issues surrounding Ge contamination that prevented this

analyte from application to artifact characterization could be avoided. Further, while ICP-MS is a more destructive technique than SIMS, it is less expensive and time-consuming. Should ICP-MS analysis of trace element concentrations in quartz samples dissolved in a four acid digestion prove as effective for source characterization as the current technique, it could provide a second option for archaeologists wishing to characterize pegmatite quartz sources and artifacts in contexts where time and money are limited.

My confidence in the results obtained through my dissertation would also be aided by SIMS analysis of quarry and artifact samples prepared in a low-Pb environment using low-Pb consumables for comparison to results of analysis presented above. Pb is a common environmental contaminant found in very low concentrations in pegmatite quartz. Though every possible step was undertaken to avoid the spectre of Pb contamination, including a thorough sample cleaning regimen, and analysis of an internal standard at the beginning of each research session, such an analysis would do much to put my mind at ease.

In terms of expanding the application of the current technique to further research into quartz technological organization in the boreal forest, four courses of future research present themselves immediately to mind. The simplest would consist of analysis of quartz formal artifacts currently in curation at the Manitoba and Royal Saskatchewan Museums recovered from sites both in other areas of the Churchill River basin and in surrounding regions, such as the Nelson River basin to assess the contribution of the Granville Lake and Pickerel Bay quarries to quartz formal toolkits on a larger geographic scale. This study would allow me to approach broader questions of social

interconnectedness, facilitated either through exchange or mobility within the boreal forest.

Analysis of quartz debitage from sites in the Churchill River basin, while complicated by difficulties attendant to identifying anthropogenic vs. naturally fractured quartz, could serve as a second potential direction of future research. Formal tools represent the terminal result of a long history of human behaviour, and are not directly associated with activities carried out on site. By attributing source provenance to artifacts directly associated with activities at sites throughout the Churchill River basin, a more complete picture of the integration of different quartz sources into toolkits through the course of seasonal mobility could be produced.

Thirdly, I could apply the current technique to formal tool fragments recovered through analysis of materials excavated from the Grandfather quarry. If quartz tools recovered from inside the quarry match raw materials from the same site, it could be argued that they represent discard of tools broken during manufacture, while tools showing chemical signatures outside that expected for Grandfather quartz may have been discarded during a 'retooling' event (Gramly, 1983) at the site.

The fourth and most challenging potential future course of research for this project would involve further survey in the study area to identify, sample, and analyze additional pegmatite quarry sites in an attempt to identify the sources represented by artifacts falling within the all too large 'unknown' area of biplots presented in Chapter 8. Doing so would give me a much better idea of the procurement ranges represented by chemical data from sites where one or more artifact plots outside of the chemical range of the Granville Lake or Pickerel Bay sources.

Finally, the boreal forest of Manitoba and Saskatchewan is not the only part of the world where pegmatite quartz was incorporated into lithic toolkits. Future research could also be directed toward determining the extent to which the current technique is applicable to characterizing quartz sources and assigning raw material provenance to quartz artifacts in these regions. Should the technique prove less appropriate in these contexts, more geographically-specific refinement might be called for.

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Appendix 1: 2007 Quarry samples

Sample Number	**Site**	**Proveniance**
GF1-01	Grandfather	Surface collection from around pit
GF1-02	Grandfather	Surface collection from around pit
GF1-03	Grandfather	Surface collection from around pit
GF-2	Grandfather	North wall of pit
GF-3	Grandfather	South wall of pit
HR-CM1	*Mimikweapisk*	Cave HR-CM1
HR-CM1-A1	*Mimikweapisk*	Cave HR-CM1-A
HR-CM1-A2	*Mimikweapisk*	Cave HR-CM1-A
HR-CM1-B1	*Mimikweapisk*	Cave HR-CM1-B
HR-CM1-B2	*Mimikweapisk*	Cave HR-CM1-B
HR-CM1-C1	*Mimikweapisk*	Cave HR-CM1-C
HR-CM1-C2	*Mimikweapisk*	Cave HR-CM1-C
HR-CM2	*Mimikweapisk*	Cave HR-CM2
HR-CM3	*Mimikweapisk*	Cave HR-CM3
HR-BM9	*Mimikweapisk*	Cave HR-BM9
WC2-01	Wheatcroft	Uncontrolled surface collection
WC2-02	Wheatcroft	Quarry face
WC2-03	Wheatcroft	Upper area of site
WC2-04	Wheatcroft	Unspecified
WC2-05	Wheatcroft	Unspecified
WC2, A1	Wheatcroft	Unspecified
SW1-1	Pickerel Bay	Sample from GcNc-1
SW2-01	Pickerel Bay	Metamorphosed outcrop
SW2-02	Pickerel Bay	Metamorphosed outcrop
SW2-03	Pickerel Bay	Metamorphosed outcrop
SW3-1	Pickerel Bay	Quartz outcrop

Appendix 2: 2009 Quarry sample

Number	**Site**	**Provenance**
SQ-01	Smoky Quartz	Smokey quartz sample from small depression
SQ-02	Smoky Quartz	Smokey quartz sample from small depression
SQ-03	Smoky Quartz	Smokey quartz sample from outcrop south over hill
SQ-04	Smoky Quartz	Smokey quartz from south face of peninsula
SQ-05	Smoky Quartz	Smokey quartz from large exposed face
SQ-06	Smoky Quartz	Smokey quartz from quarry to the north
CM1-S1	*Mimikweapisk*	HR-CM1
CM1-S2	*Mimikweapisk*	HR-CM1
CM1-S3	*Mimikweapisk*	HR-CM1
CM1- S4	*Mimikweapisk*	HR-CM1
CM1- S5	*Mimikweapisk*	HR- CM1
CM1- S6	*Mimikweapisk*	HR-CM1
CM1- S7	*Mimikweapisk*	HR-CM1
CM1- S8	*Mimikweapisk*	HR-CM1
CM1-S9	*Mimikweapisk*	HR-CM1 (white quartz)
CM1-S10	*Mimikweapisk*	Top edge of HR-CM1
CM1-S11	*Mimikweapisk*	HR-CM1
CM1- S12	*Mimikweapisk*	HR-CM1
CM1a-S13	*Mimikweapisk*	Face left of HR-CM1
CM1b-S14	*Mimikweapisk*	Above HR-CM1-B
CM1b- S15	*Mimikweapisk*	East of HR-CM1-B
FC S16	*Mimikweapisk*	Flooded cave
WC-01	Wheatcroft	Smokey quartz from surface
WC-02	Wheatcroft	Rose quartz from pegmatite (non-cultural)
WC-03	Wheatcroft	Rose quartz from pegmatite
WC-05	Wheatcroft	Rose quartz from pegmatite
WC-10	Wheatcroft	Rose quartz from quarry in pegmatite
WC-11	Wheatcroft	Quarry in pegmatite
WC-15	Wheatcroft	Quarry under tree throw
WC-16	Wheatcroft	Unworked quartz face
WC-17	Wheatcroft	Milky quartz associated with host rock
WC-19	Wheatcroft	Rose quartz from quarry in pegmatite
GF-4	Grandfather	North Wall
GF-5	Grandfather	North Wall
GF-6	Grandfather	North Wall
GF-7	Grandfather	North Wall

GF-8	Grandfather	North Wall
GF-9	Grandfather	North Wall
GF-10	Grandfather	North Wall
GF-11	Grandfather	North Wall
GF-12	Grandfather	North Wall
GF-13	Grandfather	North Wall
GF-14	Grandfather	North Wall
GF-15	Grandfather	North Wall
GF-16	Grandfather	North Wall
GF-17	Grandfather	North Wall
GF-18	Grandfather	North Wall
GF-19	Grandfather	North Wall
GF-20	Grandfather	North Wall
GF-21	Grandfather	North Wall
GF-22	Grandfather	North Wall
GF-23	Grandfather	North Wall
GF-24	Grandfather	North Wall
GF-25	Grandfather	North Wall
GF-26	Grandfather	North Wall
GF-27	Grandfather	North Wall
GF-28	Grandfather	North Wall
GF-29	Grandfather	West Wall
GF-30	Grandfather	West Wall
GF-31	Grandfather	West Wall
GF-32	Grandfather	West Wall
GF-33	Grandfather	West Wall
GF-34	Grandfather	West Wall
GF-35	Grandfather	East Wall
GF-36	Grandfather	East Wall
GF-37	Grandfather	East Wall
GF-38	Grandfather	East Wall
GF-39	Grandfather	South Wall
GF-40	Grandfather	South Wall
GF-41	Grandfather	South Wall
GF-42	Grandfather	South Wall
GF-43	Grandfather	South Wall
GF-44	Grandfather	South Wall
GF-45	Grandfather	South Wall
GF-46	Grandfather	South Wall

GF-47	Grandfather	South Wall
GF-48	Grandfather	South Wall
GF-49	Grandfather	South Wall
GF-50	Grandfather	South Wall
GF-51	Grandfather	South Wall
GF-52	Grandfather	South Wall
GF-53	Grandfather	South Wall
GF-54	Grandfather	South Wall
GF-55	Grandfather	South Wall
GF-56	Grandfather	South Wall
GF-57	Grandfather	South Wall
GF-58	Grandfather	South Wall
GF-59	Grandfather	South Wall
GF-60	Grandfather	South Wall
GF-61	Grandfather	South Wall
GF-62	Grandfather	South wall
GF-63	Grandfather	South wall
GF-64	Grandfather	South wall
GF-65	Grandfather	South wall
GF-66	Grandfather	South wall
FIB-01	Floating Island Bay	White quartz associated with white feldspar
FIB-02	Floating Island Bay	North side of peninsula
FIB-03	Floating Island Bay	Main quarry face (Abel’s Rock)

Appendix 3: Artifact Sample

Catalogue #	Object Name	Object Type	Recovery (where known)	Colour	Length (cm)	Width (cm)	Thickness (cm)	Weight (g)
HbMd-6/M241	Scraper	End	USC*	White	3.7	3.0	1.6	20.3
HcLx-1/M241	Scraper		S4W18 (2-4cm DBS)	White	2.5	2.2	1.0	7.7
HcLx-1/M381	Scraper	Combination	N0E28 (8-10cm DBS)	White	4.1	3.5	1.2	16.3
HcLx-1/M622	Scraper	Domed	USC	White	3.1	2.4	1.0	8.5
HcLx-1/M624	Scraper	Side	USC	White	3.3	1.9	0.7	5.1
HdLw-2/M80	Biface		USC	White	3.8	5.1	1.4	28.7
HdLw-6/M28	Scraper	End	USC	White	2.4	2.6	0.7	5.4
HdLw-7/M43	Scraper	Side	USC	White	2.5	2.0	0.6	3.7
HdLx-1/M254	Biface		USC	White	1.3	1.7	0.5	1.3
HdLx-20/M9	Scraper	End	USC	Rose	2.8	2.9	1.5	14.4
HdLx-23/M14	Scraper	End	USC	White	2.9	2.8	1.2	11.1
HdLx-7/M5	Scraper	End	USC	White	2.3	2.3	0.9	4.3
HeLs-16/M4	Scraper	Side	USC	White	2.3	3.0	1.1	7.9
HeLw-1/M20	Scraper		N/A	White	1.2	2.0	3.8	1.4
HeLw-1/M229	Scraper	End	N/A	White	2.2	2.1	1.3	5.3
HeLw-2/M18	Scraper		N/A	White	2.6	0.8	0.6	1.4
HeLw-2/M19	Scraper	End	N/A	White	2.3	2.4	0.4	2.8
HeLw-2/M229	Scraper	Side	USC	Rose	4.8	1.9	0.7	7.9
HeLw-2/M240	Scraper		N/A	White	2.6	2.0	1.1	7.9
HeLw-20/M455	Scraper		N2W8 Lv1	White	1.8	1.5	0.6	1.7
HgLt-7/M27	Scraper	Combination	USC	White	2.6	2.0	0.7	4.0
HgLt-7/M28	Scraper	Side	USC	Rose	7.8	5.6	1.6	87.8
HgLt-7/M50	Spokeshave		USC	Rose				
HhLp-11/M45	Scraper	End	USC	Rose	2.2	2.3	0.8	4.8
HhLp-16/M24	Biface		Locus 2	White	3.8	1.9	0.8	5.2
HhLp-16/M31	Scraper	End	Locus 1	White	2.5	1.6	0.9	4.5

HhLp-7/M12	Scraper		USC	White	1.7	1.8	0.5	1.8
HhLp-7/M8	Scraper	End	USC	White	3.5	2.3	2.0	21.4
HhLr-4/M5	Biface		USC	Rose	3.5	5.1	1.5	27.4
HhLt-6/M15	Scraper	Side	USC	White	3.9	2.3	0.9	8.4
HiLp-1/M12132	Scraper	Side	N/A	White	1.6	1.4	0.4	1.4
HiLp-1/M12322	Scraper	End; Side	N/A	White	1.6	1.6	0.6	2.0
HiLp-1/M12323	Biface		N/A	White	1.8	1.3	0.5	0.8
HiLp-1/M12485	Scraper	End	N/A	White	2.2	1.7	0.6	2.6
HiLp-1/M2980	Scraper	Primary	N/A	White	3.9	2.2	1	12
HiLp-1/M4703	Biface		N/A	Rose	7.2	4.4	1.7	60
HiLp-1/M4976	Scraper		N/A	White	2	1.7	0.9	3.4
HiLp-1/M6498	Biface	Projectile Point Base	N/A	White	2.6	2.2	0.5	3.5
HiLp-1/M7412	Scraper	Side	N/A	White	1.4	1.5	0.5	1.3
HiLp-1/M7425	Biface		N/A	Smoky	1.0	2	0.6	1.4
HiLp-1/M7456	Scraper	Side	N/A	White	1.8	2.1	0.7	2.7
HiLp-1/M7929	Scraper		N/A	Smoky	2.7	1.4	0.7	2.9
HiLp-1/M8243	Biface		N/A	Smoky	3.6	1.6	0.7	3.9
HiLp-1/M8715	Biface		N/A	White	0.9	1.3	0.5	0.6
HjLp-1/M21	Biface		USC	Smoky	5.3	4.3	1.7	40.8
HjLp-15/M58	Scraper	End	USC	White	1.6	2.6	0.7	2.8
HjLp-15/M61	Biface		USC	White	2.5	1.5	0.9	4.0
HjLp-15/M67	Scraper	End	USC	White	2.0	2.3	0.7	4.3
HjLp-6/M5	Biface		Test pit	White	2.4	2.0	0.8	3.6
GlLr-28/M11	Scraper	Side	USC	Rose				
GkLs-16/152	Scraper		USC	Smoky				

* Uncontrolled surface collection

Appendix 4: 2007 Acid digestion ICP-MS results

Results of 2007 acid digestion ICP-MS trace element analysis of Churchill River basin quartz samples.

Analyte Symbol	**Li**	**Be**	**B**	**Na**	**Mg**	**Al**	**P**	**S**	**K**	**Ca**	**V**	**Cr**	**Ti**	**Mn**	**Fe**
Unit Symbol	ppm	ppm	ppm	%	%	%	%	%	%	%	ppm	ppm	%	ppm	%
Detection Limit	0.1	0.1	1	0.001	0.01	0.01	0.001	0.001	0.01	0.01	1	0.5	0.01	1	0.01
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-ICP	AR-ICP	AR-MS	AR-MS	AR-MS	AR-MS	AR-ICP	AR-MS	AR-MS
GF 1-01	1.6	<0.1	<1	0.04	<0.01	0.05	<0.001	0.004	0.02	<0.01	2	13.5	<0.01	107	1.91
GF 1-02	2.2	<0.1	<1	0.033	<0.01	0.04	<0.001	<0.001	<0.01	<0.01	<1	3	<0.01	35	0.61
GF 1-03	2.2	<0.1	3	0.029	<0.01	0.03	<0.001	<0.001	<0.01	0.02	<1	4.9	<0.01	39	0.64
GF -3	1.4	<0.1	<1	0.03	<0.01	0.04	<0.001	<0.001	<0.01	<0.01	<1	8.1	<0.01	70	1.19
HR -CM1	2.8	<0.1	2	0.06	<0.01	0.09	<0.001	0.001	0.03	<0.01	3	25.7	<0.01	181	3.47
HR -CM1-A1	1.5	<0.1	<1	0.035	<0.01	0.04	<0.001	<0.001	<0.01	<0.01	<1	3.9	<0.01	46	0.86
HR -CM1-A2	1.3	<0.1	<1	0.035	<0.01	0.03	<0.001	<0.001	<0.01	<0.01	<1	5.6	<0.01	51	0.81
HR -CM1-B1	1.3	<0.1	<1	0.053	<0.01	0.07	<0.001	<0.001	0.03	0.02	<1	4.7	<0.01	49	0.86
HR -CM1-C1	1	<0.1	<1	0.032	<0.01	0.03	<0.001	<0.001	<0.01	<0.01	<1	3.1	<0.01	31	0.59
HR -CM2	1.3	<0.1	<1	0.034	<0.01	0.04	<0.001	<0.001	<0.01	<0.01	<1	3.1	<0.01	39	0.7
HR -CM3	1.3	<0.1	<1	0.04	<0.01	0.05	<0.001	<0.001	0.02	<0.01	<1	10.7	<0.01	88	1.53
HR -BM9	1.4	<0.1	<1	0.041	<0.01	0.06	<0.001	<0.001	0.02	<0.01	<1	3.7	<0.01	47	0.85
SW 1-1	0.5	<0.1	<1	0.029	<0.01	0.03	<0.001	<0.001	<0.01	<0.01	<1	5.9	<0.01	53	0.86
SW 2-01	0.6	<0.1	<1	0.027	<0.01	0.03	<0.001	<0.001	<0.01	<0.01	<1	2.6	<0.01	31	0.57
SW2 -02	0.3	<0.1	<1	0.023	<0.01	0.02	<0.001	<0.001	<0.01	<0.01	<1	4.1	<0.01	38	0.69
SW 2-03	0.5	<0.1	<1	0.024	<0.01	0.02	<0.001	<0.001	<0.01	<0.01	<1	2	<0.01	23	0.4
SW 3-1	0.4	<0.1	<1	0.025	<0.01	0.03	<0.001	<0.001	<0.01	<0.01	<1	6.6	<0.01	58	0.91

Analyte Symbol	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Y	Zr
Unit Symbol	ppm	ppm	ppm	ppm	ppm	Ppm	Ppm	Ppm	ppm	ppm	ppm	ppm
Detection Limit	0.1	0.1	0.01	0.1	0.02	0.1	0.1	0.1	0.1	0.5	0.01	0.1
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
GF 1-01	0.8	8.1	33.1	3.9	0.44	<0.1	0.4	0.6	3.9	0.8	2.75	24.5
GF 1-02	0.2	1.3	3.21	7.1	0.25	<0.1	0.2	0.3	6.7	0.6	4.91	20.4
GF 1-03	0.3	2.8	10.1	5.3	0.16	<0.1	0.2	0.3	1.6	<0.5	0.83	4.9
GF -3	0.5	5	12.8	2.6	0.24	<0.1	0.4	0.2	1.5	0.8	0.93	7.3
HR -CM1	1.5	14.8	34.3	5	0.59	<0.1	0.5	<0.1	1.8	1.1	1.19	12.2
HR -CM1-A1	0.2	1.8	5.14	2.3	0.18	<0.1	<0.1	<0.1	1.1	0.6	0.87	6
HR -CM1-A2	0.4	3.4	10	3.9	0.17	<0.1	<0.1	<0.1	0.7	1	0.37	3.4
HR -CM1-B1	0.3	2.5	7.71	5	0.26	<0.1	<0.1	<0.1	1.4	0.9	0.84	4.6
HR -CM1-C1	0.2	1.2	5.24	2	0.14	<0.1	0.4	<0.1	0.7	0.6	0.55	3.8
HR -CM2	0.2	1.4	4.34	7.6	0.15	<0.1	0.2	<0.1	0.7	<0.5	0.5	3.4
HR -CM3	0.6	6.7	16.5	3.6	0.29	<0.1	0.4	0.1	0.8	0.8	0.44	4.8
HR -BM9	0.3	1.9	4.96	4.4	0.21	<0.1	<0.1	<0.1	0.9	0.8	0.62	7.7
SW 1-1	0.4	3.8	8.8	2.4	0.18	<0.1	<0.1	<0.1	0.4	0.9	0.26	2.1
SW 2-01	0.2	1.3	4.05	2.6	0.14	<0.1	<0.1	<0.1	0.4	0.6	0.26	1.5
SW2 -02	0.3	2.8	6.78	2.3	0.12	<0.1	0.4	<0.1	0.2	<0.5	0.12	1.1
SW 2-03	<0.1	1.1	4.88	4.4	0.1	<0.1	0.3	<0.1	0.4	1.1	0.2	1.7
SW 3-1	0.4	4.3	11.3	2.9	0.16	<0.1	<0.1	<0.1	0.3	<0.5	0.16	1.6

Analyte Symbol	Sc	Pr	Gd	Dy	Ho	Er	Tm	Nb	Mo	Ag	Cd	In
Unit Symbol	ppm	ppm	ppm	ppm	ppm	Ppm	Ppm	Ppm	ppm	ppm	ppm	ppm
Detection Limit	0.1	0.1	0.1	0.001	0.1	0.1	0.1	0.1	0.01	0.002	0.01	0.02
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
GF 1-01	<0.1	<0.1	0.2	0.9	0.2	0.9	0.2	4.7	2.33	<0.002	<0.01	0.03
GF 1-02	<0.1	0.2	0.4	1.7	0.4	1.4	0.3	7.6	1.23	<0.002	<0.01	0.03
GF 1-03	<0.1	<0.1	<0.1	0.3	<0.1	0.2	<0.1	2.7	0.82	0.009	<0.01	<0.02
GF -3	<0.1	<0.1	<0.1	0.3	<0.1	0.3	<0.1	2.8	1.66	0.156	<0.01	<0.02
HR -CM1	<0.1	0.1	<0.1	0.4	<0.1	0.4	<0.1	2.1	4.87	0.012	<0.01	<0.02
HR -CM1-A1	<0.1	<0.1	<0.1	0.3	<0.1	0.3	<0.1	2.3	1.34	<0.002	<0.01	<0.02
HR -CM1-A2	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	1.3	1.18	<0.002	<0.01	<0.02
HR -CM1-B1	<0.1	<0.1	<0.1	0.3	<0.1	0.3	<0.1	2.9	1.06	<0.002	<0.01	<0.02
HR -CM1-C1	<0.1	<0.1	<0.1	0.2	<0.1	0.2	<0.1	2	0.81	<0.002	<0.01	<0.02
HR -CM2	<0.1	<0.1	<0.1	0.2	<0.1	0.2	<0.1	1.5	0.67	<0.002	<0.01	<0.02
HR -CM3	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	1.3	2.17	<0.002	<0.01	<0.02
HR -BM9	<0.1	<0.1	<0.1	0.2	<0.1	0.2	<0.1	2.1	1.27	<0.002	<0.01	<0.02
SW 1-1	<0.1	0.3	<0.1	0.1	<0.1	<0.1	<0.1	0.7	1.16	0.009	<0.01	<0.02
SW 2-01	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.8	0.5	<0.002	<0.01	<0.02
SW2 -02	<0.1	<0.1	<0.1	<0.001	<0.1	<0.1	<0.1	0.5	0.66	<0.002	<0.01	<0.02
SW 2-03	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.8	0.32	<0.002	<0.01	<0.02
SW 3-1	<0.1	<0.1	<0.1	<0.001	<0.1	<0.1	<0.1	0.6	1.31	<0.002	<0.01	<0.02

Analyte Symbol	Sn	Sb	Te	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb
Unit Symbol	ppm	ppm	ppm	ppm	ppm	Ppm	Ppm	Ppm	ppm	ppm	ppm	ppm
Detection Limit	0.05	0.02	0.02	0.02	0.5	0.5	0.01	0.02	0.1	0.1	0.1	0.1
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
GF 1-01	2.67	0.17	<0.02	0.2	7.3	<0.5	1.99	0.39	0.2	<0.1	<0.1	1.1
GF 1-02	2.98	0.08	<0.02	0.2	7.6	<0.5	2.55	0.63	0.3	<0.1	0.2	1.7
GF 1-03	0.97	0.07	<0.02	<0.02	7.3	<0.5	1.02	0.13	<0.1	<0.1	<0.1	0.3
GF -3	1.46	0.12	<0.02	0.2	6.9	<0.5	1.01	0.12	<0.1	<0.1	<0.1	0.4
HR -CM1	3.12	0.29	<0.02	0.1	6.8	<0.5	1.25	0.2	<0.1	<0.1	<0.1	0.5
HR -CM1-A1	1.09	0.06	<0.02	0.1	7.2	<0.5	1.05	0.12	<0.1	<0.1	<0.1	0.4
HR -CM1-A2	0.84	0.1	<0.02	0.25	6.3	<0.5	0.81	0.06	<0.1	<0.1	<0.1	<0.1
HR -CM1-B1	0.98	0.09	<0.02	0.1	7.6	<0.5	1.2	0.18	<0.1	<0.1	<0.1	0.3
HR -CM1-C1	0.63	0.04	<0.02	0.1	6.5	<0.5	0.89	0.08	<0.1	<0.1	<0.1	0.2
HR -CM2	0.72	0.04	<0.02	<0.02	6.4	<0.5	0.8	0.07	<0.1	<0.1	<0.1	0.2
HR -CM3	1.45	0.14	<0.02	0.1	6.3	<0.5	0.84	0.08	<0.1	<0.1	<0.1	0.2
HR -BM9	0.77	0.06	<0.02	0.1	7	<0.5	0.94	0.1	<0.1	<0.1	<0.1	0.3
SW 1-1	0.67	0.08	<0.02	<0.02	7	1.5	2.57	1.17	0.2	<0.1	<0.1	<0.1
SW 2-01	0.41	0.03	<0.02	<0.02	6.7	<0.5	0.83	0.09	<0.1	<0.1	<0.1	<0.1
SW2 -02	0.53	0.06	<0.02	<0.02	6.7	<0.5	0.66	0.03	<0.1	<0.1	<0.1	<0.1
SW 2-03	0.32	0.03	<0.02	0.1	6.6	<0.5	0.7	0.05	<0.1	<0.1	<0.1	<0.1
SW 3-1	0.75	0.08	<0.02	<0.02	6	<0.5	0.68	0.04	<0.1	<0.1	<0.1	<0.1

Analyte Symbol	Lu	Hf	Ta	W	Re	Au	Tl	Pb	Bi	Th	U
Unit Symbol	ppm	ppm	ppm	ppm	ppm	Ppb	Ppm	Ppm	ppm	ppm	ppm
Detection Limit	0.1	0.1	0.05	0.1	0.001	0.5	0.02	0.01	0.02	0.1	0.1
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
GF 1-01	0.2	1.5	<0.05	<0.1	<0.001	4	<0.02	9.68	0.27	14.2	3.8
GF 1-02	0.2	1.5	<0.05	<0.1	<0.001	4.1	0.03	20.7	0.42	21.2	5.5
GF 1-03	<0.1	0.3	<0.05	<0.1	<0.001	1	<0.02	3.21	0.13	5.8	1.2
GF -3	<0.1	0.5	<0.05	<0.1	<0.001	1.4	<0.02	3.83	0.23	6.2	1.7
HR -CM1	<0.1	0.6	<0.05	<0.1	<0.001	1	<0.02	4.65	0.13	8.3	1.8
HR -CM1-A1	<0.1	0.4	<0.05	<0.1	<0.001	<0.5	<0.02	4.09	0.13	4.7	1.1
HR -CM1-A2	<0.1	0.2	<0.05	<0.1	<0.001	<0.5	<0.02	1.69	0.06	2.6	0.6
HR -CM1-B1	<0.1	0.3	<0.05	0.2	<0.001	0.6	<0.02	3.94	0.12	4.4	1
HR -CM1-C1	<0.1	0.2	<0.05	<0.1	<0.001	<0.5	<0.02	2.67	0.13	2.4	0.7
HR -CM2	<0.1	0.2	<0.05	<0.1	<0.001	0.9	<0.02	2.36	0.07	2.2	0.6
HR -CM3	<0.1	0.2	<0.05	<0.1	<0.001	<0.5	<0.02	1.92	0.21	2.9	0.7
HR -BM9	<0.1	0.4	<0.05	<0.1	<0.001	<0.5	<0.02	3.02	0.14	3.2	0.8
SW 1-1	<0.1	<0.1	<0.05	<0.1	<0.001	0.8	<0.02	0.7	0.03	1.1	0.3
SW 2-01	<0.1	<0.1	<0.05	<0.1	<0.001	<0.5	<0.02	1.24	0.05	1.2	0.3
SW2 -02	<0.1	n/a	<0.05	<0.1	<0.001	<0.5	<0.02	0.57	<0.02	0.5	0.2
SW 2-03	<0.1	<0.1	<0.05	<0.1	<0.001	<0.5	<0.02	1.42	0.05	0.7	0.2
SW 3-1	<0.1	<0.1	<0.05	<0.1	<0.001	0.8	<0.02	0.76	<0.02	0.8	0.2

Appendix 5: 2009 Acid digestion ICP-MS results

Results of 2009 acid digestion ICP-MS analysis of Churchill River basin quartz samples

Analyte Symbol	Li	Be	B	Na	Mg	Al	P	S	K	Ca	V	Cr	Ti	Mn	Fe
Unit Symbol	ppm	ppm	ppm	%	%	%	%	%	%	%	ppm	ppm	%	ppm	%
Detection Limit	0.1	0.1	1	0.001	0.01	0.01	0.001	0.001	0.01	0.01	1	0.5	0.01	1	0.01
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-ICP	AR-ICP	AR-MS	AR-MS	AR-MS	AR-MS	AR-ICP	AR-MS	AR-MS
GF-4	1.3	0.9	27	0.05	< 0.01	0.06	0.002	0.148	0.02	< 0.01	1	46.1	< 0.01	205	2.88
GF-5	1	< 0.1	20	0.022	< 0.01	0.04	< 0.001	0.004	0.01	< 0.01	10	383	< 0.01	59	0.63
GF-6	0.8	< 0.1	19	0.015	< 0.01	0.03	< 0.001	0.003	< 0.01	< 0.01	< 1	1.4	< 0.01	39	0.82
GF-7	1.6	0.4	25	0.052	< 0.01	0.08	< 0.001	0.023	0.03	< 0.01	< 1	37.8	< 0.01	143	2.15
GF-8	1	< 0.1	25	0.021	< 0.01	0.03	< 0.001	0.002	0.01	< 0.01	10	348	< 0.01	48	0.53
GF-9	0.7	< 0.1	22	0.018	< 0.01	0.04	< 0.001	0.002	0.01	< 0.01	< 1	4.5	< 0.01	62	1.69
GF-10	0.8	0.2	25	0.018	< 0.01	0.03	< 0.001	0.008	< 0.01	< 0.01	< 1	27.9	< 0.01	78	1.22
GF-11	0.8	< 0.1	24	0.016	< 0.01	0.02	< 0.001	0.001	< 0.01	< 0.01	14	493	< 0.01	60	0.69
GF-12	1.2	< 0.1	22	0.011	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	1	0.7	< 0.01	27	0.52
GF-13	0.9	0.2	28	0.017	< 0.01	0.02	< 0.001	0.005	< 0.01	< 0.01	< 1	22.1	< 0.01	79	1.22
GF-14	1.4	< 0.1	24	0.032	< 0.01	0.06	< 0.001	0.001	0.02	< 0.01	15	505	< 0.01	78	1.05
GF-15	1.5	< 0.1	21	0.035	< 0.01	0.07	< 0.001	0.002	0.02	< 0.01	< 1	6.2	< 0.01	73	2.29
GF-16	1	< 0.1	23	0.023	< 0.01	0.04	< 0.001	0.004	0.01	< 0.01	< 1	29.1	< 0.01	107	1.69
GF-17	1.3	< 0.1	21	0.032	< 0.01	0.06	< 0.001	0.001	0.02	< 0.01	12	460	< 0.01	68	0.93
GF-18	0.4	< 0.1	23	0.01	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	19	0.35
GF-19	0.5	0.1	19	0.018	< 0.01	0.03	< 0.001	0.003	0.01	< 0.01	< 1	26	< 0.01	101	1.58
GF-21	0.8	< 0.1	20	0.019	0.01	0.12	< 0.001	0.002	0.02	< 0.01	< 1	1.1	< 0.01	18	0.09
GF-22	0.8	< 0.1	22	0.021	< 0.01	0.03	< 0.001	< 0.001	0.01	< 0.01	14	376	< 0.01	48	0.57
GF-23	0.9	< 0.1	23	0.023	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	< 1	1.9	< 0.01	34	0.8
GF-24	0.4	< 0.1	19	0.014	< 0.01	0.02	< 0.001	0.003	< 0.01	< 0.01	< 1	15.6	< 0.01	68	1.06
GF-25	1	< 0.1	22	0.021	< 0.01	0.04	< 0.001	0.001	0.01	< 0.01	16	584	< 0.01	77	1.06
GF-26	0.9	< 0.1	22	0.018	< 0.01	0.03	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.6	< 0.01	28	0.58
GF-27	1.6	< 0.1	23	0.017	< 0.01	0.02	< 0.001	0.002	< 0.01	< 0.01	< 1	13.7	< 0.01	58	0.88
GF-28	1.3	< 0.1	22	0.019	< 0.01	0.03	< 0.001	< 0.001	< 0.01	< 0.01	8	319	< 0.01	42	0.51
GF-29	0.7	< 0.1	21	0.011	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	25	0.32
GF-30	1.2	< 0.1	18	0.014	< 0.01	0.02	< 0.001	0.002	< 0.01	< 0.01	< 1	18.6	< 0.01	35	0.5
GF-31	1.9	< 0.1	23	0.042	< 0.01	0.07	0.019	0.001	0.03	< 0.01	17	568	< 0.01	77	1.06
GF-32	1.8	< 0.1	23	0.025	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	1	2.8	< 0.01	38	0.98
GF-33	2.3	0.1	22	0.057	< 0.01	0.08	< 0.001	0.002	0.03	< 0.01	2	79.2	< 0.01	100	1.66
GF-34	1.2	< 0.1	19	0.021	< 0.01	0.03	< 0.001	< 0.001	0.01	< 0.01	10	358	< 0.01	45	0.54

GF-35	0.9	< 0.1	22	0.021	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	2	5.6	< 0.01	60	1.75
GF-36	0.6	< 0.1	20	0.015	< 0.01	0.02	< 0.001	0.008	< 0.01	< 0.01	1	17.4	< 0.01	41	0.56
GF-37	0.8	< 0.1	22	0.018	< 0.01	0.03	< 0.001	0.002	0.01	< 0.01	2	259	< 0.01	35	0.42
GF-38	1.4	< 0.1	2	0.027	< 0.01	0.04	< 0.001	0.002	0.01	< 0.01	2	1	< 0.01	29	0.65
GF-39	1.8	< 0.1	1	0.03	< 0.01	0.05	< 0.001	0.002	0.01	< 0.01	< 1	43.6	< 0.01	107	1.71
GF-40	2	< 0.1	2	0.042	< 0.01	0.06	< 0.001	0.001	0.02	< 0.01	13	463	< 0.01	63	0.86
GF-41	1.3	< 0.1	1	0.026	< 0.01	0.03	< 0.001	< 0.001	0.01	< 0.01	< 1	2.1	< 0.01	32	0.7
GF-42	1.8	< 0.1	< 1	0.042	< 0.01	0.07	< 0.001	0.002	0.02	< 0.01	< 1	43.2	< 0.01	118	1.9
GF-43	1.7	< 0.1	19	0.024	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	13	416	< 0.01	54	0.73
GF-44	1.7	< 0.1	24	0.016	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	3.1	< 0.01	39	1.08
GF-45	2	< 0.1	21	0.035	< 0.01	0.06	< 0.001	0.002	0.02	< 0.01	3	39.1	< 0.01	111	1.75
GF-46	2.2	< 0.1	22	0.024	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	14	504	< 0.01	62	0.86
GF-47	1.7	< 0.1	21	0.022	< 0.01	0.04	< 0.001	0.001	0.01	< 0.01	1	6.6	< 0.01	73	2.34
GF-48	1.2	< 0.1	17	0.024	< 0.01	0.04	< 0.001	0.002	0.01	< 0.01	< 1	30.7	< 0.01	109	1.73
GF-49	0.9	< 0.1	1	0.023	< 0.01	0.03	< 0.001	< 0.001	< 0.01	< 0.01	9	333	< 0.01	38	0.46
GF-50	0.7	< 0.1	3	0.014	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	18	0.37
GF-51	1.1	< 0.1	1	0.024	< 0.01	0.1	< 0.001	0.003	0.01	< 0.01	< 1	< 0.5	< 0.01	13	0.05
GF-52	1.1	0.1	2	0.082	< 0.01	0.13	< 0.001	0.003	0.03	< 0.01	1	< 0.5	< 0.01	8	0.02
GF-53	0.4	< 0.1	< 1	0.017	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	10.2	< 0.01	41	0.57
GF-54	1.1	< 0.1	< 1	0.016	< 0.01	0.05	< 0.001	0.002	< 0.01	< 0.01	< 1	< 0.5	< 0.01	6	0.01
GF-55	1.9	< 0.1	1	0.021	< 0.01	0.03	< 0.001	< 0.001	0.01	< 0.01	13	400	< 0.01	48	0.59
GF-56	0.5	< 0.1	< 1	0.015	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.7	< 0.01	28	0.67
GF-57	0.6	< 0.1	< 1	0.014	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	10.2	< 0.01	45	0.62
GF-58	0.6	< 0.1	< 1	0.016	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	235	< 0.01	29	0.35
GF-59	0.6	< 0.1	< 1	0.015	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.1	< 0.01	23	0.51
GF-60	0.9	< 0.1	< 1	0.021	< 0.01	0.02	< 0.001	0.001	< 0.01	< 0.01	2	18.4	< 0.01	71	1.09
GF-61	0.9	< 0.1	< 1	0.016	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	1	205	< 0.01	26	0.31
GF-62	0.4	< 0.1	< 1	0.013	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	18	0.36
GF-63	1.2	< 0.1	3	0.017	< 0.01	0.05	< 0.001	0.002	< 0.01	< 0.01	< 1	< 0.5	< 0.01	4	< 0.01
GF-64	0.6	< 0.1	< 1	0.015	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	16.7	< 0.01	35	0.51
GF-65	0.8	< 0.1	1	0.025	< 0.01	0.03	< 0.001	< 0.001	0.01	< 0.01	8	320	< 0.01	37	0.44
GF-66	2.1	< 0.1	< 1	0.023	< 0.01	0.03	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.1	< 0.01	31	0.8
GF-67	1.2	< 0.1	< 1	0.019	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	2	21.3	< 0.01	53	0.87
SQ-01	1	< 0.1	< 1	0.018	< 0.01	0.01	< 0.001	0.001	< 0.01	< 0.01	9	302	< 0.01	36	0.41
SQ-02	1	< 0.1	< 1	0.016	< 0.01	0.01	< 0.001	0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	19	0.34
SQ-03	1.3	< 0.1	< 1	0.029	< 0.01	0.04	< 0.001	0.001	0.01	< 0.01	2	42.5	< 0.01	111	1.83
SQ-04	1	< 0.1	< 1	0.027	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	8	351	< 0.01	57	0.51
SQ-05	0.4	< 0.1	< 1	0.015	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	0.7	< 0.01	17	0.35
SQ-06	1	< 0.1	< 1	0.019	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	23.2	< 0.01	58	0.95
WC-02	0.6	< 0.1	< 1	0.011	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	5.1	< 0.01	24	0.33
WC-03	0.8	< 0.1	< 1	0.014	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	231	< 0.01	28	0.34
WC-05	0.7	< 0.1	< 1	0.013	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	23	0.51

WC-11	0.8	< 0.1	< 1	0.013	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	11	< 0.01	29	0.41
WC-15	1	< 0.1	< 1	0.023	< 0.01	0.03	< 0.001	< 0.001	0.01	< 0.01	9	311	< 0.01	35	0.43
WC-16	0.5	< 0.1	< 1	0.009	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	17	0.33
WC-17	0.5	< 0.1	< 1	0.022	< 0.01	0.03	< 0.001	< 0.001	< 0.01	< 0.01	< 1	13.5	< 0.01	39	0.56
WC-19	1.5	< 0.1	< 1	0.033	< 0.01	0.05	< 0.001	< 0.001	0.01	< 0.01	12	452	< 0.01	53	0.65
WC-20	0.9	< 0.1	< 1	0.017	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	3	1.9	< 0.01	30	0.82
WC-23	0.6	< 0.1	< 1	0.014	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	6.2	< 0.01	19	0.26
WC-24	1.3	< 0.1	< 1	0.027	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	11	369	< 0.01	40	0.48
CMI-S1	0.6	< 0.1	< 1	0.015	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.1	< 0.01	18	0.39
CMI-S2	0.3	< 0.1	< 1	0.012	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	8.1	< 0.01	21	0.29
CMI-S3	0.9	< 0.1	< 1	0.019	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	9	336	< 0.01	38	0.47
CMI-S5	0.8	< 0.1	< 1	0.02	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.6	< 0.01	23	0.51
CMI-S6	1.3	< 0.1	< 1	0.026	< 0.01	0.04	< 0.001	< 0.001	0.01	< 0.01	< 1	19.9	< 0.01	55	0.88
CMI-S7	1	< 0.1	< 1	0.019	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	11	360	< 0.01	42	0.53
CMI-S8	0.5	< 0.1	< 1	0.012	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	< 0.5	< 0.01	21	0.46
CMI-S9	1.1	< 0.1	< 1	0.02	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	17	< 0.01	46	0.66
CMI-S10	0.9	< 0.1	< 1	0.013	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	173	< 0.01	21	0.26
CMI-S11	0.7	< 0.1	< 1	0.016	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	1.5	< 0.01	25	0.55
CMI-S12	1.2	< 0.1	< 1	0.021	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	1	27	< 0.01	85	1.35
CMI-S13	0.4	< 0.1	< 1	0.012	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	118	< 0.01	14	0.17
CMI-S14	0.9	< 0.1	< 1	0.022	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	1	1.2	< 0.01	22	0.45
CMI-S17	0.9	< 0.1	< 1	0.015	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	9.5	< 0.01	38	0.54
CMI-S18	1.6	< 0.1	< 1	0.031	< 0.01	0.05	< 0.001	< 0.001	0.02	< 0.01	12	382	< 0.01	45	0.56
FC-S16	0.8	< 0.1	< 1	0.02	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	< 1	0.7	< 0.01	21	0.43
FIB-01	1.3	< 0.1	1	0.035	< 0.01	0.05	< 0.001	< 0.001	0.01	< 0.01	< 1	15.2	< 0.01	57	0.88
FIB-02	1.4	< 0.1	< 1	0.02	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	1	277	< 0.01	36	0.42
FIB-03	0.5	< 0.1	< 1	0.015	< 0.01	< 0.01	< 0.001	< 0.001	< 0.01	< 0.01	< 1	0.6	< 0.01	23	0.45
GFNW-10	1	< 0.1	< 1	0.018	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	2	2.4	< 0.01	38	1.01
GFNW-11	0.7	< 0.1	< 1	0.018	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	3	21.2	< 0.01	68	1.08
GFNW-12	2.1	< 0.1	< 1	0.023	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	1	244	< 0.01	30	0.37
GFNW-13	1	< 0.1	< 1	0.014	< 0.01	0.01	< 0.001	< 0.001	< 0.01	< 0.01	1	0.8	< 0.01	21	0.47
GFNW-14	1.9	< 0.1	< 1	0.021	< 0.01	0.02	< 0.001	< 0.001	< 0.01	< 0.01	2	16.2	< 0.01	57	0.89

Analyte Symbol	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Y	Zr	Sc	Pr	Gd
Unit Symbol	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	0.1	0.1	0.01	0.1	0.02	0.1	0.1	0.1	0.1	0.5	0.01	0.1	0.1	0.1	0.1
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
GF-4	2.2	2190	32.8	27.5	0.61	< 0.1	1	< 0.1	0.9	1.8	7.5	31.5	< 0.1	0.8	0.8
GF-5	1.2	10.7	10.6	18	0.26	< 0.1	< 0.1	0.2	0.3	1.3	0.14	1.6	< 0.1	< 0.1	< 0.1
GF-6	0.3	2.8	6.58	6.1	0.22	< 0.1	0.3	0.2	0.3	0.7	0.15	2.5	< 0.1	< 0.1	< 0.1
GF-7	1.5	307	35.1	16.5	0.55	< 0.1	0.5	0.1	0.8	2	3.3	15.6	< 0.1	0.4	0.3
GF-8	0.8	8.9	9.63	4.3	0.29	< 0.1	0.9	0.2	0.3	1.1	0.12	1.4	< 0.1	< 0.1	< 0.1
GF-9	0.6	5.3	16.6	32	0.32	< 0.1	< 0.1	0.2	0.4	1	0.24	5.5	< 0.1	< 0.1	< 0.1
GF-10	0.8	102	13.6	5.1	0.32	< 0.1	0.3	< 0.1	0.3	0.8	2.59	8.5	< 0.1	0.2	0.3
GF-11	1.1	11.9	13.6	15	0.31	< 0.1	0.9	0.4	0.2	0.9	0.06	1.4	< 0.1	< 0.1	< 0.1
GF-12	0.2	1.6	4.35	3.1	0.16	< 0.1	< 0.1	0.2	0.2	< 0.5	0.1	1.7	< 0.1	< 0.1	< 0.1
GF-13	0.8	63.7	19	20.1	0.33	< 0.1	< 0.1	0.2	0.3	0.7	1.1	6.4	< 0.1	0.1	0.1
GF-14	1.2	12.6	21.6	19	0.4	< 0.1	0.7	< 0.1	0.4	1.8	0.13	1.6	< 0.1	< 0.1	< 0.1
GF-15	0.7	5.9	20.9	16.7	0.44	< 0.1	< 0.1	0.4	0.9	2.1	0.28	7.7	< 0.1	< 0.1	< 0.1
GF-16	1.1	60.2	21	26.5	0.41	< 0.1	< 0.1	0.1	0.4	1.1	1.06	7.1	< 0.1	0.1	< 0.1
GF-17	1.2	12.2	16.3	16	0.32	< 0.1	0.3	0.3	0.4	1.6	0.29	2.2	< 0.1	< 0.1	< 0.1
GF-18	0.2	1.1	4.14	2.3	0.15	< 0.1	< 0.1	0.3	0.1	< 0.5	0.06	1	< 0.1	< 0.1	< 0.1
GF-19	1	47.7	17.1	13.3	0.36	< 0.1	0.2	0.1	0.4	0.6	0.89	6.1	< 0.1	< 0.1	< 0.1
GF-21	0.9	1.7	1.48	12.6	0.49	< 0.1	0.4	< 0.1	0.8	2.3	0.57	1.3	< 0.1	0.1	0.1
GF-22	0.9	8.5	11.6	11.3	0.31	< 0.1	0.7	0.5	0.3	0.9	0.05	1.2	< 0.1	< 0.1	< 0.1
GF-23	0.3	2.4	11.8	10.3	0.26	< 0.1	< 0.1	< 0.1	0.3	1	0.14	2.5	< 0.1	< 0.1	< 0.1
GF-24	0.8	31	16.4	23.9	0.27	< 0.1	< 0.1	0.3	0.3	0.6	5.7	4.6	< 0.1	< 0.1	0.5
GF-25	1.3	13.7	22.4	28.6	0.34	< 0.1	0.5	0.1	0.3	1	0.27	2	< 0.1	< 0.1	< 0.1
GF-26	0.2	1.7	9.11	11.6	0.24	< 0.1	0.9	0.2	0.2	0.8	0.24	2.2	< 0.1	< 0.1	< 0.1
GF-27	0.5	23.7	15.1	17.5	0.26	< 0.1	0.5	0.2	0.3	0.6	0.54	3.6	< 0.1	< 0.1	< 0.1
GF-28	0.7	7.9	10.5	9.1	0.25	< 0.1	< 0.1	0.1	0.3	0.9	0.04	1	< 0.1	< 0.1	< 0.1
GF-29	0.1	0.9	4.93	4.7	0.18	< 0.1	0.2	< 0.1	0.2	< 0.5	0.14	1.7	< 0.1	< 0.1	< 0.1
GF-30	0.4	20.6	8.46	7.8	0.2	< 0.1	< 0.1	0.3	0.2	0.6	0.39	2.4	< 0.1	< 0.1	< 0.1
GF-31	1.2	14.2	22.8	36.7	0.45	0.3	< 0.1	1.7	0.6	2.2	36.2	1.5	< 0.1	37.5	29
GF-32	0.3	2.6	13.2	7.7	0.32	< 0.1	0.2	0.4	0.4	1.3	5.92	6.3	< 0.1	< 0.1	0.4
GF-33	1	40.1	29.4	29.2	0.48	< 0.1	1.1	0.3	0.7	2.4	0.64	4.9	< 0.1	< 0.1	< 0.1

GF-34	0.7	8.1	11.4	19.7	0.29	< 0.1	0.9	0.2	0.3	0.9	0.25	1.1	< 0.1	0.2	0.2
GF-35	1	4.3	17	9.7	0.35	< 0.1	1	0.4	0.4	0.9	0.25	5.2	< 0.1	< 0.1	< 0.1
GF-36	0.4	15.1	11.5	14.2	0.27	< 0.1	0.8	0.2	0.4	0.8	0.37	2.4	< 0.1	< 0.1	< 0.1
GF-37	0.6	6.3	8.63	11.4	0.25	< 0.1	1	0.3	0.3	0.8	0.07	0.9	< 0.1	< 0.1	< 0.1
GF-38	0.2	1.8	10.6	12.7	0.24	< 0.1	< 0.1	0.1	0.3	1.2	1.11	2.3	< 0.1	< 0.1	< 0.1
GF-39	1.1	29.5	23.6	24.5	0.41	< 0.1	0.7	0.3	0.5	1.3	0.45	4.7	< 0.1	< 0.1	< 0.1
GF-40	1	11.3	14.8	20	0.38	< 0.1	< 0.1	0.3	0.6	2	0.45	1.3	< 0.1	0.2	0.2
GF-41	0.8	2.6	9.46	15.2	0.26	< 0.1	0.8	< 0.1	0.4	1	0.3	2.2	< 0.1	< 0.1	< 0.1
GF-42	1.3	31.6	28.1	26.9	0.46	< 0.1	0.4	0.5	0.8	1.6	0.45	4.8	< 0.1	< 0.1	< 0.1
GF-43	1	10.1	13.8	12.5	0.3	< 0.1	< 0.1	0.2	0.4	1.1	0.06	1.2	< 0.1	< 0.1	< 0.1
GF-44	0.3	2.6	13.4	9.4	0.26	< 0.1	< 0.1	0.3	0.3	0.7	0.12	3.2	< 0.1	< 0.1	< 0.1
GF-45	1.1	28.8	24.1	12.8	0.49	< 0.1	0.6	< 0.1	0.6	1.6	0.47	5.3	< 0.1	< 0.1	< 0.1
GF-46	1	12.2	16.6	17.2	0.35	< 0.1	1.2	0.6	0.4	1.3	0.13	1.4	< 0.1	< 0.1	< 0.1
GF-47	0.7	5	17.5	8.1	0.36	< 0.1	0.3	0.2	0.4	1.2	0.18	7.2	< 0.1	< 0.1	< 0.1
GF-48	1.2	26.3	27.5	30.3	0.4	< 0.1	0.4	0.3	0.4	1	0.4	4.2	< 0.1	< 0.1	< 0.1
GF-49	0.6	7.5	10.8	7.8	0.28	< 0.1	< 0.1	< 0.1	0.2	0.8	0.05	1	< 0.1	< 0.1	< 0.1
GF-50	0.2	1	4.22	5.7	0.2	< 0.1	< 0.1	0.2	0.1	< 0.5	0.09	1.2	< 0.1	< 0.1	< 0.1
GF-51	1	1.4	1.37	20.4	0.36	< 0.1	< 0.1	0.2	0.8	2.6	0.46	1.2	< 0.1	0.1	< 0.1
GF-52	0.6	0.8	1.02	17	0.62	< 0.1	1.4	< 0.1	1.2	5.8	0.38	1.1	< 0.1	< 0.1	< 0.1
GF-53	0.4	10.5	10.4	11	0.25	< 0.1	< 0.1	0.1	0.3	0.6	0.2	1.8	< 0.1	< 0.1	< 0.1
GF-54	0.5	0.6	19.1	24	0.23	< 0.1	< 0.1	0.3	0.5	1.1	0.2	0.5	< 0.1	< 0.1	< 0.1
GF-55	0.8	9.4	13.6	11.4	0.31	< 0.1	0.8	0.2	0.3	1	0.31	1.7	< 0.1	< 0.1	< 0.1
GF-56	0.3	1.7	9.55	10.6	0.22	< 0.1	0.8	< 0.1	0.2	< 0.5	0.09	2.1	< 0.1	< 0.1	< 0.1
GF-57	0.5	11.2	8.8	6	0.22	< 0.1	< 0.1	< 0.1	0.2	0.6	0.19	1.9	< 0.1	< 0.1	< 0.1
GF-58	0.5	6	7.76	7.2	0.24	< 0.1	< 0.1	< 0.1	0.2	0.6	0.05	0.8	< 0.1	< 0.1	< 0.1
GF-59	0.4	1.3	6.74	5.3	0.24	< 0.1	0.7	0.2	0.3	0.6	0.07	1.6	< 0.1	< 0.1	< 0.1
GF-60	0.8	16.8	18.3	9.8	0.35	< 0.1	< 0.1	< 0.1	0.6	0.9	0.24	3.2	< 0.1	< 0.1	< 0.1
GF-61	0.4	5.1	6.15	7.9	0.24	< 0.1	< 0.1	< 0.1	0.2	0.5	0.03	0.8	< 0.1	< 0.1	< 0.1
GF-62	0.2	1	5.84	4.6	0.16	< 0.1	< 0.1	< 0.1	0.2	< 0.5	0.04	1	< 0.1	< 0.1	< 0.1
GF-63	0.3	0.7	13.3	22.7	0.29	< 0.1	< 0.1	0.1	0.4	1.2	0.17	0.5	< 0.1	< 0.1	< 0.1
GF-64	0.4	9.5	7.46	3.7	0.19	< 0.1	< 0.1	< 0.1	0.2	0.5	0.16	1.6	< 0.1	< 0.1	< 0.1
GF-65	0.6	7.1	10.3	12.7	0.33	< 0.1	1.2	0.1	0.3	1.1	0.08	1	< 0.1	< 0.1	< 0.1
GF-66	0.3	1.9	10.8	6.7	0.24	< 0.1	< 0.1	< 0.1	0.3	0.9	0.08	2.1	< 0.1	< 0.1	< 0.1
GF-67	0.6	14.4	19.6	10.9	0.28	< 0.1	< 0.1	0.3	0.3	0.8	0.34	2.3	< 0.1	< 0.1	< 0.1
SQ-01	0.6	6.7	8.03	4	0.26	< 0.1	1.1	0.2	0.2	1.4	0.05	1	< 0.1	< 0.1	< 0.1
SQ-02	0.1	1	6.54	4.4	0.19	< 0.1	0.6	0.2	0.3	2.1	0.09	1.1	< 0.1	< 0.1	< 0.1

SQ-03	1.1	26	28.1	22.1	0.4	< 0.1	1.3	0.2	0.5	2.3	0.35	4.1	< 0.1	< 0.1	< 0.1
SQ-04	0.7	8	13.2	21.7	0.33	< 0.1	1.7	0.4	0.5	1.3	0.18	1.1	< 0.1	< 0.1	< 0.1
SQ-05	0.2	0.9	4.84	4.4	0.22	< 0.1	0.6	0.4	0.2	0.9	0.07	1.2	< 0.1	< 0.1	< 0.1
SQ-06	0.6	13.9	19.4	25.2	0.27	< 0.1	< 0.1	0.1	0.4	1.5	0.21	2.5	< 0.1	< 0.1	< 0.1
WC-02	0.2	6	7.85	6.6	0.17	< 0.1	< 0.1	< 0.1	0.1	0.5	0.09	1.2	< 0.1	< 0.1	< 0.1
WC-03	0.4	5.6	7.69	7	0.22	< 0.1	0.5	0.3	0.1	0.6	0.02	0.8	< 0.1	< 0.1	< 0.1
WC-05	0.2	1.4	9.04	9	0.19	< 0.1	< 0.1	0.3	0.1	< 0.5	0.07	1.5	< 0.1	< 0.1	< 0.1
WC-11	0.3	7	7.55	5	0.23	< 0.1	< 0.1	0.3	0.1	< 0.5	0.11	1.4	< 0.1	< 0.1	< 0.1
WC-15	0.6	7.5	14.2	24.8	0.24	< 0.1	0.3	0.2	0.4	1.2	0.07	0.9	< 0.1	< 0.1	< 0.1
WC-16	0.2	0.9	4.81	5	0.16	< 0.1	< 0.1	0.3	< 0.1	< 0.5	0.03	1	< 0.1	< 0.1	< 0.1
WC-17	0.4	8.7	12	10	0.28	< 0.1	0.3	0.4	0.3	1.4	0.12	1.6	< 0.1	< 0.1	< 0.1
WC-19	0.8	10.3	19.5	19.4	0.36	< 0.1	1	0.1	0.4	1.6	0.11	1.3	< 0.1	< 0.1	< 0.1
WC-20	0.3	2	13.9	14.7	0.22	< 0.1	< 0.1	0.3	0.2	0.6	0.12	2.5	< 0.1	< 0.1	< 0.1
WC-23	0.2	4.1	4.25	2.9	0.16	< 0.1	< 0.1	< 0.1	0.1	0.5	0.06	0.8	< 0.1	< 0.1	< 0.1
WC-24	0.7	8.2	11.3	11	0.36	< 0.1	1.3	< 0.1	0.4	1.4	0.07	1.1	< 0.1	< 0.1	< 0.1
CMI-S1	0.2	1	5.34	8.3	0.21	< 0.1	0.2	0.3	0.1	0.5	0.04	1.3	< 0.1	< 0.1	< 0.1
CMI-S2	0.2	5.1	4.94	4.2	0.18	< 0.1	< 0.1	0.2	0.1	< 0.5	0.06	0.9	< 0.1	< 0.1	< 0.1
CMI-S3	0.7	7.7	13.5	18.2	0.27	< 0.1	0.5	< 0.1	0.2	0.9	0.03	0.9	< 0.1	< 0.1	< 0.1
CMI-S5	0.2	1.3	5.89	7.2	0.24	< 0.1	0.2	0.3	0.2	1.1	0.08	1.6	< 0.1	< 0.1	< 0.1
CMI-S6	0.6	11.8	20.3	17.8	0.29	< 0.1	< 0.1	< 0.1	0.4	1.2	0.15	2.1	< 0.1	< 0.1	< 0.1
CMI-S7	0.7	8.6	11.1	12	0.25	< 0.1	< 0.1	0.1	0.2	0.9	0.05	1	< 0.1	< 0.1	< 0.1
CMI-S8	0.2	1.2	7.66	8.4	0.14	< 0.1	< 0.1	< 0.1	0.1	< 0.5	0.06	1.3	< 0.1	< 0.1	< 0.1
CMI-S9	0.5	9.6	12.1	14.3	0.24	< 0.1	< 0.1	0.1	0.3	1.2	0.12	1.7	< 0.1	< 0.1	< 0.1
CMI-S10	0.3	4.4	4.45	3.7	0.2	< 0.1	0.5	0.2	0.1	< 0.5	0.1	0.7	< 0.1	< 0.1	< 0.1
CMI-S11	0.2	1.5	7.54	13.1	0.23	< 0.1	< 0.1	0.2	0.1	0.6	0.06	1.7	< 0.1	< 0.1	< 0.1
CMI-S12	0.8	17.1	20.1	29.5	0.37	< 0.1	0.5	0.3	0.3	0.9	0.17	2.9	< 0.1	< 0.1	< 0.1
CMI-S13	0.2	2.9	3.06	2.2	0.2	< 0.1	1.1	0.3	< 0.1	< 0.5	< 0.01	0.4	< 0.1	< 0.1	< 0.1
CMI-S14	0.2	1.3	13.2	18.2	0.26	< 0.1	1.1	0.3	0.2	1.2	0.08	1.3	< 0.1	< 0.1	< 0.1
CMI-S17	0.4	7.9	11.7	10.3	0.2	< 0.1	< 0.1	0.3	0.1	0.6	0.07	1.4	< 0.1	< 0.1	< 0.1
CMI-S18	0.8	9.7	23.8	37.4	0.37	< 0.1	1	< 0.1	0.5	1.8	0.1	1.1	< 0.1	< 0.1	< 0.1
FC-S16	0.2	1.3	9.09	11.4	0.24	< 0.1	0.8	0.2	0.3	0.8	0.08	1.3	< 0.1	< 0.1	< 0.1
FIB-01	0.5	11.1	15.6	25	0.33	< 0.1	< 0.1	< 0.1	0.5	2.3	0.16	2.1	< 0.1	< 0.1	< 0.1
FIB-02	0.6	6.9	9.2	12.3	0.22	< 0.1	0.2	< 0.1	0.3	1.9	0.09	0.9	< 0.1	< 0.1	< 0.1
FIB-03	0.2	1.2	9.4	9.5	0.17	< 0.1	0.2	0.3	0.2	0.9	0.04	1.1	< 0.1	< 0.1	< 0.1
GFNW-10	0.4	2.5	18.3	24.5	0.25	< 0.1	0.2	< 0.1	0.3	0.8	0.1	2.9	< 0.1	< 0.1	< 0.1
GFNW-11	0.7	13.8	17.6	19.5	0.29	< 0.1	0.8	0.2	0.3	0.7	0.13	2.5	< 0.1	< 0.1	< 0.1

GFNW-12	0.5	6.2	11	18.7	0.25	< 0.1	0.5	< 0.1	0.4	0.9	0.05	0.8	< 0.1	< 0.1	< 0.1
GFNW-13	0.2	1.2	8.1	16.5	0.18	< 0.1	< 0.1	< 0.1	0.3	< 0.5	0.08	1.4	< 0.1	< 0.1	< 0.1
GFNW-14	0.6	11.1	16.1	14	0.31	< 0.1	1.1	< 0.1	0.3	0.8	0.13	2	< 0.1	< 0.1	< 0.1

Analyte Symbol	Dy	Ho	Er	Tm	Nb	Mo	Ag	Cd	In	Sn	Sb	Te	Cs	Ba	La
Unit Symbol	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Detection Limit	0.001	0.1	0.1	0.1	0.1	0.01	0.002	0.01	0.02	0.05	0.02	0.02	0.02	0.5	0.5
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
GF-4	1.31	0.3	1	0.2	5.6	11.7	0.034	< 0.01	< 0.02	3.04	0.7	0.06	0.09	1.7	2.5
GF-5	0.031	< 0.1	< 0.1	< 0.1		33.4	0.005	< 0.01	< 0.02	0.47	0.04	< 0.02	0.04	0.6	< 0.5
GF-6	0.026	< 0.1	< 0.1	< 0.1	0.4	0.38	< 0.002	< 0.01	< 0.02	0.49	< 0.02	< 0.02	0.04	1	< 0.5
GF-7	0.558	0.1	0.4	< 0.1	2.3	9.33	0.02	< 0.01	< 0.02	2.13	0.21	0.03	0.05	1.1	1.1
GF-8	0.027	< 0.1	< 0.1	< 0.1		28.9	0.005	< 0.01	< 0.02	0.45	0.03	< 0.02	0.03	1.4	< 0.5
GF-9	0.042	< 0.1	< 0.1	< 0.1	0.9	0.72	0.011	< 0.01	< 0.02	1.11	0.05	0.03	0.04	1	< 0.5
GF-10	0.429	< 0.1	0.3	< 0.1	1.2	5.68	0.008	< 0.01	< 0.02	1.02	0.05	< 0.02	0.02	0.5	0.6
GF-11	0.02	< 0.1	< 0.1	< 0.1		42.2	0.021	< 0.01	< 0.02	0.58	0.07	< 0.02	0.02	< 0.5	< 0.5
GF-12	0.014	< 0.1	< 0.1	< 0.1	0.3	0.32	< 0.002	< 0.01	< 0.02	0.35	< 0.02	< 0.02	< 0.02	0.7	< 0.5
GF-13	0.179	< 0.1	0.1	< 0.1	0.8	5.17	0.011	< 0.01	< 0.02	1.07	0.06	< 0.02	0.03	1.1	< 0.5
GF-14	0.031	< 0.1	< 0.1	< 0.1		42.6	0.012	< 0.01	< 0.02	0.88	0.12	< 0.02	0.02	0.7	< 0.5
GF-15	0.043	< 0.1	< 0.1	< 0.1	1.2	0.98	0.014	< 0.01	< 0.02	1.57	0.1	0.03	0.09	2.3	< 0.5
GF-16	0.169	< 0.1	0.1	< 0.1	0.7	6.87	0.009	< 0.01	< 0.02	1.28	0.09	< 0.02	0.02	1.1	< 0.5
GF-17	0.068	< 0.1	< 0.1	< 0.1		39.6	0.007	< 0.01	< 0.02	0.7	0.08	< 0.02	0.02	0.6	< 0.5
GF-18	0.01	< 0.1	< 0.1	< 0.1	0.1	0.25	< 0.002	< 0.01	< 0.02	0.25	< 0.02	0.02	0.02	0.6	< 0.5
GF-19	0.16	< 0.1	0.1	< 0.1	0.6	6.43	0.019	< 0.01	< 0.02	1.07	0.07	< 0.02	0.04	0.6	< 0.5
GF-21	0.107	< 0.1	< 0.1	< 0.1		0.04	< 0.002	< 0.01	< 0.02	< 0.05	< 0.02	< 0.02	0.04	9.5	< 0.5
GF-22	0.016	< 0.1	< 0.1	< 0.1		31.4	0.006	< 0.01	< 0.02	0.51	0.04	< 0.02	0.03	< 0.5	< 0.5
GF-23	0.022	< 0.1	< 0.1	< 0.1	0.4	0.39	0.003	< 0.01	< 0.02	0.59	< 0.02	< 0.02	0.03	0.8	< 0.5
GF-24	0.968	0.2	0.5	0.1	0.4	3.84	0.012	< 0.01	< 0.02	0.87	0.02	< 0.02	0.03	1.2	< 0.5
GF-25	0.051	< 0.1	< 0.1	< 0.1		48.2	0.01	< 0.01	< 0.02	0.91	0.13	0.02	< 0.02	0.9	< 0.5
GF-26	0.041	< 0.1	< 0.1	< 0.1	0.3	0.36	0.012	0.01	< 0.02	0.5	< 0.02	0.03	0.05	0.8	< 0.5
GF-27	0.087	< 0.1	< 0.1	< 0.1	0.3	3.35	0.028	< 0.01	< 0.02	0.68	< 0.02	< 0.02	0.06	1	< 0.5
GF-28	0.013	< 0.1	< 0.1	< 0.1		27.4	0.005	< 0.01	< 0.02	0.43	< 0.02	< 0.02	0.05	< 0.5	< 0.5
GF-29	0.021	< 0.1	< 0.1	< 0.1	0.2	0.23	0.003	< 0.01	< 0.02	0.47	< 0.02	< 0.02	0.06	< 0.5	< 0.5
GF-30	0.068	< 0.1	< 0.1	< 0.1	0.2	3.31	0.003	< 0.01	< 0.02	0.44	< 0.02	< 0.02	0.03	0.7	< 0.5
GF-31	13.1	1.3	2.3	0.2		46.5	0.015	< 0.01	< 0.02	0.88	0.12	< 0.02	0.04	1.2	75.6

GF-32	1	0.2	0.6	0.1	0.5	0.53	0.009	< 0.01	< 0.02	0.78	0.03	0.02	0.04	< 0.5	< 0.5
GF-33	0.096	< 0.1	< 0.1	< 0.1	0.3	12.2	0.017	< 0.01	< 0.02	1.4	0.08	0.03	0.04	0.7	< 0.5
GF-34	0.082	< 0.1	< 0.1	< 0.1		28.9	0.009	< 0.01	< 0.02	0.46	0.03	< 0.02	0.03	< 0.5	< 0.5
GF-35	0.047	< 0.1	< 0.1	< 0.1	0.8	0.84	0.016	< 0.01	< 0.02	1.29	0.12	< 0.02	0.03	< 0.5	< 0.5
GF-36	0.06	< 0.1	< 0.1	< 0.1	0.2	3.18	0.015	< 0.01	< 0.02	0.55	< 0.02	< 0.02	0.08	1.4	< 0.5
GF-37	0.015	< 0.1	< 0.1	< 0.1		22.7	0.003	< 0.01	< 0.02	0.37	< 0.02	< 0.02	0.02	< 0.5	< 0.5
GF-38	0.169	< 0.1	0.1	< 0.1	0.3	0.35	0.004	< 0.01	< 0.02	0.56	< 0.02	< 0.02	0.04	5.3	< 0.5
GF-39	0.065	< 0.1	< 0.1	< 0.1	0.2	8.22	0.015	< 0.01	< 0.02	1.24	0.08	< 0.02	0.19	5.4	< 0.5
GF-40	0.138	< 0.1	< 0.1	< 0.1		38.9	0.032	< 0.01	< 0.02	0.66	0.08	< 0.02	0.08	5.8	0.5
GF-41	0.076	< 0.1	< 0.1	< 0.1	0.4	0.45	0.01	< 0.01	< 0.02	0.64	< 0.02	< 0.02	0.2	5.5	< 0.5
GF-42	0.069	< 0.1	< 0.1	< 0.1	0.2	8.33	0.017	< 0.01	< 0.02	1.41	0.1	< 0.02	0.12	5.8	< 0.5
GF-43	0.025	< 0.1	< 0.1	< 0.1	0.1	34.8	0.071	< 0.01	< 0.02	0.55	0.06	< 0.02	0.05	< 0.5	< 0.5
GF-44	0.018	< 0.1	< 0.1	< 0.1	0.5	0.57	0.011	< 0.01	< 0.02	0.84	0.03	< 0.02	0.04	< 0.5	< 0.5
GF-45	0.078	< 0.1	< 0.1	< 0.1	0.2	7.81	0.016	< 0.01	< 0.02	1.35	0.08	< 0.02	0.04	0.6	< 0.5
GF-46	0.026	< 0.1	< 0.1	< 0.1		41.4	0.017	< 0.01	< 0.02	0.7	0.1	< 0.02	0.08	0.7	< 0.5
GF-47	0.028	< 0.1	< 0.1	< 0.1	1.2	1.08	0.02	< 0.01	< 0.02	1.59	0.16	< 0.02	0.07	0.7	< 0.5
GF-48	0.066	< 0.1	< 0.1	< 0.1	0.3	7.01	0.016	< 0.01	< 0.02	1.32	0.06	< 0.02	0.02	< 0.5	< 0.5
GF-49	0.015	< 0.1	< 0.1	< 0.1	0.3	27.4	0.005	< 0.01	< 0.02	0.43	< 0.02	< 0.02	0.02	5.7	< 0.5
GF-50	0.012	< 0.1	< 0.1	< 0.1	0.2	0.24	< 0.002	< 0.01	< 0.02	0.29	< 0.02	< 0.02	< 0.02	6.2	< 0.5
GF-51	0.081	< 0.1	< 0.1	< 0.1		0.05	0.003	0.03	< 0.02	< 0.05	0.09	< 0.02	0.07	22.3	< 0.5
GF-52	0.066	< 0.1	< 0.1	< 0.1	0.1	0.24	0.008	0.01	< 0.02	< 0.05	0.06	< 0.02	0.13	18.5	< 0.5
GF-53	0.031	< 0.1	< 0.1	< 0.1		2.42	0.016	< 0.01	< 0.02	0.5	< 0.02	< 0.02	0.05	5.4	< 0.5
GF-54	0.037	< 0.1	< 0.1	< 0.1		0.03	0.014	0.01	< 0.02	0.3	< 0.02	< 0.02	0.22	14.2	< 0.5
GF-55	0.052	< 0.1	< 0.1	< 0.1		33.1	0.021	< 0.01	< 0.02	0.58	0.06	< 0.02	0.05	4.5	< 0.5
GF-56	0.014	< 0.1	< 0.1	< 0.1	0.3	0.39	0.004	< 0.01	< 0.02	0.56	< 0.02	< 0.02	0.05	5.9	< 0.5
GF-57	0.029	< 0.1	< 0.1	< 0.1		2.67	0.003	< 0.01	< 0.02	0.5	< 0.02	< 0.02	0.04	3.8	< 0.5
GF-58	0.012	< 0.1	< 0.1	< 0.1		21.6	0.009	< 0.01	< 0.02	0.31	< 0.02	< 0.02	0.05	4.4	< 0.5
GF-59	0.008	< 0.1	< 0.1	< 0.1	0.2	0.31	0.005	< 0.01	< 0.02	0.44	< 0.02	0.03	0.06	5.3	< 0.5
GF-60	0.035	< 0.1	< 0.1	< 0.1	0.1	4.28	0.017	< 0.01	< 0.02	0.88	0.05	< 0.02	0.11	5.9	< 0.5
GF-61	0.006	< 0.1	< 0.1	< 0.1		18	< 0.002	< 0.01	< 0.02	0.26	< 0.02	0.02	< 0.02	4.4	< 0.5
GF-62	0.007	< 0.1	< 0.1	< 0.1	0.1	0.22	0.003	< 0.01	< 0.02	0.28	< 0.02	< 0.02	0.03	4.7	< 0.5
GF-63	0.029	< 0.1	< 0.1	< 0.1		0.02	0.012	< 0.01	< 0.02	0.24	< 0.02	0.03	0.14	12.3	< 0.5
GF-64	0.026	< 0.1	< 0.1	< 0.1		3.33	< 0.002	< 0.01	< 0.02	0.41	< 0.02	< 0.02	0.04	4.8	< 0.5
GF-65	0.018	< 0.1	< 0.1	< 0.1		26	0.012	< 0.01	< 0.02	0.4	0.04	< 0.02	0.05	4.6	< 0.5
GF-66	0.012	< 0.1	< 0.1	< 0.1	0.3	0.4	0.005	< 0.01	< 0.02	0.61	< 0.02	< 0.02	0.32	5	< 0.5
GF-67	0.049	< 0.1	< 0.1	< 0.1		4.6	0.019	< 0.01	< 0.02	0.76	< 0.02	< 0.02	0.06	4.7	< 0.5
SQ-01	0.01	< 0.1	< 0.1	< 0.1		23.9	< 0.002	< 0.01	< 0.02	0.37	< 0.02	< 0.02	0.13	5.1	< 0.5
SQ-02	0.016	< 0.1	< 0.1	< 0.1	0.2	0.24	< 0.002	< 0.01	< 0.02	0.27	< 0.02	< 0.02	0.19	6.3	< 0.5
SQ-03	0.052	< 0.1	< 0.1	< 0.1	0.1	8.5	0.014	< 0.01	< 0.02	1.36	0.09	0.03	0.12	6.7	< 0.5
SQ-04	0.03	< 0.1	< 0.1	< 0.1	0.2	28.9	0.004	< 0.01	< 0.02	0.44	0.19	0.02	0.34	6	< 0.5
SQ-05	0.011	< 0.1	< 0.1	< 0.1	0.2	0.21	< 0.002	< 0.01	< 0.02	0.29	< 0.02	< 0.02	0.04	5.9	< 0.5
SQ-06	0.032	< 0.1	< 0.1	< 0.1		4.89	0.01	< 0.01	< 0.02	0.78	0.03	0.05	0.17	6	< 0.5

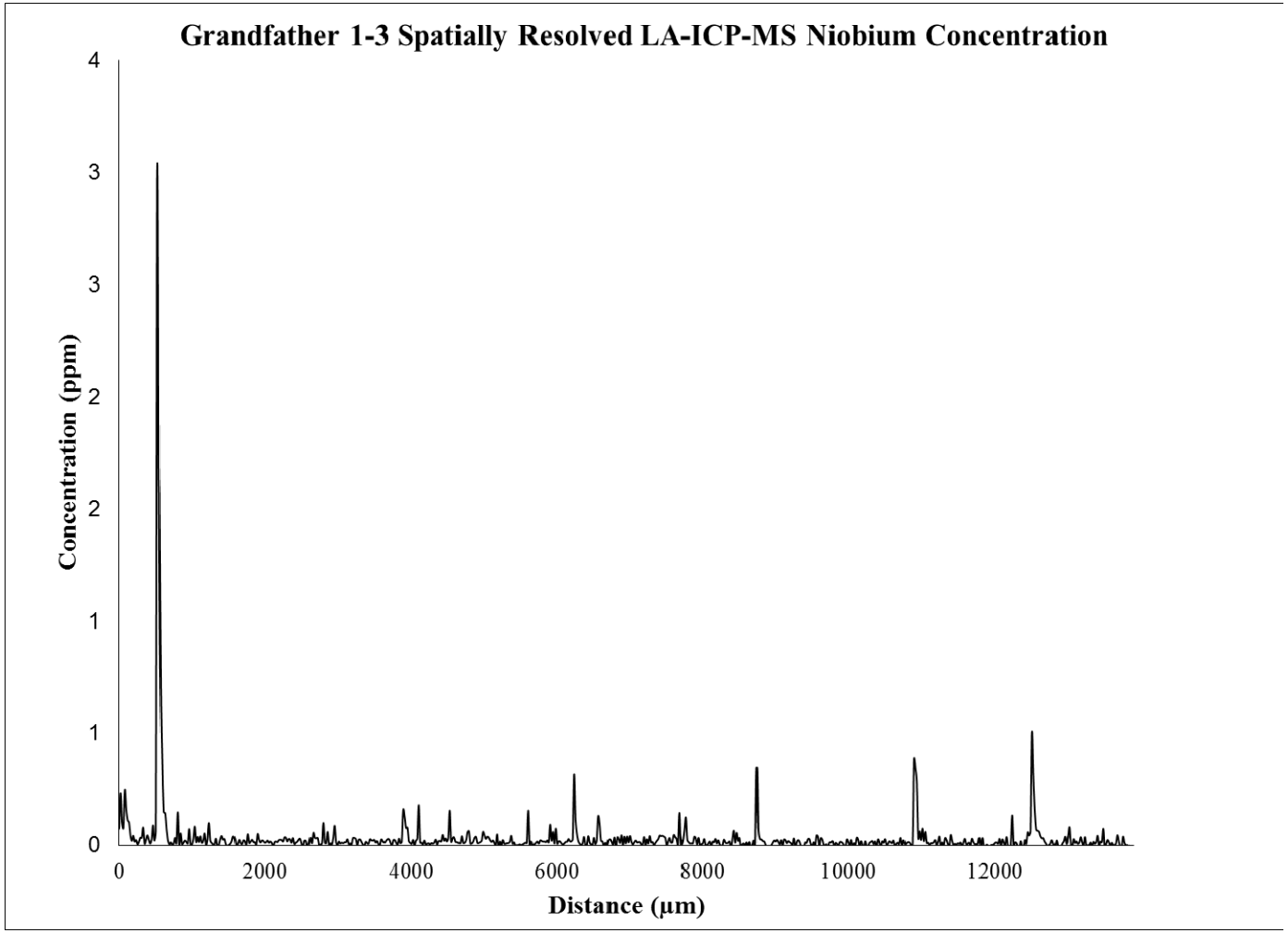
WC-02	0.016	< 0.1	< 0.1	< 0.1		1.46	0.006	< 0.01	< 0.02	0.31	< 0.02	< 0.02	0.19	5.2	< 0.5
WC-03	0.009	< 0.1	< 0.1	< 0.1		20.8	0.003	< 0.01	< 0.02	0.33	0.05	0.03	0.18	5.8	< 0.5
WC-05	0.009	< 0.1	< 0.1	< 0.1	0.2	0.28	0.008	< 0.01	< 0.02	0.44	< 0.02	< 0.02	0.05	5.2	< 0.5
WC-11	0.015	< 0.1	< 0.1	< 0.1		2.17	0.006	< 0.01	< 0.02	0.34	< 0.02	0.03	0.05	5.4	< 0.5
WC-15	0.016	< 0.1	< 0.1	< 0.1		25.8	0.175	< 0.01	< 0.02	0.46	0.19	< 0.02	0.12	5.6	< 0.5
WC-16	0.005	< 0.1	< 0.1	< 0.1		0.22	0.04	< 0.01	< 0.02	0.27	< 0.02	< 0.02	0.06	5.1	< 0.5
WC-17	0.017	< 0.1	< 0.1	< 0.1		2.75	0.003	< 0.01	< 0.02	0.51	< 0.02	< 0.02	< 0.02	5.6	< 0.5
WC-19	0.021	< 0.1	< 0.1	< 0.1		36.9	0.011	< 0.01	< 0.02	0.73	0.06	< 0.02	0.07	5.8	< 0.5
WC-20	0.017	< 0.1	< 0.1	< 0.1	0.4	0.42	0.006	< 0.01	< 0.02	0.7	< 0.02	< 0.02	< 0.02	5.7	< 0.5
WC-23	0.011	< 0.1	< 0.1	< 0.1		1.26	0.034	< 0.01	< 0.02	0.22	< 0.02	< 0.02	0.18	5.4	< 0.5
WC-24	0.016	< 0.1	< 0.1	< 0.1		30.7	0.007	< 0.01	< 0.02	0.47	0.04	< 0.02	0.08	7.2	< 0.5
CMI-S1	0.007	< 0.1	< 0.1	< 0.1	0.2	0.25	< 0.002	< 0.01	< 0.02	0.31	< 0.02	< 0.02	< 0.02	5.7	< 0.5
CMI-S2	0.009	< 0.1	< 0.1	< 0.1		1.69	0.006	< 0.01	< 0.02	0.23	< 0.02	< 0.02	0.02	5.6	< 0.5
CMI-S3	0.007	< 0.1	< 0.1	< 0.1		28	0.006	< 0.01	< 0.02	0.5	< 0.02	< 0.02	0.05	5.9	< 0.5
CMI-S5	0.009	< 0.1	< 0.1	< 0.1	0.2	0.33	< 0.002	< 0.01	< 0.02	0.43	< 0.02	< 0.02	0.09	5.9	< 0.5
CMI-S6	0.021	< 0.1	< 0.1	< 0.1		4.13	0.01	< 0.01	< 0.02	0.79	< 0.02	< 0.02	0.03	5.4	< 0.5
CMI-S7	0.016	< 0.1	< 0.1	< 0.1		30.5	0.008	< 0.01	< 0.02	0.46	0.03	< 0.02	0.03	6	< 0.5
CMI-S8	0.011	< 0.1	< 0.1	< 0.1	0.2	0.27	< 0.002	< 0.01	< 0.02	0.4	< 0.02	< 0.02	0.05	5.5	< 0.5
CMI-S9	0.018	< 0.1	< 0.1	< 0.1		3.53	0.006	< 0.01	< 0.02	0.58	0.02	< 0.02	0.15	6	< 0.5
CMI-S10	0.021	< 0.1	< 0.1	< 0.1		15	0.004	< 0.01	< 0.02	0.19	< 0.02	0.03	0.07	5.4	< 0.5
CMI-S11	0.007	< 0.1	< 0.1	< 0.1	0.2	0.32	0.072	< 0.01	< 0.02	0.45	< 0.02	< 0.02	0.03	5.4	< 0.5
CMI-S12	0.025	< 0.1	< 0.1	< 0.1		5.62	0.009	< 0.01	< 0.02	1.05	0.05	0.03	0.06	5.8	< 0.5
CMI-S13	0.003	< 0.1	< 0.1	< 0.1		10.8	< 0.002	< 0.01	< 0.02	0.13	< 0.02	< 0.02	0.29	5.1	< 0.5
CMI-S14	0.012	< 0.1	< 0.1	< 0.1	0.2	0.24	0.003	< 0.01	< 0.02	0.49	< 0.02	< 0.02	0.08	4.9	< 0.5
CMI-S17	0.012	< 0.1	< 0.1	< 0.1		2.27	0.004	< 0.01	< 0.02	0.47	< 0.02	< 0.02	0.07	5.1	< 0.5
CMI-S18	0.02	< 0.1	< 0.1	< 0.1		32.6	0.011	< 0.01	< 0.02	0.75	0.03	< 0.02	0.05	4.7	< 0.5
FC-S16	0.012	< 0.1	< 0.1	< 0.1	0.2	0.28	0.002	< 0.01	< 0.02	0.41	< 0.02	< 0.02	0.04	5.7	< 0.5
FIB-01	0.027	< 0.1	< 0.1	< 0.1		3.58	0.005	< 0.01	< 0.02	0.68	0.03	< 0.02	0.41	5.7	< 0.5
FIB-02	0.02	< 0.1	< 0.1	< 0.1		25.7	0.004	< 0.01	< 0.02	0.37	0.02	< 0.02	0.3	6	< 0.5
FIB-03	0.006	< 0.1	< 0.1	< 0.1	0.2	0.29	< 0.002	< 0.01	< 0.02	0.39	< 0.02	< 0.02	0.22	6.1	< 0.5
SIL8-01	0.018	< 0.1	< 0.1	< 0.1		3.19	0.009	< 0.01	< 0.02	0.71	< 0.02	< 0.02	< 0.02	6.2	< 0.5
SIL8-18	0.018	< 0.1	< 0.1	< 0.1		40	0.01	< 0.01	< 0.02	0.73	0.07	< 0.02	0.03	5.2	< 0.5
GFNW-10	0.016	< 0.1	< 0.1	< 0.1	0.4	0.49	0.02	< 0.01	< 0.02	0.94	0.05	< 0.02	0.02	5	< 0.5
GFNW-11	0.018	< 0.1	< 0.1	< 0.1		4.76	0.008	< 0.01	< 0.02	0.88	0.02	< 0.02	0.1	5.3	< 0.5
GFNW-12	0.012	< 0.1	< 0.1	< 0.1		23.1	0.015	< 0.01	< 0.02	0.35	0.04	< 0.02	0.15	5.3	< 0.5
GFNW-13	0.014	< 0.1	< 0.1	< 0.1	0.2	0.35	0.016	< 0.01	< 0.02	0.41	< 0.02	< 0.02	0.11	5.2	< 0.5
GFNW-14	0.018	< 0.1	< 0.1	< 0.1		3.76	0.01	< 0.01	< 0.02	0.74	0.05	< 0.02	0.17	5.1	< 0.5

	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Hf	Ta	W	Re	Au	Tl	Pb	Bi	Th	U
Analyte Symbol	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm
Unit Symbol	0.01	0.02	0.1	0.1	0.1	0.1	0.1	0.1	0.05	0.1	0.001	0.5	0.02	0.01	0.02	0.1	0.1
Detection Limit	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS
Analysis Method	6.72	3.07	0.7	< 0.1	0.2	1	0.1	0.8	< 0.05	2.8	0.001	1.7	< 0.02	2.62	< 0.02	16.5	0.7
GF-4	0.29	0.12	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	6.7	0.001	< 0.5	< 0.02	0.52	< 0.02	0.3	0.2
GF-5	0.23	0.11	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	< 0.001	< 0.5	< 0.02	0.39	< 0.02	0.1	0.1
GF-6	2.97	1.33	0.3	< 0.1	< 0.1	0.5	< 0.1	0.4	< 0.05	2.4	0.001	< 0.5	< 0.02	2.35	< 0.02	6.3	0.4
GF-7	0.21	0.08	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	3.2	< 0.001	< 0.5	< 0.02	0.41	< 0.02	0.1	0.2
GF-8	0.34	0.14	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.9	< 0.001	< 0.5	< 0.02	0.94	< 0.02	0.1	< 0.1
GF-9	1.73	0.78	0.2	< 0.1	< 0.1	0.3	< 0.1	0.2	< 0.05	1.8	< 0.001	< 0.5	< 0.02	0.92	< 0.02	3.2	0.8
GF-10	0.19	0.08	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	3.6	0.001	< 0.5	< 0.02	0.43	< 0.02	< 0.1	< 0.1
GF-11	0.12	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	< 0.001	< 0.5	< 0.02	0.14	< 0.02	< 0.1	< 0.1
GF-12	1	0.45	0.1	< 0.1	< 0.1	0.2	< 0.1	0.2	< 0.05	1.8	< 0.001	< 0.5	< 0.02	1.31	0.02	2	0.1
GF-13	0.24	0.11	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	4.1	0.002	< 0.5	< 0.02	0.99	< 0.02	0.1	0.1
GF-14	0.41	0.17	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.1	< 0.001	< 0.5	< 0.02	1.11	< 0.02	< 0.1	0.1
GF-15	1	0.44	0.1	< 0.1	< 0.1	0.1	< 0.1	0.2	< 0.05	1.6	0.001	< 0.5	< 0.02	0.91	< 0.02	1.7	< 0.1
GF-16	0.41	0.17	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	4.5	< 0.001	< 0.5	< 0.02	0.62	< 0.02	< 0.1	< 0.1
GF-17	0.11	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.3	< 0.001	< 0.5	< 0.02	0.2	< 0.02	< 0.1	< 0.1
GF-18	0.73	0.34	< 0.1	< 0.1	< 0.1	0.1	< 0.1	0.1	< 0.05	1.6	< 0.001	< 0.5	< 0.02	1.05	0.03	1.4	1
GF-19	1.23	0.59	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.9	0.001	< 0.5	< 0.02	13.1	< 0.02	0.2	< 0.1
GF-21	0.13	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	3.8	< 0.001	< 0.5	< 0.02	0.4	< 0.02	< 0.1	< 0.1
GF-22	0.17	0.08	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.6	< 0.001	< 0.5	< 0.02	0.66	< 0.02	< 0.1	< 0.1
GF-23	0.56	0.29	0.2	< 0.1	0.1	0.7	0.1	0.1	< 0.05	2.1	0.001	< 0.5	< 0.02	0.98	< 0.02	1.4	1
GF-24	0.22	0.11	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	4.1	0.002	< 0.5	< 0.02	1.18	< 0.02	0.1	0.6
GF-25	0.11	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	< 0.001	< 0.5	< 0.02	1.06	0.03	< 0.1	2.7
GF-26	0.46	0.22	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.65	0.03	0.7	0.3
GF-27	0.09	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.6	0.001	< 0.5	< 0.02	0.35	< 0.02	< 0.1	0.2
GF-28	0.05	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.05	1.1	< 0.001	< 0.5	< 0.02	0.34	0.02	< 0.1	0.4
GF-29	0.35	0.15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	1.48	< 0.02	0.6	0.8
GF-30	272	134	50.5	< 0.1	3.6	1.1	< 0.1	< 0.1	< 0.05	< 0.1	0.003	< 0.5	< 0.02	14.2	0.04	120	11.7
GF-31	0.44	0.26	0.2	< 0.1	0.1	0.9	0.1	0.3	< 0.05	1.4	< 0.001	< 0.5	< 0.02	0.89	0.07	2	1.2
GF-32	0.58	0.26	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	< 0.001	< 0.5	< 0.02	1.45	< 0.02	1.1	0.9
GF-33	1.39	0.71	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.1	0.001	< 0.5	< 0.02	0.65	< 0.02	0.7	0.7
GF-34	0.29	0.14	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	5.7	< 0.001	< 0.5	< 0.02	0.93	0.08	0.1	3
GF-35	0.34	0.16	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.66	0.09	0.7	< 0.1
GF-36	0.15	0.07	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.9	0.001	< 0.5	< 0.02	0.38	0.04	< 0.1	0.3
GF-37	0.75	0.06	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.05	1.3	< 0.001	< 0.5	< 0.02	0.75	< 0.02	0.1	0.2

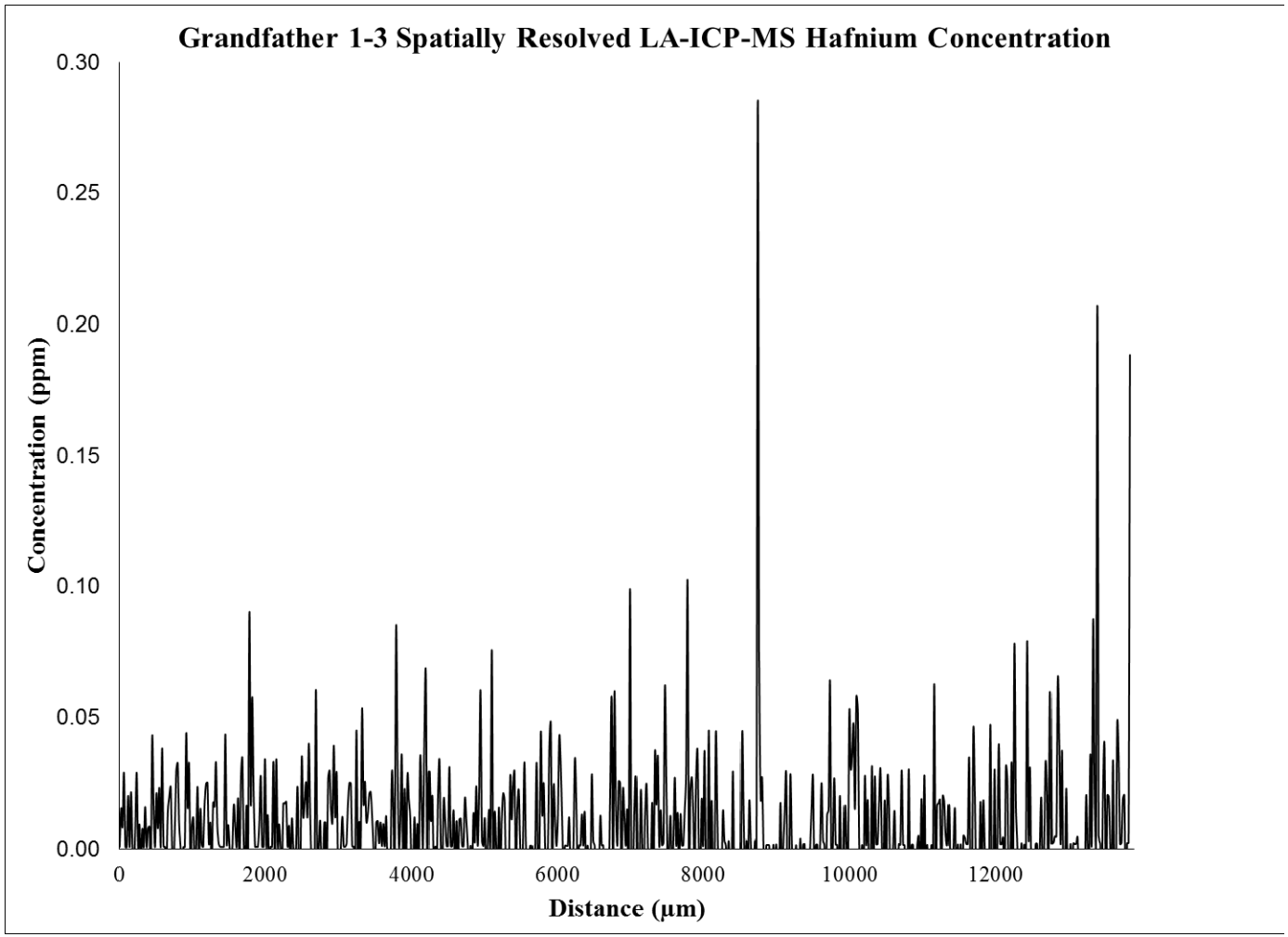
GF-38	1.02	0.19	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.6	< 0.001	< 0.5	< 0.02	0.94	< 0.02	0.6	0.3
GF-39	2.42	0.9	0.4	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.4	0.002	< 0.5	< 0.02	0.63	< 0.02	0.9	1
GF-40	0.87	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	4.4	< 0.001	< 0.5	< 0.02	2.67	0.04	< 0.1	10.3
GF-41	1.13	0.19	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2	< 0.001	< 0.5	< 0.02	1.19	< 0.02	0.5	1.2
GF-42	0.16	0.07	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	3.9	0.002	< 0.5	< 0.02	1.66	< 0.02	< 0.1	6.5
GF-43	0.14	0.07	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.67	< 0.02	< 0.1	0.1
GF-44	0.47	0.22	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.85	< 0.02	0.5	0.3
GF-45	0.22	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.8	0.002	< 0.5	< 0.02	0.73	< 0.02	< 0.1	< 0.1
GF-46	0.22	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.8	< 0.001	< 0.5	< 0.02	0.73	< 0.02	< 0.1	< 0.1
GF-47	0.37	0.17	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2	0.001	< 0.5	< 0.02	1.41	< 0.02	0.4	0.6
GF-48	0.8	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.7	0.002	< 0.5	< 0.02	0.64	0.21	< 0.1	0.4
GF-49	0.82	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.18	0.02	< 0.1	0.1
GF-50	1.65	0.41	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.7	< 0.001	< 0.5	< 0.02	14.7	< 0.02	0.1	< 0.1
GF-51	1.48	0.33	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.7	0.001	< 0.5	0.02	11.4	0.03	0.1	0.6
GF-52	0.87	0.09	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.3	< 0.001	< 0.5	< 0.02	0.6	0.03	0.2	0.2
GF-53	0.91	0.14	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.7	< 0.001	< 0.5	< 0.02	6.41	0.03	< 0.1	< 0.1
GF-54	0.72	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2	0.001	< 0.5	< 0.02	0.57	0.04	< 0.1	1.1
GF-55	0.7	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	< 0.001	< 0.5	< 0.02	0.61	< 0.02	< 0.1	< 0.1
GF-56	0.65	0.09	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.47	< 0.02	0.2	0.3
GF-57	0.6	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2	0.001	< 0.5	< 0.02	0.45	< 0.02	< 0.1	0.3
GF-58	0.77	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.9	0.001	< 0.5	< 0.02	0.42	0.15	< 0.1	< 0.1
GF-59	0.79	0.12	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.8	0.001	< 0.5	< 0.02	1.03	0.05	0.3	0.7
GF-60	0.59	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	< 0.001	< 0.5	< 0.02	0.2	< 0.02	< 0.1	< 0.1
GF-61	0.58	0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.6	< 0.001	< 0.5	< 0.02	0.32	< 0.02	< 0.1	< 0.1
GF-62	0.8	0.13	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.7	< 0.001	< 0.5	< 0.02	5	0.05	< 0.1	0.2
GF-63	0.73	0.07	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.25	< 0.02	0.2	< 0.1
GF-64	0.67	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.5	0.002	< 0.5	< 0.02	0.52	0.03	< 0.1	0.1
GF-65	0.68	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.1	0.001	< 0.5	< 0.02	0.64	0.04	< 0.1	0.7
GF-66	0.82	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.3	0.001	< 0.5	< 0.02	0.89	0.08	0.2	0.5
GF-67	0.71	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.2	0.001	< 0.5	< 0.02	0.45	< 0.02	< 0.1	0.2
SQ-01	0.82	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.9	0.001	1.5	< 0.02	0.5	0.03	< 0.1	0.4
SQ-02	1.09	0.15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.3	0.001	4.1	< 0.02	1.33	< 0.02	0.3	0.4
SQ-03	0.79	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.6	0.001	0.9	< 0.02	0.76	0.24	< 0.1	0.7
SQ-04	0.83	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	1.5	< 0.02	0.37	< 0.02	< 0.1	< 0.1
SQ-05	0.95	0.09	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.96	0.03	0.2	0.6
SQ-06	0.81	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	0.002	0.6	< 0.02	0.37	< 0.02	< 0.1	< 0.1
WC-02	0.85	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.29	< 0.02	< 0.1	< 0.1
WC-03	0.84	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.9	< 0.001	< 0.5	< 0.02	0.47	< 0.02	< 0.1	< 0.1
WC-05	0.83	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	0.27	< 0.02	< 0.1	< 0.1
WC-11	0.85	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.5	0.001	< 0.5	< 0.02	0.79	< 0.02	< 0.1	< 0.1
WC-15	0.74	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.22	< 0.02	< 0.1	< 0.1
WC-16	0.83	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	0.54	< 0.02	< 0.1	< 0.1

WC-17	0.87	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.6	0.002	< 0.5	< 0.02	0.9	< 0.02	< 0.1	< 0.1
WC-19	0.87	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.1	< 0.001	< 0.5	< 0.02	0.74	< 0.02	< 0.1	< 0.1
WC-20	0.79	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	0.2	< 0.02	< 0.1	< 0.1
WC-23	0.84	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.9	< 0.001	< 0.5	< 0.02	0.46	< 0.02	< 0.1	0.1
WC-24	0.83	0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	0.24	< 0.02	< 0.1	< 0.1
CMI-S1	0.85	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.7	< 0.001	< 0.5	< 0.02	0.22	< 0.02	< 0.1	< 0.1
CMI-S2	0.86	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	2.2	< 0.001	< 0.5	< 0.02	0.8	< 0.02	< 0.1	< 0.1
CMI-S3	0.82	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.26	< 0.02	< 0.1	< 0.1
CMI-S5	0.82	0.07	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	1.07	< 0.02	< 0.1	< 0.1
CMI-S6	0.81	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.7	0.001	< 0.5	< 0.02	0.44	< 0.02	< 0.1	< 0.1
CMI-S7	0.77	0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.43	< 0.02	< 0.1	< 0.1
CMI-S8	0.84	0.05	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.9	< 0.001	< 0.5	< 0.02	1.09	0.02	< 0.1	< 0.1
CMI-S9	0.78	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	< 0.001	< 0.5	< 0.02	0.17	< 0.02	< 0.1	0.2
CMI-S10	0.79	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.4	< 0.02	< 0.1	< 0.1
CMI-S11	0.99	0.09	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.1	< 0.001	< 0.5	< 0.02	0.73	< 0.02	< 0.1	< 0.1
CMI-S12	0.72	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.9	0.001	< 0.5	< 0.02	0.12	< 0.02	< 0.1	< 0.1
CMI-S13	0.73	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	0.87	< 0.02	< 0.1	< 0.1
CMI-S14	0.78	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	0.76	< 0.02	< 0.1	< 0.1
CMI-S17	0.8	0.08	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	0.001	< 0.5	< 0.02	1.33	< 0.02	< 0.1	< 0.1
CMI-S18	0.74	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	0.001	< 0.5	< 0.02	0.54	< 0.02	< 0.1	< 0.1
FC-S16	0.94	0.11	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	1.31	0.11	< 0.1	< 0.1
FIB-01	1.05	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.4	0.001	< 0.5	< 0.02	0.66	0.06	< 0.1	0.2
FIB-02	0.84	0.03	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	0.001	< 0.5	< 0.02	0.71	< 0.02	< 0.1	< 0.1
FIB-03	0.86	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.8	< 0.001	< 0.5	< 0.02	1.04	< 0.02	< 0.1	< 0.1
GFNW-10	0.85	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.62	< 0.02	< 0.1	< 0.1
GFNW-11	0.89	0.08	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.2	0.001	< 0.5	< 0.02	0.63	0.12	< 0.1	1.9
GFNW-12	0.81	0.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1	< 0.001	< 0.5	< 0.02	0.61	3.07	< 0.1	0.9
GFNW-13	0.89	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	0.9	< 0.001	< 0.5	< 0.02	0.73	0.09	< 0.1	< 0.1
GFNW-14	0.84	0.06	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.05	1.1	0.001	< 0.5	< 0.02	0.52	0.02	< 0.1	< 0.1

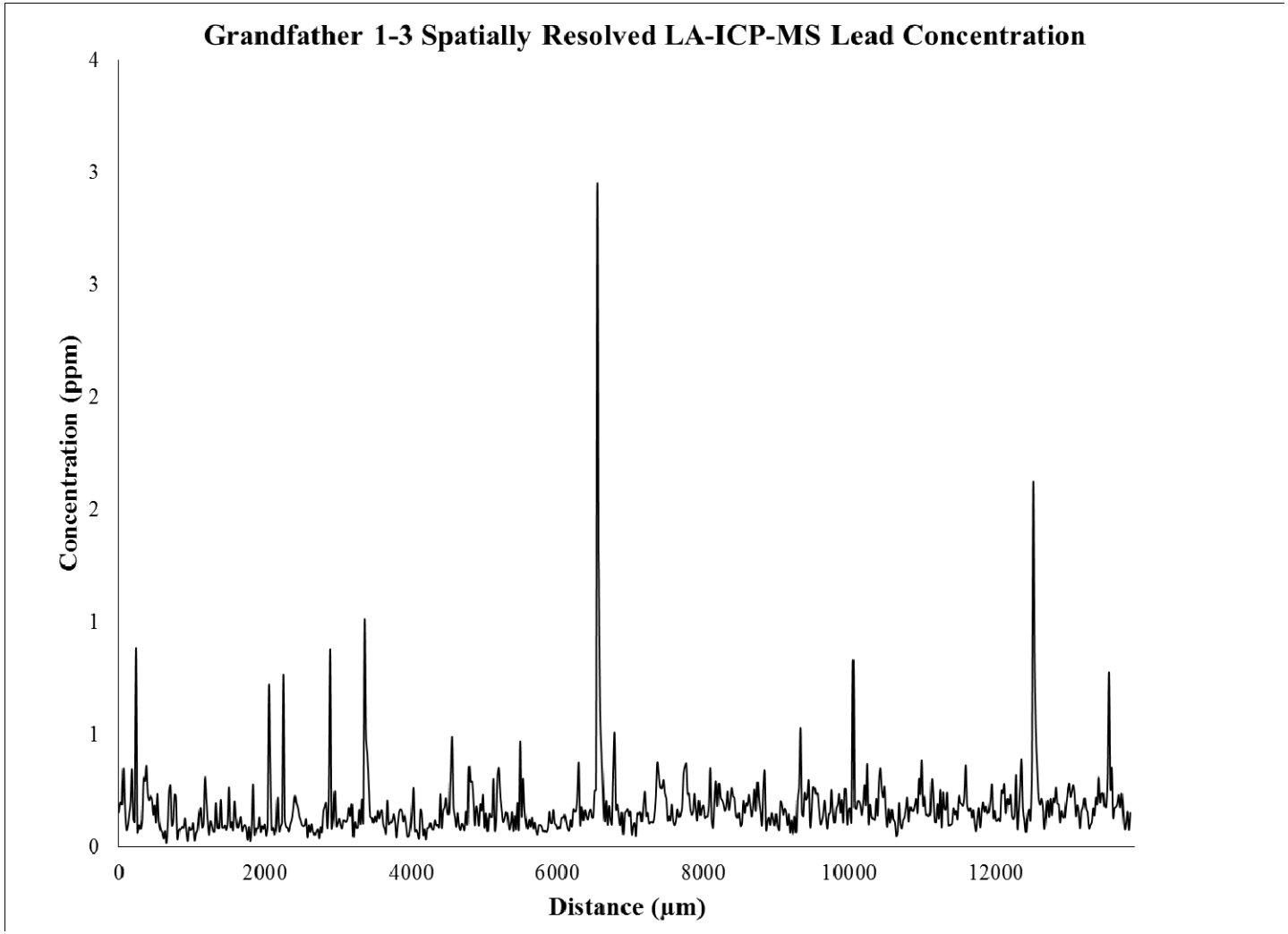
Appendix 6: LA-ICP-MS trace element plots



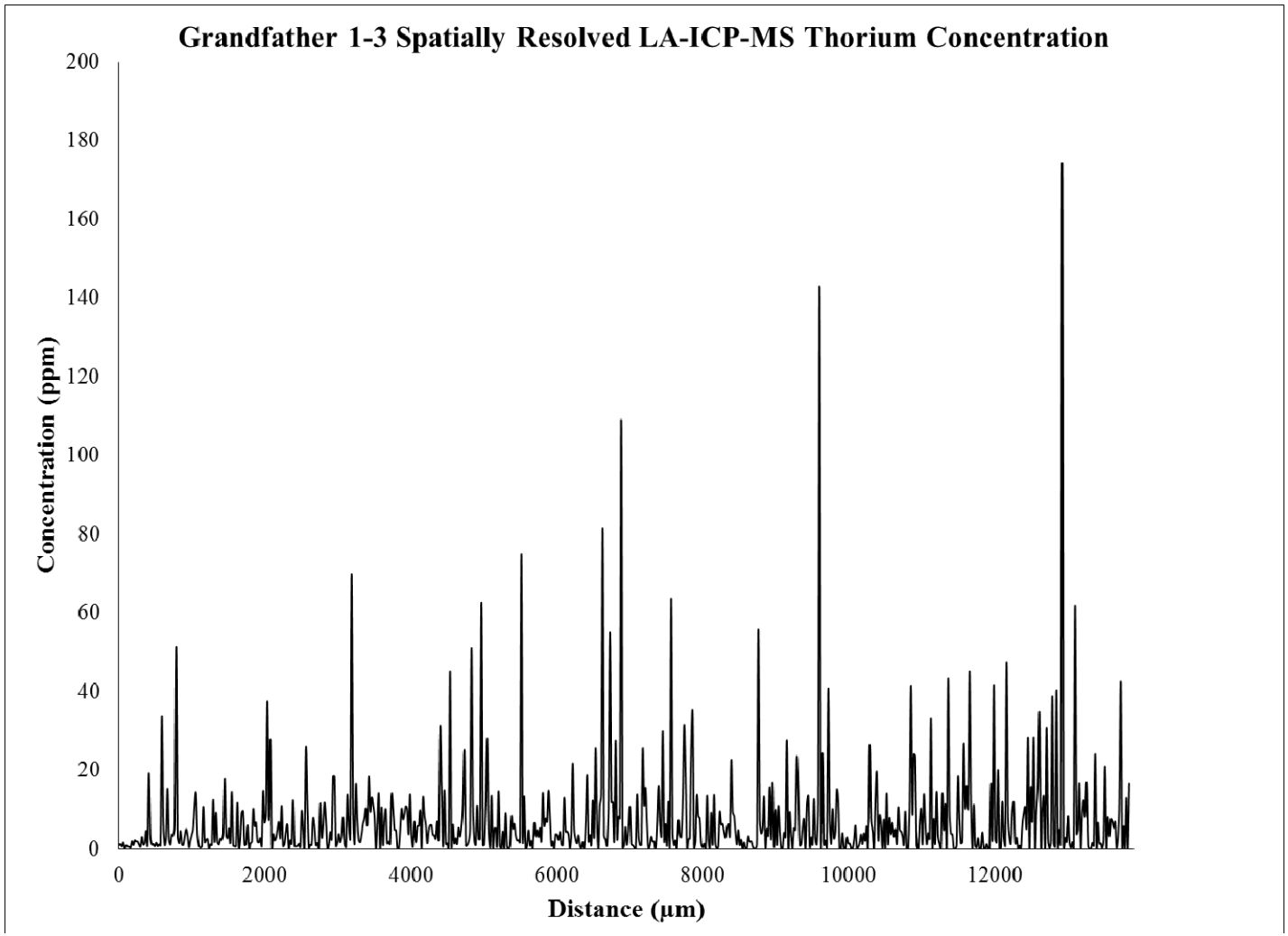
Nb concentration (ppm) plotted against distance in µm over the course of a line scan of GF (Grandfather) 1-3



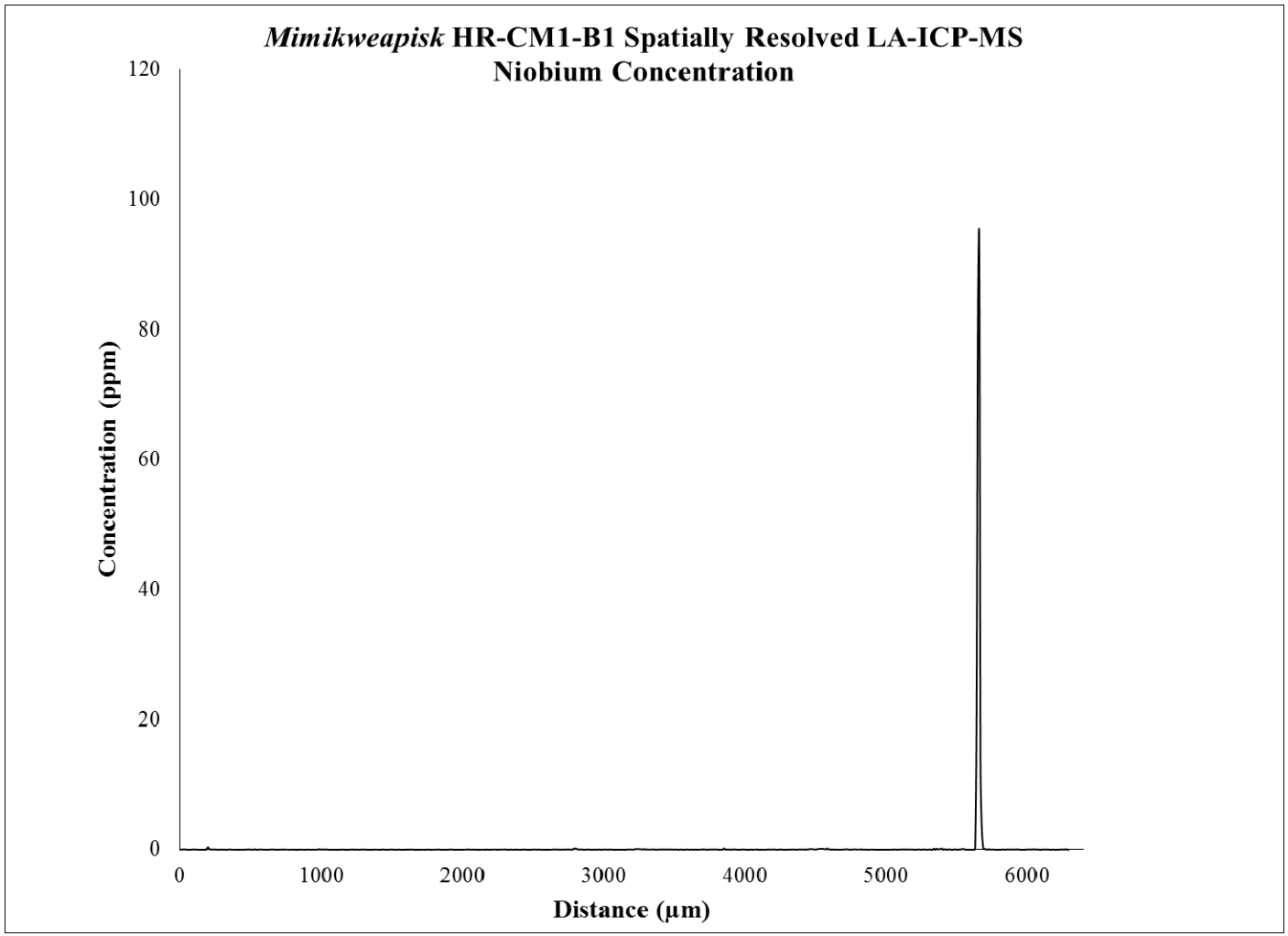
Hf concentration (ppm) plotted against distance in µm over the course of a line scan of GF (Grandfather) 1-3



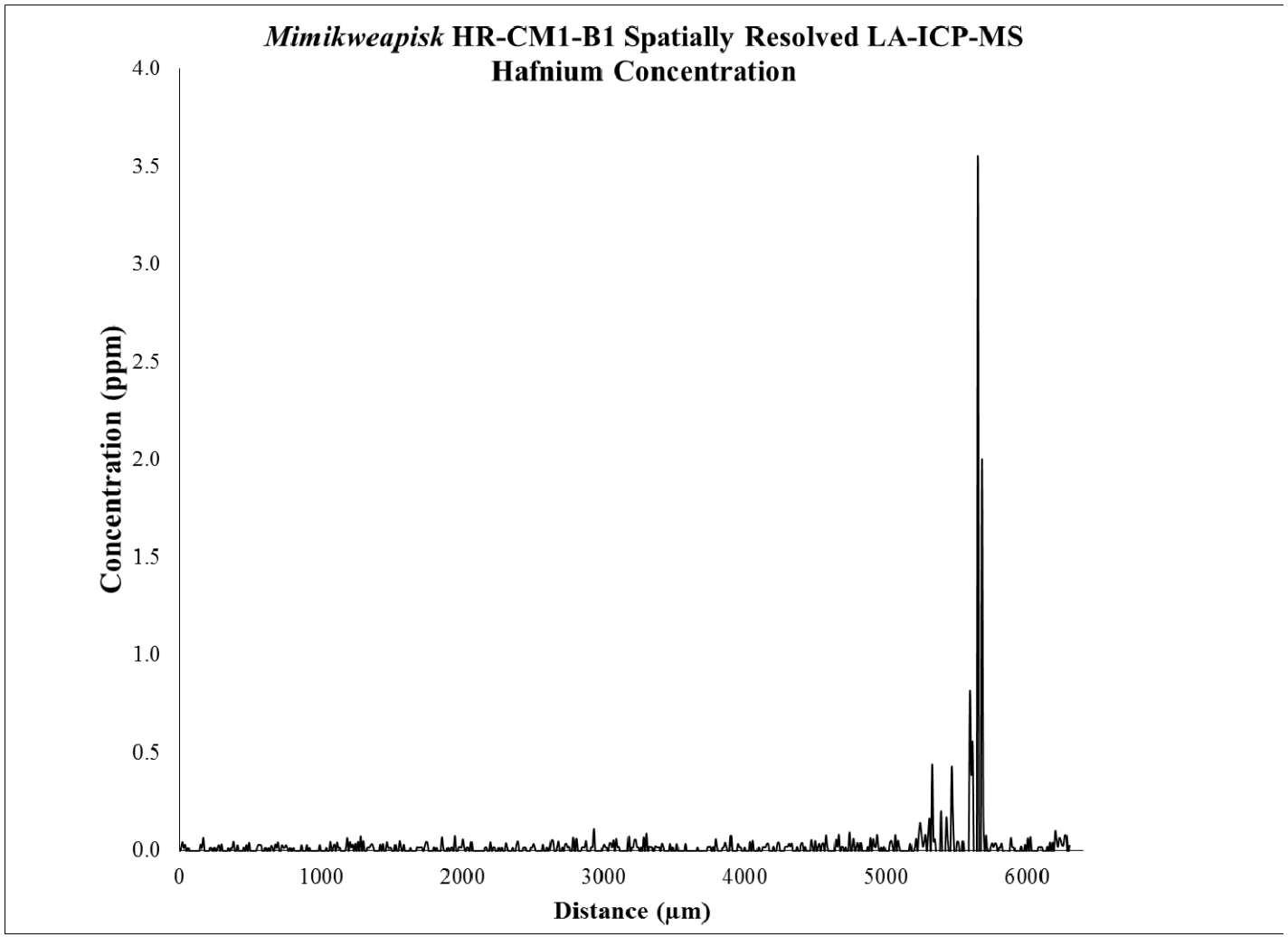
Pb concentration (ppm) plotted against distance in µm over the course of a line scan of GF (Grandfather) 1-3



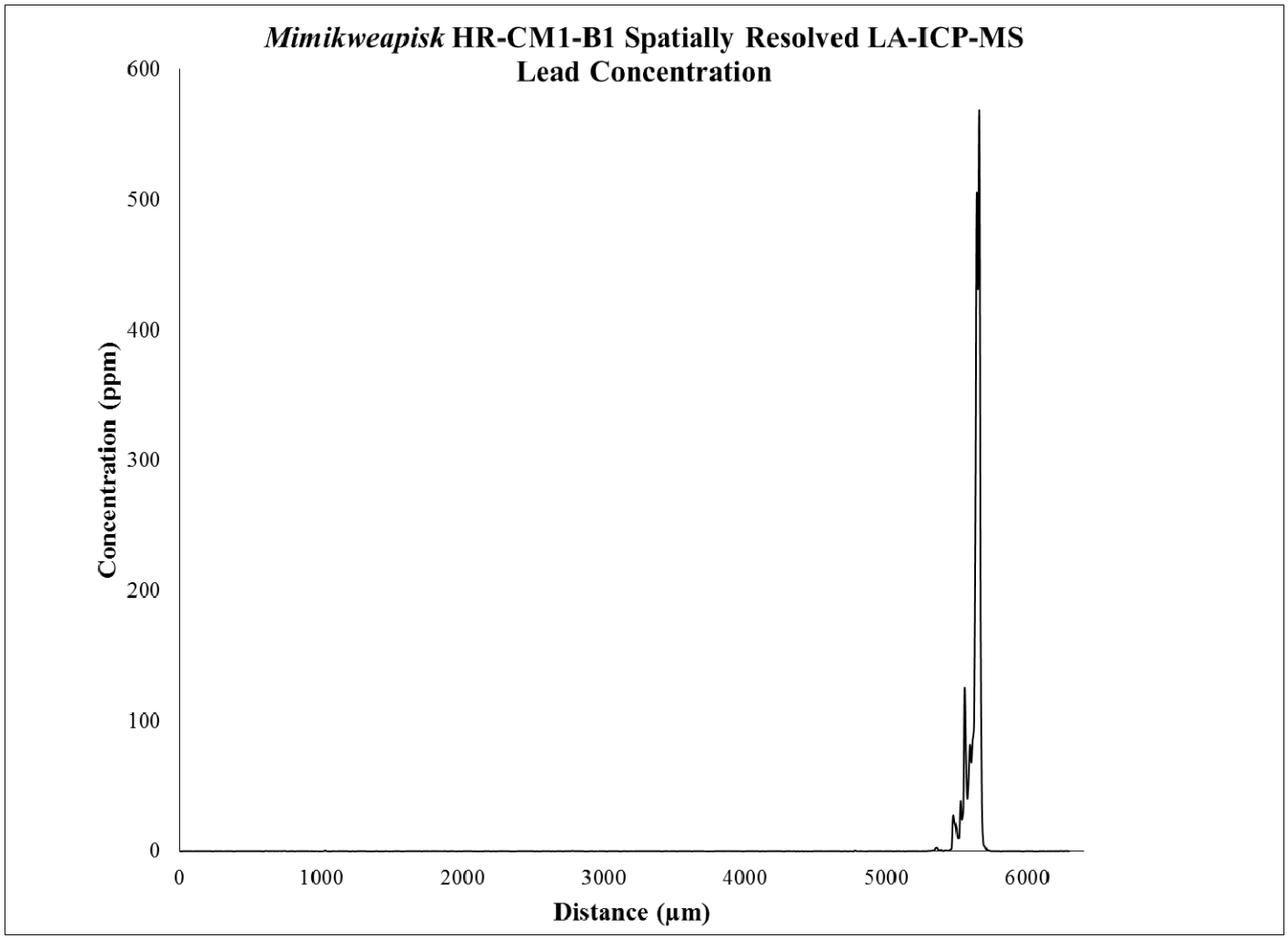
Th concentration (ppm) plotted against distance in µm over the course of a line scan of GF (Grandfather) 1-3



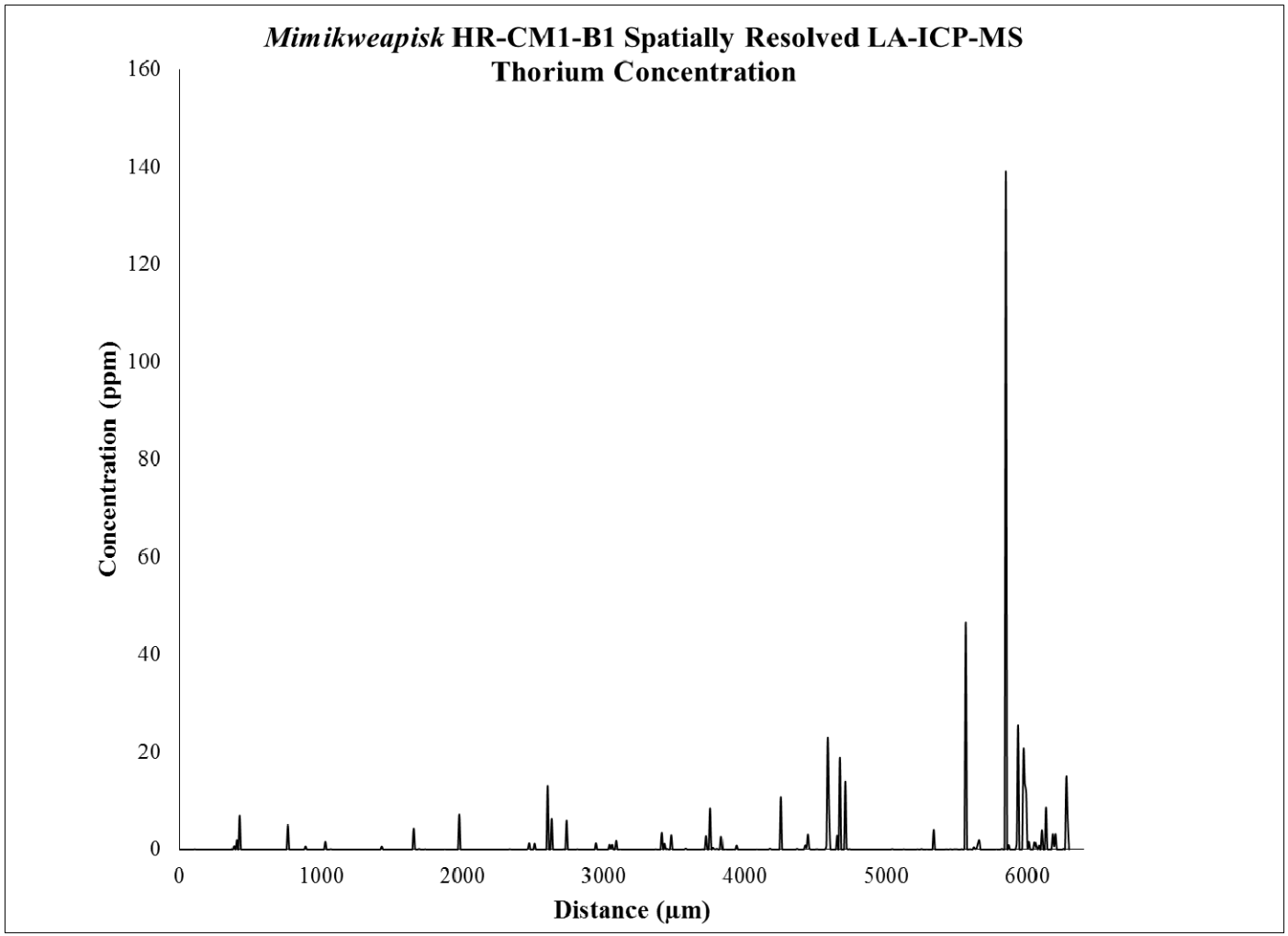
Nb concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM1-B1



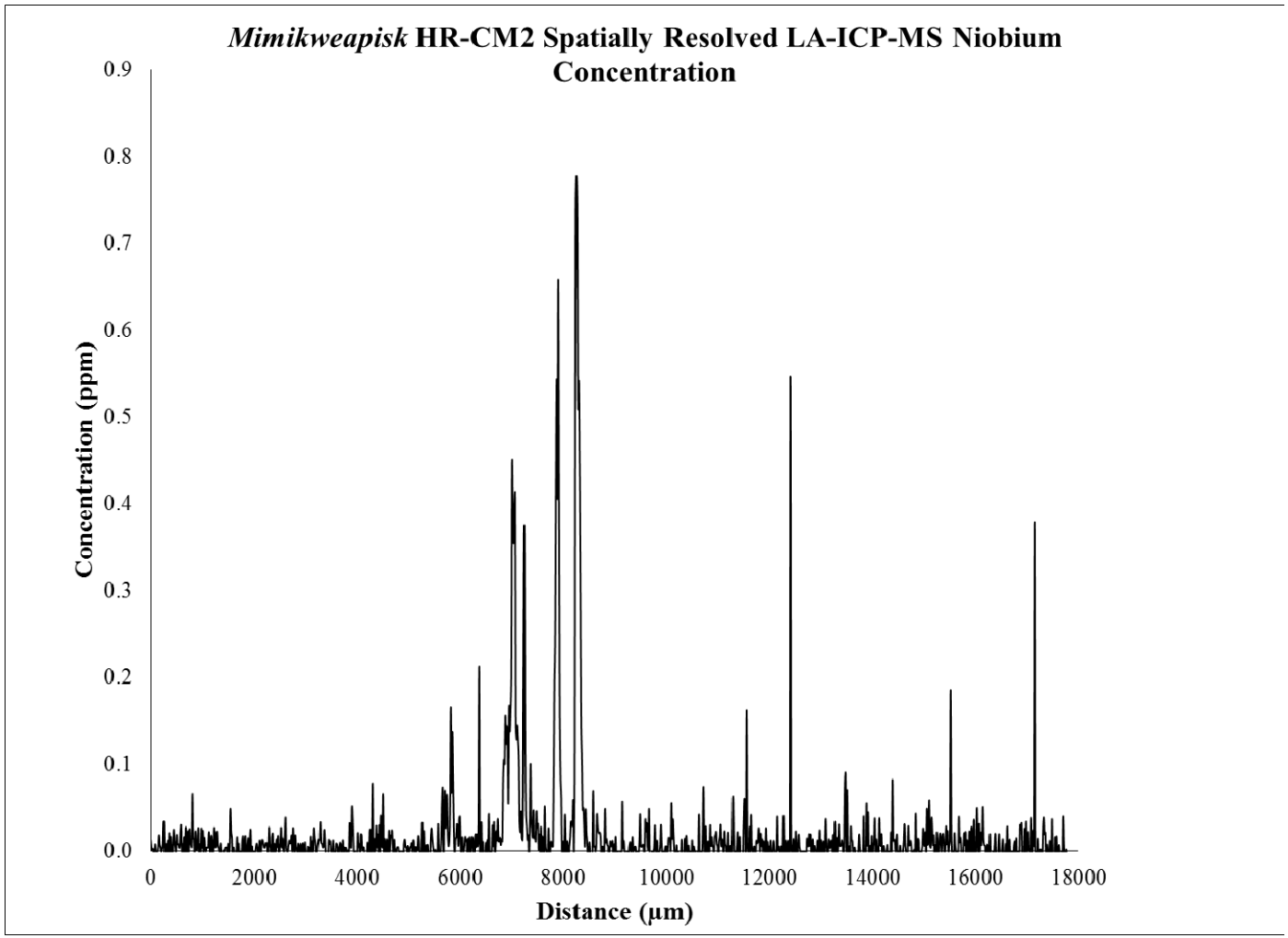
Hf concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM1-B1



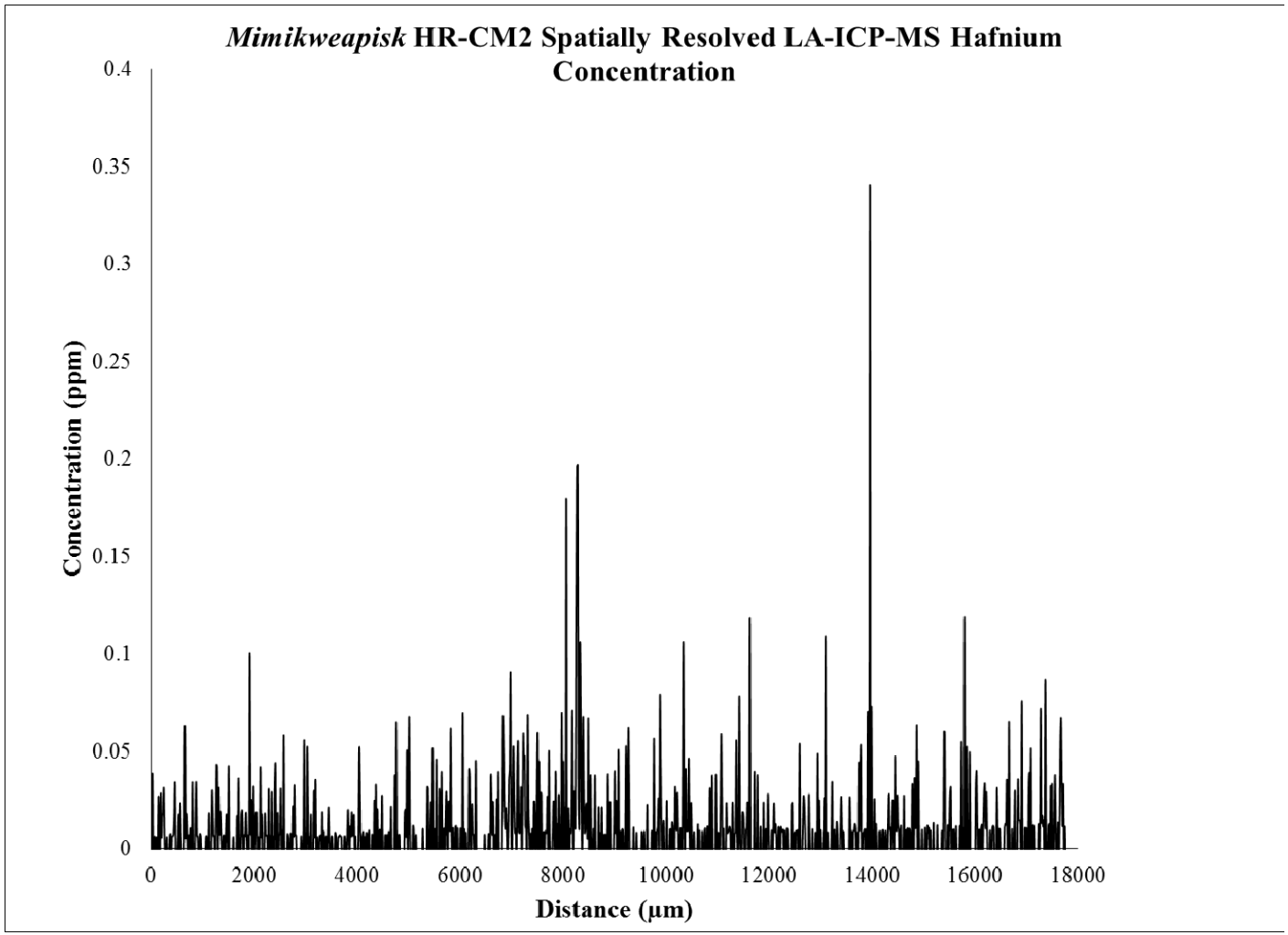
Pb concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM1-B1



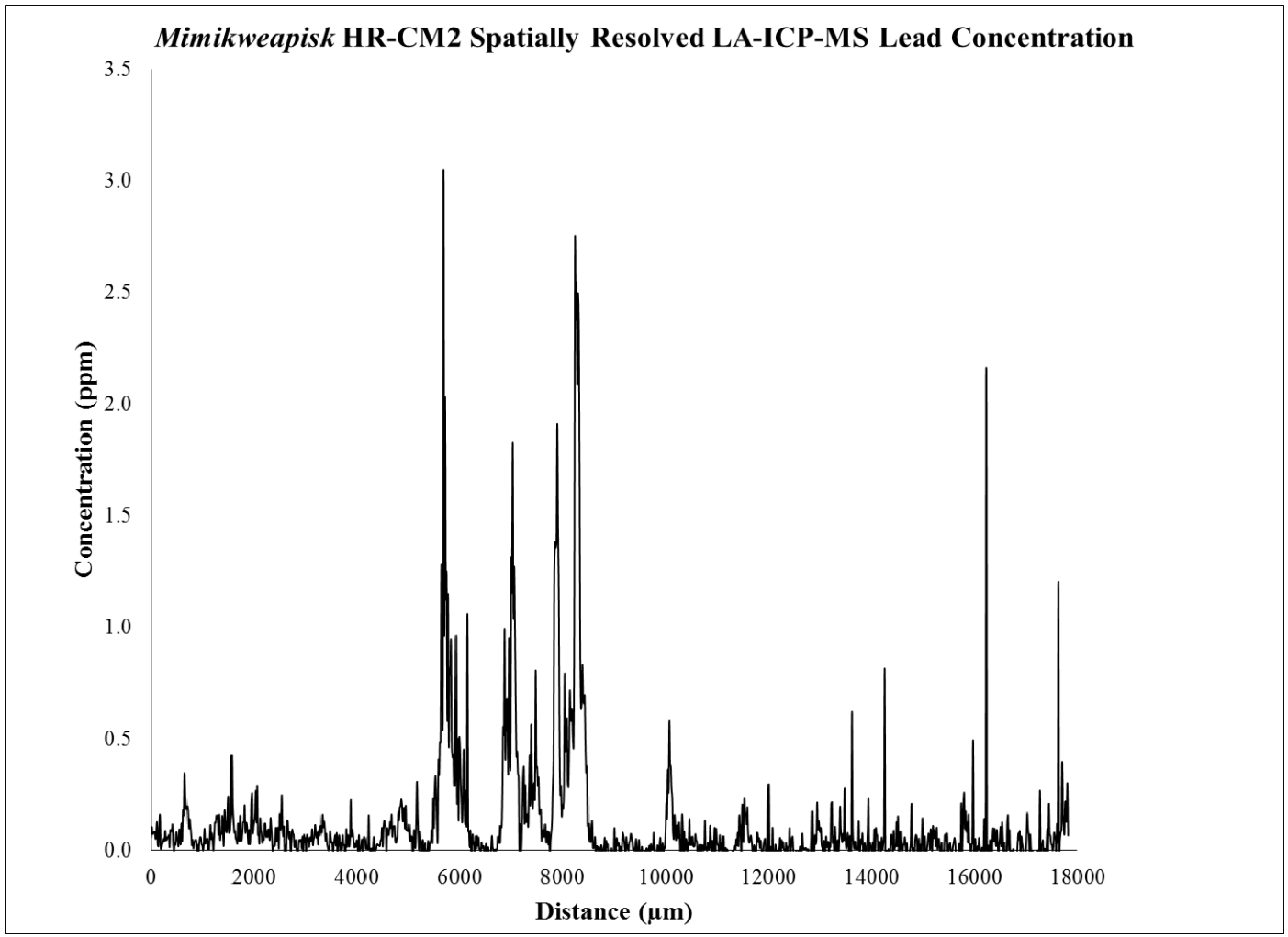
Th concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM1-B1



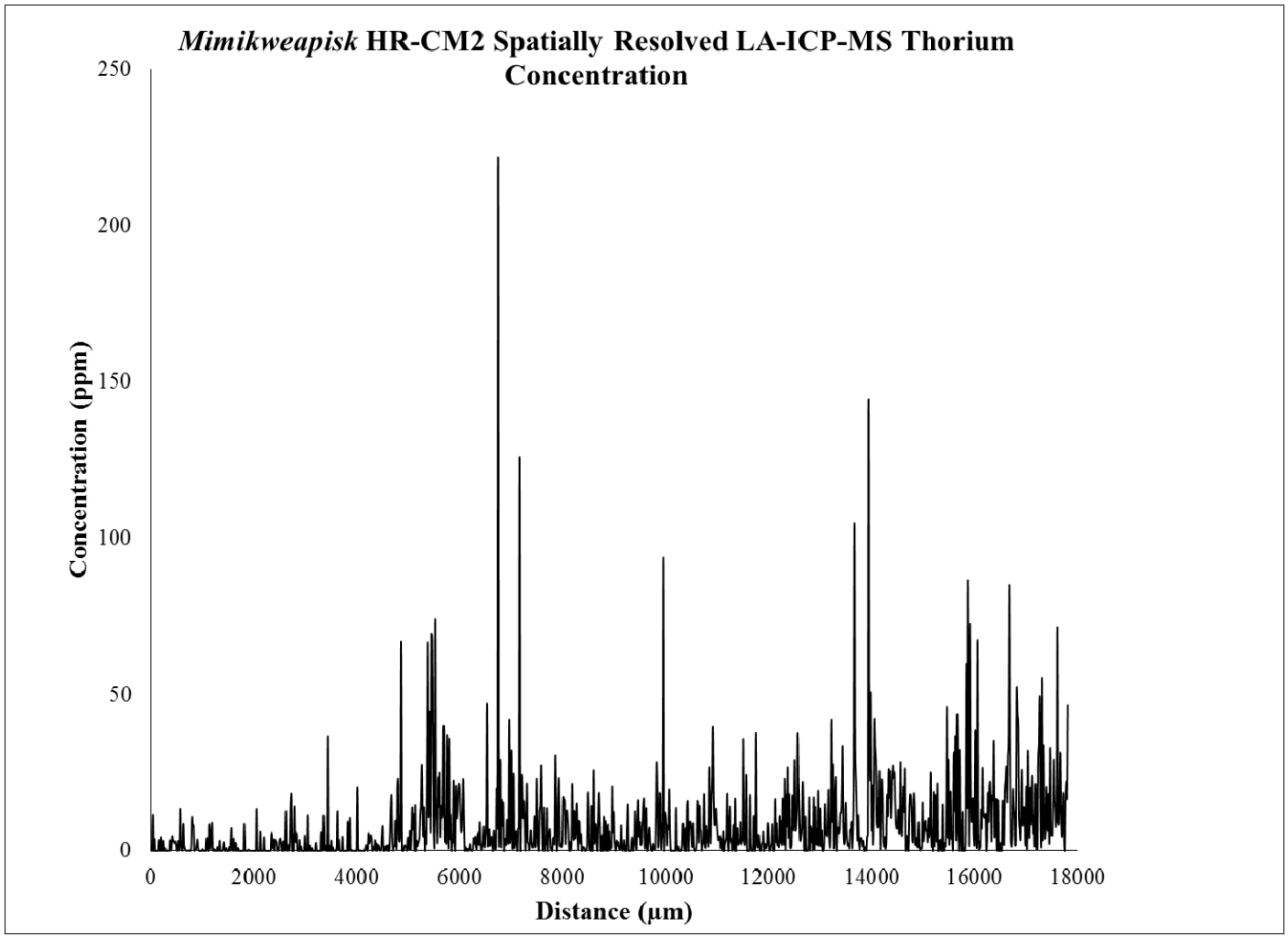
Nb concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM2



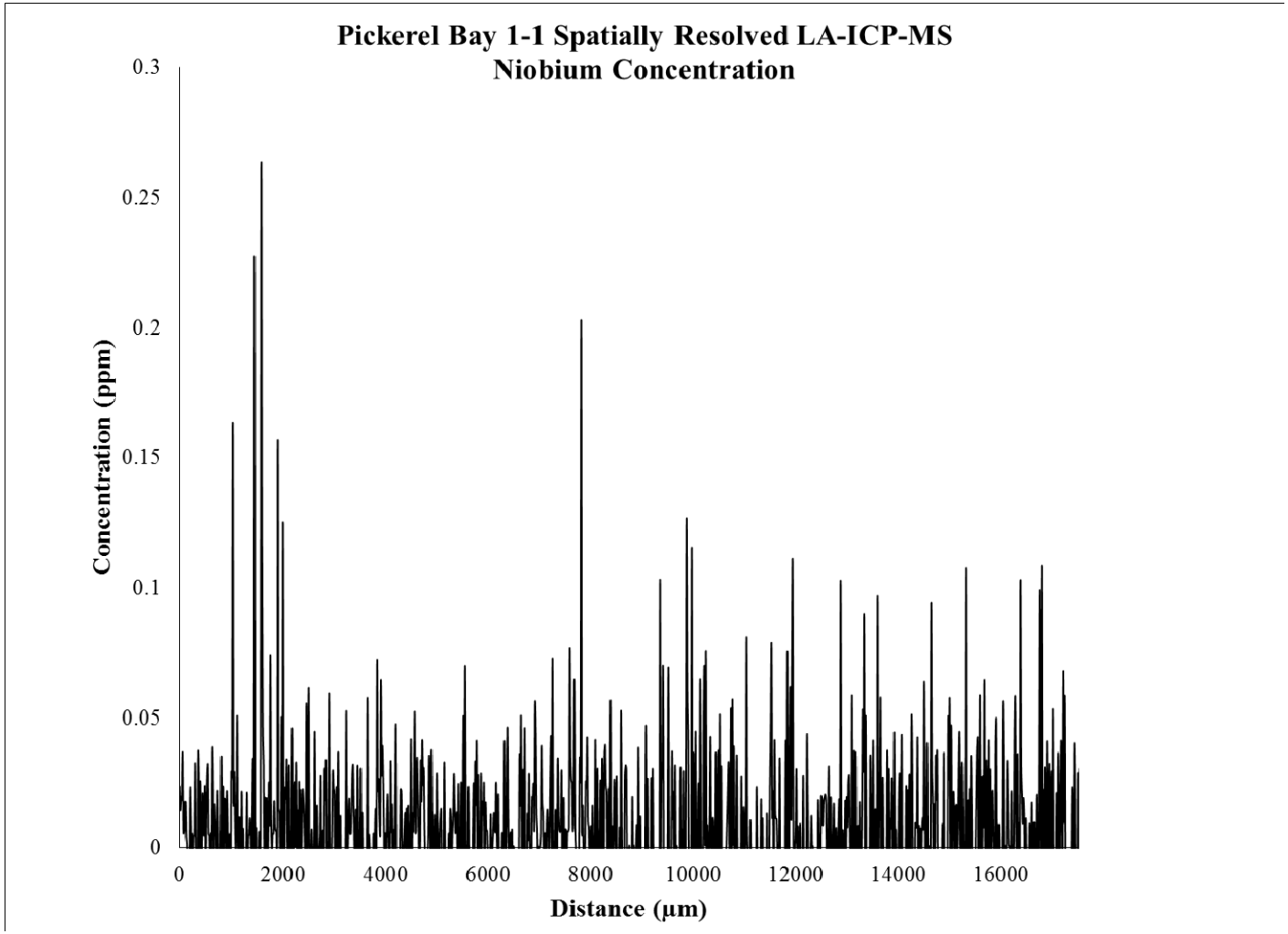
Nb concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM2



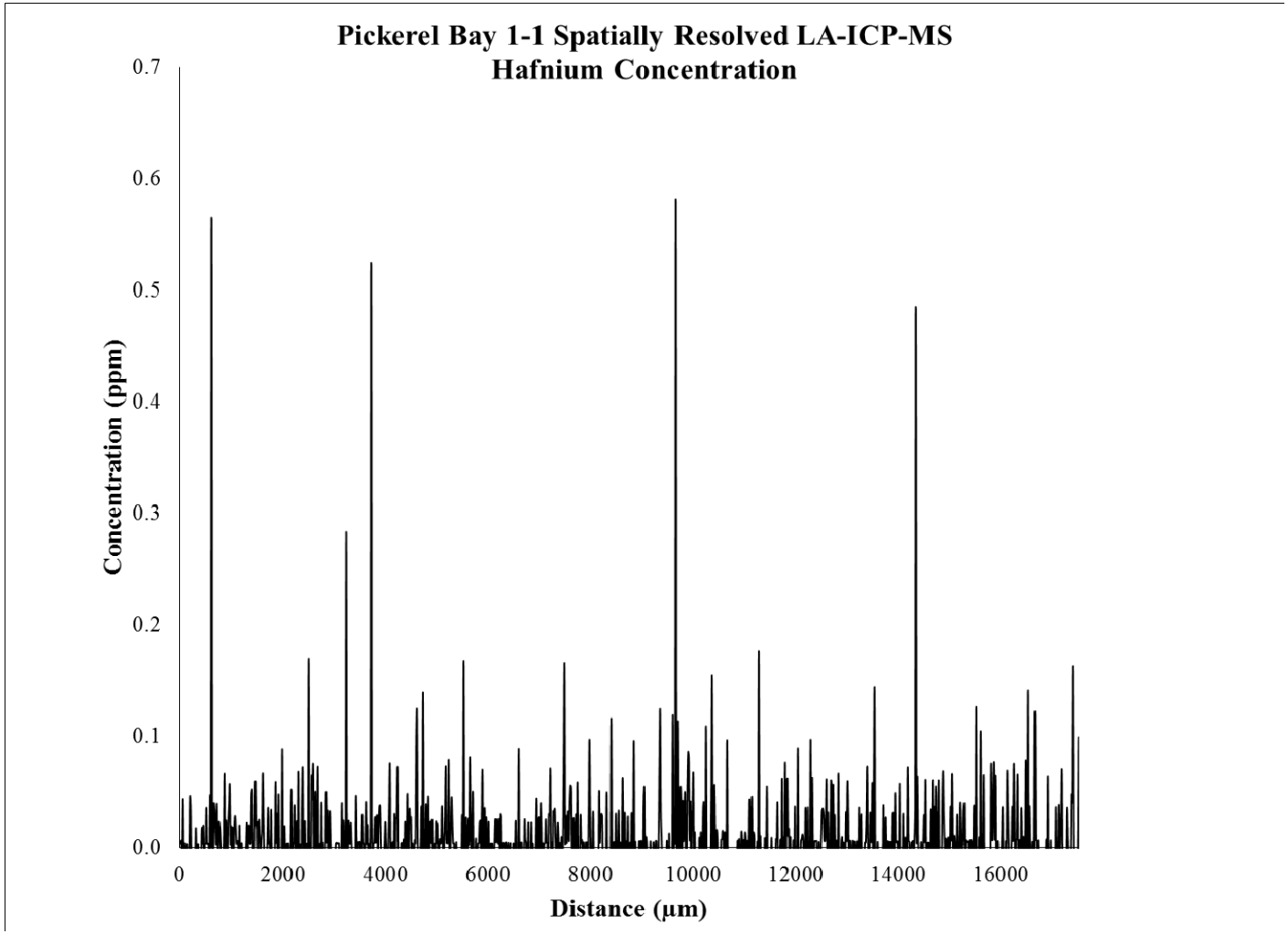
Pb concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM2



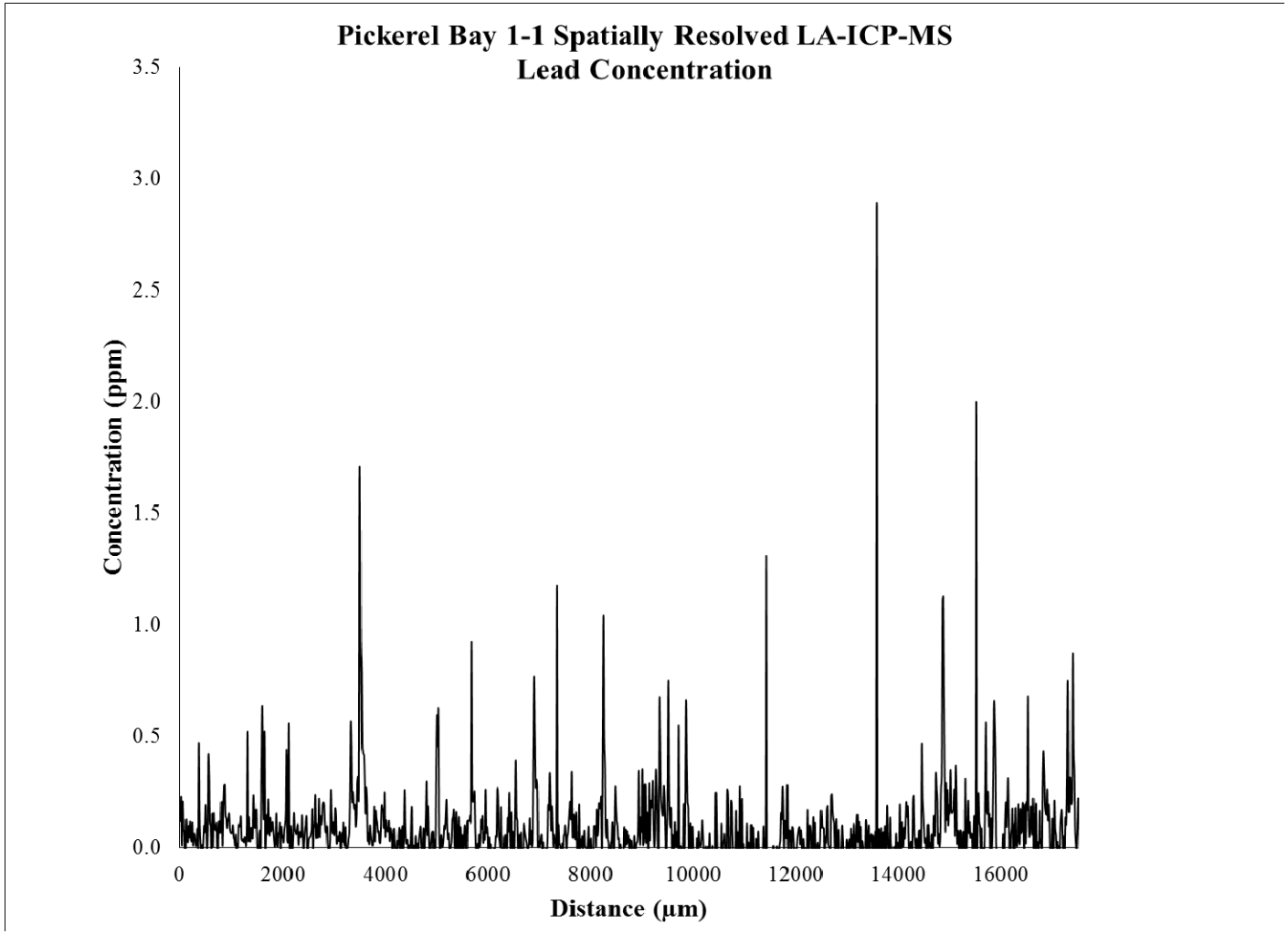
Th concentration (ppm) plotted against distance in µm over the course of a line scan of *Mimikweapisk* sample HR-CM2



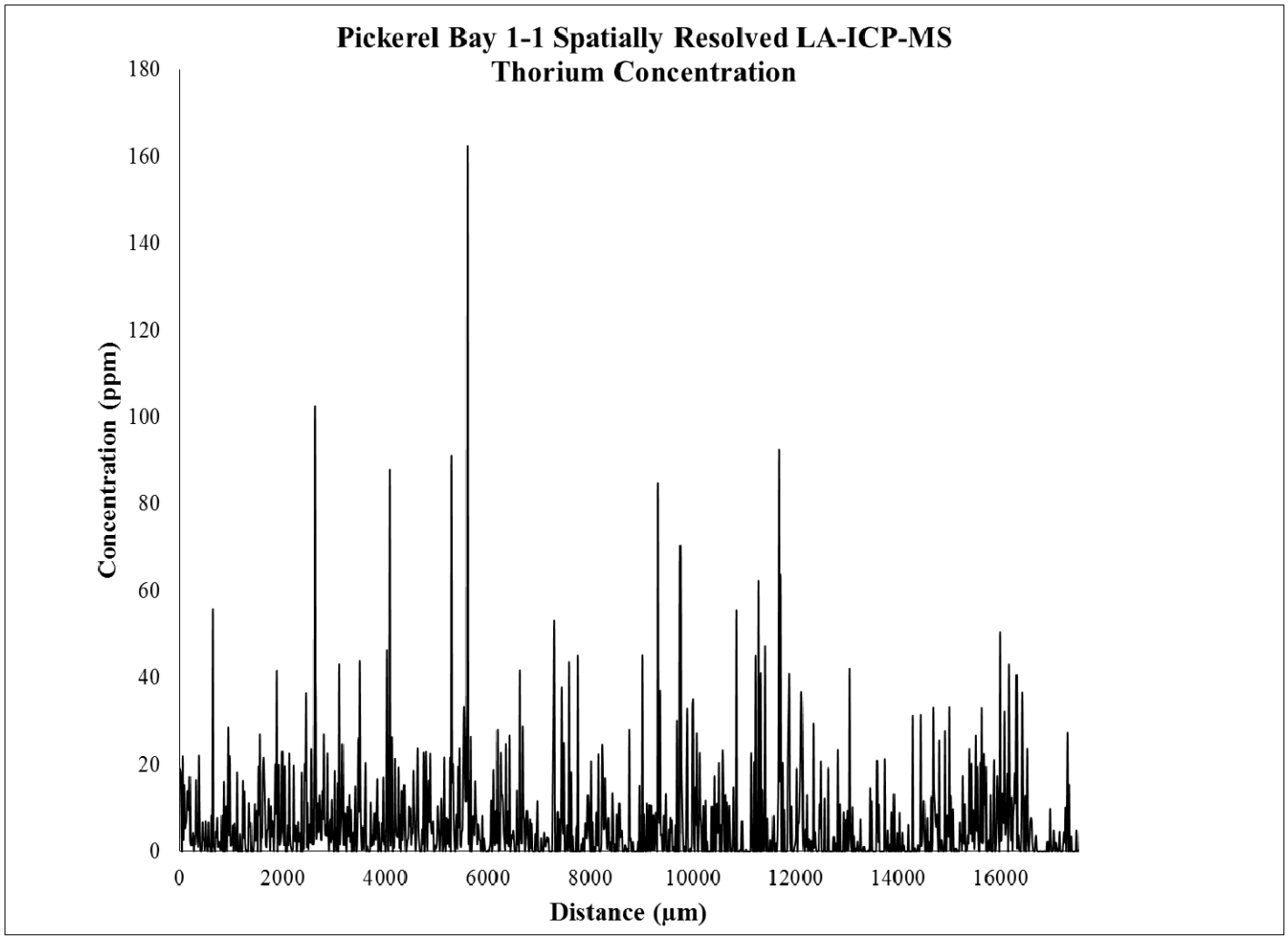
Nb concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW1-1



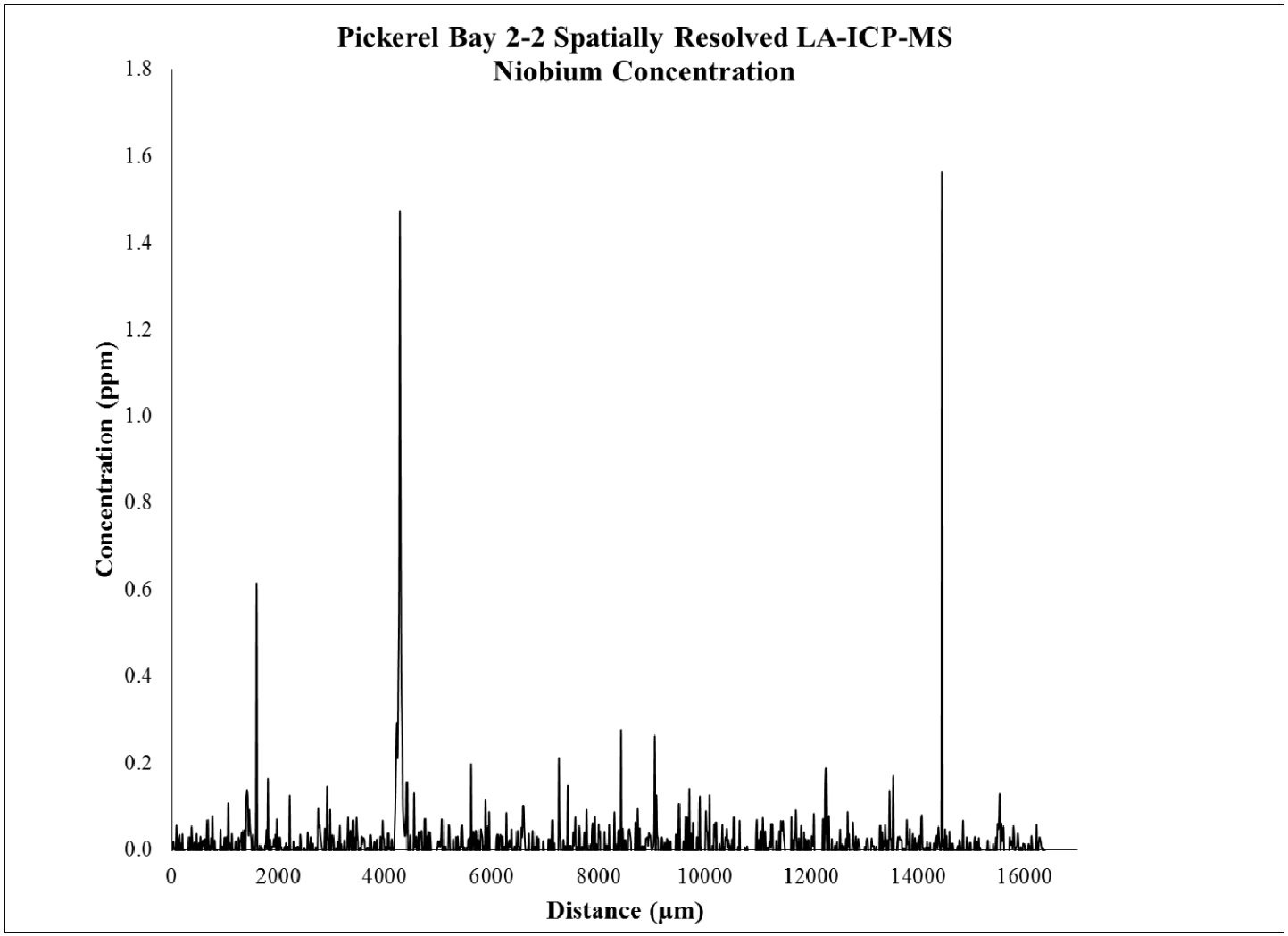
Hf concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW1-1



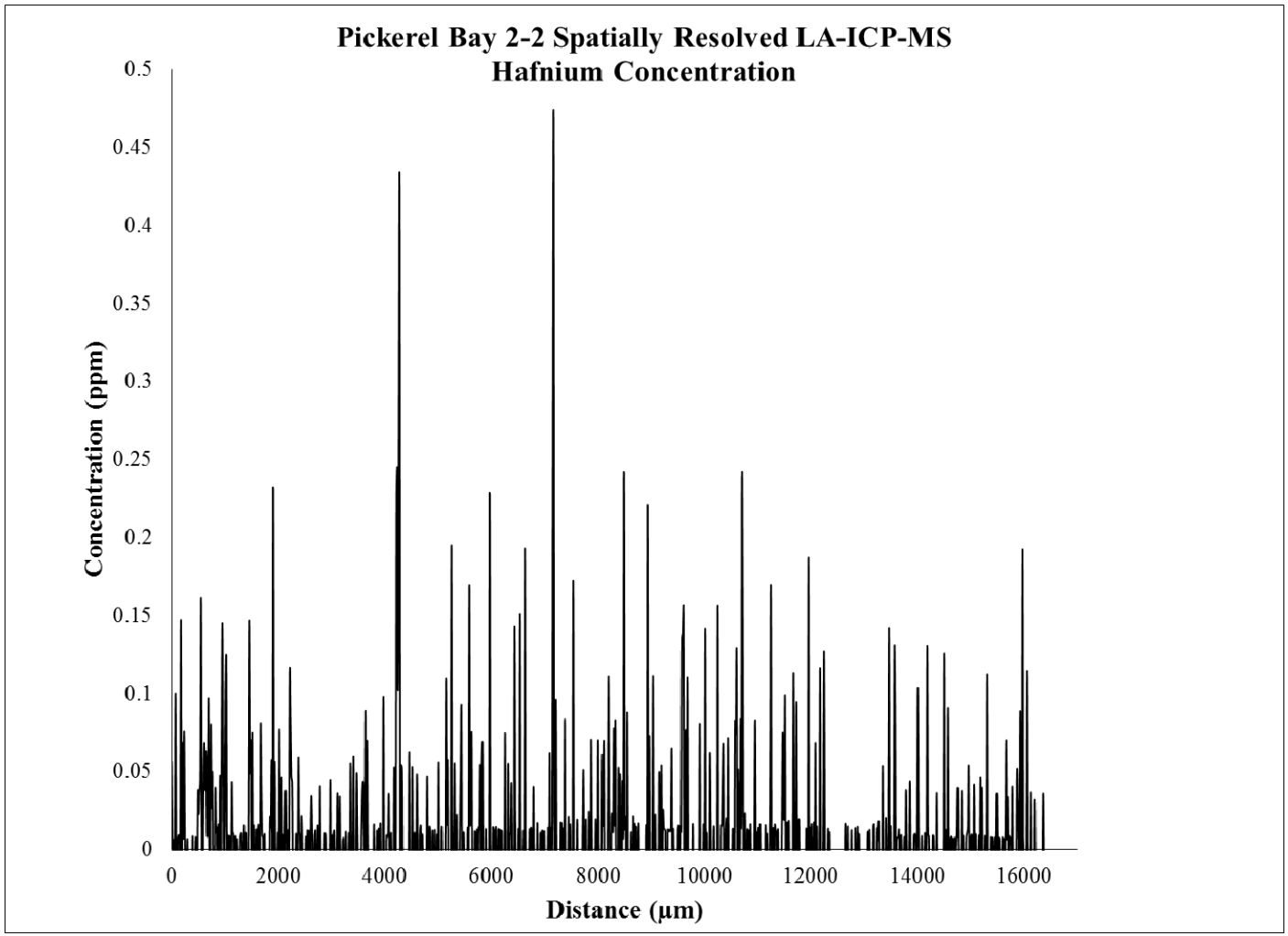
Pb concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW1-1



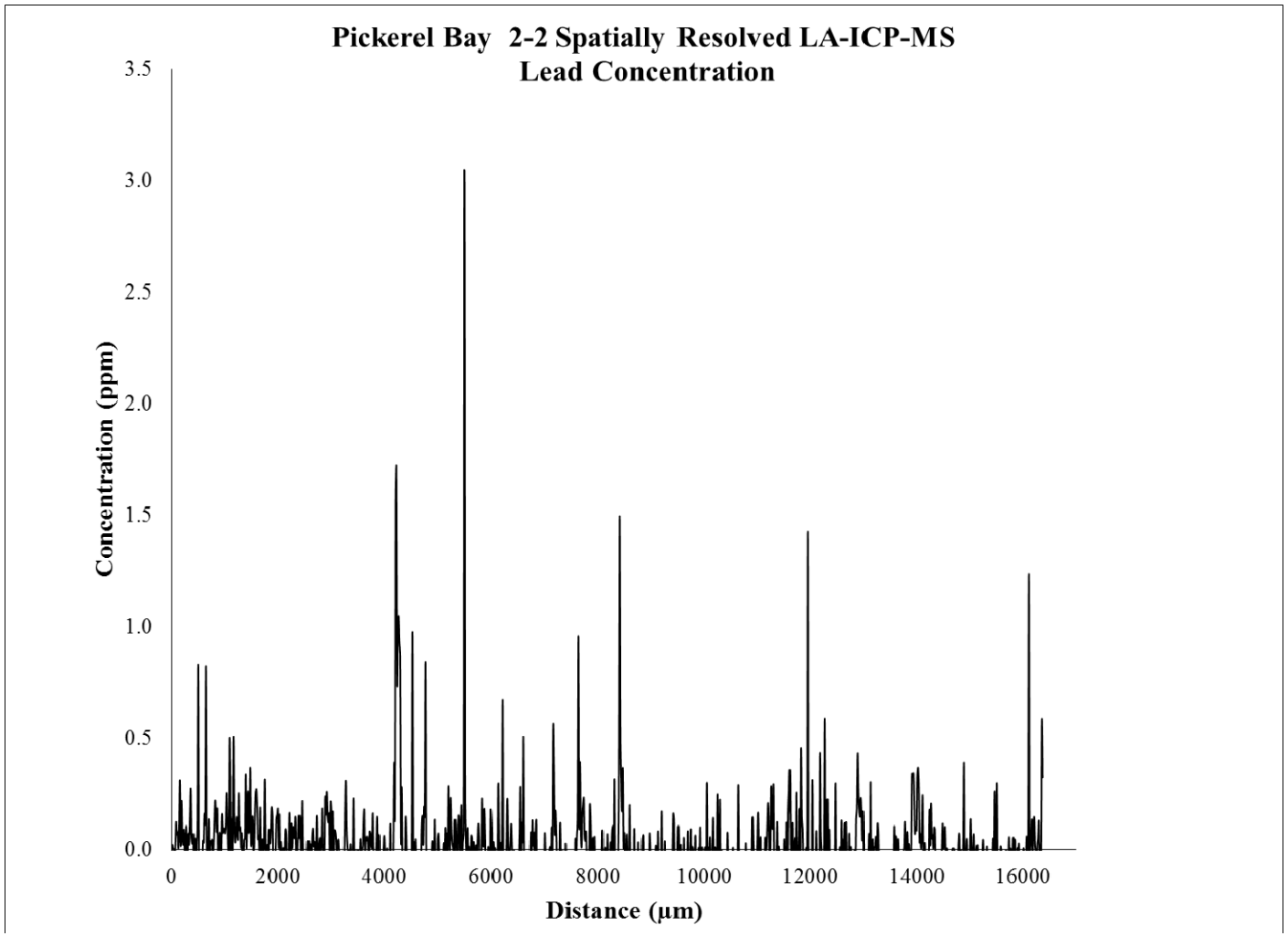
Th concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW1-1



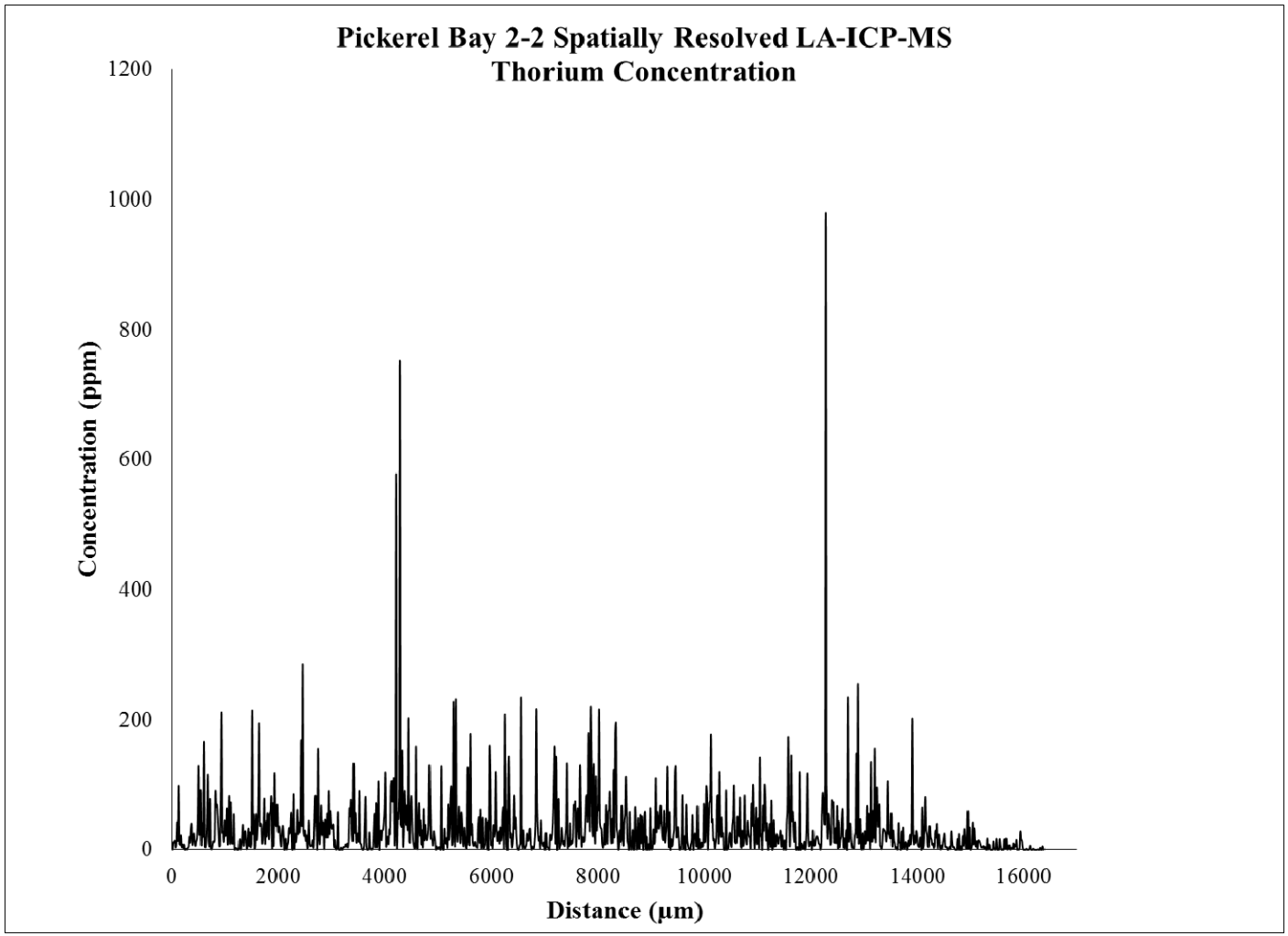
Nb concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW2-2



Hf concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW2-2



Pb concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW2-2



Th concentration (ppm) plotted against distance in µm over the course of a line scan of Pickerel Bay sample SW2-2

Appendix 7: ^{14}C accelerator mass spectrometry (AMS) and optically stimulated luminescence (OSL) dates from Grandfather quarry

Sample Number	Technique	Lab number	AD/BC Intercept (AMS)	BP Intercept (AMS)	BP 2 sigma with error (OSL)	BP 2 Sigma Calibrated Results (95%)	Unit
HbMd-4/S1	AMS	266110	Cal BC 4360	Cal BP 6320		Cal BP 6410 to 6290	1
HbMd-4/S2	AMS	266111	Cal BC 4330	Cal BP 6280		Cal BP 6300 to 6190	5
HbMd-4/S3	OSL	UIC2911			BP 1170 +/- 180	BP 1350 - 990	1
HbMd-4/S4	OSL	UIC2912			BP 2465 +/- 540	BP 3005 - 1925	1
HbMd-4/S5	OSL	UIC2910			BP 3610 +/- 1650	BP 5260 - 1960	1
HbMd-4/S6	OSL	UIC2913			BP 5735 +/- 1730	BP 7465 - 4005	1
HbMd-4/S7	OSL	UIC2914			BP 6360 +/- 1050	BP 7410 - 5310	1
HbMd-4/B2	OSL	UIC2931			BP 7300 +/- 1780	BP 9080 - 5520	1
HbMd-4/S8	AMS	295504	Cal AD 1890 Cal AD 1910 Cal AD 1950	Cal BP 60 Cal BP 40 Cal BP 0		Cal BP 270 to 210 Cal BP 140 to 20 Cal BP 0 to 0	5
HbMd-4/S9	AMS	295505	Cal AD 1650	Cal BP 300		Cal BP 430 to 370 Cal BP 320 to 280	5
HbMd-4/S10	AMS	296314	Cal AD 1650	Cal BP 300		Cal BP 440 to 350 Cal BP 340 to 280 Cal BP 170 to 150 Cal BP 0 to 0	1
HbMd-4/S11	AMS	296315	Cal BC 840	Cal BP 2790		Cal BP 2880 to 2750	1
HbMd-4/S12	AMS	296316	Cal BC 820	Cal BP 2770		Cal BP 2860 to 2820	1
HbMd-4/S13	AMS	296317	Cal BC 1130	Cal BP 3080		Cal BP 3210 to 2990	1
HbMd-4/S14	AMS	296318	Cal BC 1000	Cal BP 2950		Cal BP 3030 to 2870	1