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Using pXRF to Determine Lithic Source Materials

Introduction

Understanding the source of raw materials used to make stone tools could be key to understand trade and migration patterns in northern Quebec. New portable X-Ray Fluorescence (pXRF) technology has made the process of determining the chemical composition of lithics relatively inexpensive, fast, and possible to perform without destruction of the artifact. Using the pXRF data this paper will show that element correlation presented in the form of principal component analysis coupled with geographic observations can aid the process of sourcing lithic raw materials in Quebec in some cases. However, without a database of pXRF raw material source data, pXRF cannot definitively source materials in Quebec and archaeologists must continue to use visual analysis in tandem with the new technology to attempt to source raw materials.

Context

In August 2012, the seventh season of the Social Change and the Environment in Nordic Prehistory (SCENOP) archaeology project was conducted in the Wemindji, Quebec area. SCENOP is a collaborative project between academics in Canada and Finland to understand human responses to rapid climate change in prehistory. The goal of the 2012 season was to test a new computational model created by Colin Wren and Andre Costopoulos which attempts to predict the most likely areas in the James Bay area where prehistoric settlements may have occurred. Costopoulos and Wren mapped the changing shorelines starting at 6850 BP and identified the areas which would have most stable during ongoing climate change (Costopoulos and Wren, 2012).

The two week survey and excavation from August 3, 2012 to August 18, 2012 was predominantly a reconnaissance mission to identify sites that show evidence of prehistoric occupation, such as lithic materials on the ground surface, test pits, or noticeable disturbances in

the stratigraphy of the soil during coring. Over one hundred lithics (tools and flakes) were collected and brought back to McGill University for further analysis. A few of the lithics were made from very intriguing raw materials that at first glance looked they were not from local sources. Identifying the sources of the raw materials was thought to provide many clues about prehistoric trade routes.

In 2010, one of the SCENOP lead researchers, Colin Wren, performed a chemical analysis of Iroquois ceramics that were found at Old Factory Lake during the 2007 SCENOP season. The Old Factory Lake ceramics were definitely sourced to South-West Ontario, approximately 1200km south of where the ceramics were found in 2010. The findings suggest that migration or exchange were occurring for ceramics or ceramic making materials in the 17th century (Wren 2010). The success of the ceramic sourcing gave rise to the question of sourcing the lithic materials because they are the majority of the finds from each field season since 2007.

Portable X-Ray Florescence was decided to be the method of analysis for the study. PXRF is the sister to larger, lab-based XRF stations, which use the same method. XRF uses X-Ray technology to penetrate a geological material and determine it's chemical composition of 10 – 30 elements (Craig et al. 2007). XRF has been used for geological and environmental analysis since 1980 and soon became an important tool for sourcing obsidian lithics in South America because each volcano has a very distinct chemical signature. There are several kinds of chemical sourcing that can be done, such as Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma-Mass Spectrometry (ICPMS). However, these methods can be both costly and may require destruction of the artifact in order to process them. XRF became popular in the archaeological community as a relatively low-cost, precise, quick, non-destructive means of obtaining chemical composition (Craig et al. 2007).

In October 2012, nine lithic samples from the 2010 and 2012 SCENOP seasons were analyzed using pXRF to attempt the source of the raw materials and thus scientifically prove that some raw materials used to create lithics are not from local sources.

A Brief Introduction to the Prehistoric Ecological Environment in Quebec

The Wisconsin Glaciation, the most recent glaciation in the region of Quebec, started approximately 100,000 years BP and slowly receded starting approximately 15,000 years ago (Seguin 1985:81). Gradual environmental warming caused the glacier, known as the Laurentian Icefield, to rupture in the centre and divide, creating the Tyrrell Sea. Around 7500-7000 years BP the Tyrrell Sea engulfed the modern day Hudson and James Bays, as well as stretching 200-300km inland of what is now northern Quebec and Ontario (Seguin 1985:81). As the environment continued to warm, the glaciers receded north and the water level of the Tyrrell Sea started to shrink to the modern-day shoreline of James Bay. However, the rapid retreat of the glaciers triggered glacio-isostatic rebound causing the land to rise 6.5m per 100 years, displacing the shoreline rapidly (Pendera et al. 2010). The glacio-isostatic rebound slowed to approximately 1.5m per 100 years during the late Holocene and continues to rise at a similar pace (Pendera et al. 2010; Hétu et al. 2010).

From 7500 to 1600 BP, the average temperature was approximately two degrees warmer than the present day, meaning the climate was more hospitable for vegetation. Black Spruce began to appear on the landscape around 6500-6000 BP, creating an ecological environment to support animals and humans, as well as fuel for the regular forest fires that began to occur every 50 to 100 years (Sanguin, 1985:83).

History of archaeology in Quebec

Costopoulos et al. (2012) found possible anthropogenic signals from charcoal signal cores dating as early as 5600 cal yr BP near Old Factory Lake, meaning human occupation may have started in the area very soon after the water level of the Tyrrell Sea dropped considerably. Previous archaeological studies show evidence of human activity only on the Labrador coast and the lower part of the St. Lawrence River as early as 7500 years BP with the discovery of a wide variety of chipped stone tools, specifically for harvesting salt water species (Sanguin 1985:91).

The earliest confirmed archaeological sites in north-western Quebec (known as the La Grand Complex) have been dated to 1500 years BP (Sanguin 1985:98-100; Ethnoscop 1988:14). Evidence of seasonal occupations from 1500 years BP until historical periods all over the La

Grande Complex has been well documented and thoroughly investigated by various CRM projects and independent archeology consultants before massive hydro projects flooded the area (Chism 1974; Ethnoscop 1988-1989; Arkeos 2004; Denton 1989). The archaeological evidence found in sites dated 1500 years BP to the historical period is usually in the form of hearths, charcoal, animal bones, cairns, middens, and a wide assortment of stone tools and flakes made of local and imported raw materials (Senguin 1985:149). Some raw materials can be sourced by visual analysis such as Hudson Bay Lowland chert, Nastapoka chert, and Abitibi rhyolite due to their distinctive composition or colour (Senguin 1985; Archaeotec 2012).

Until recently, sourcing of raw materials has been through visual analysis using comparative collections, which can be time consuming and inaccurate. Kristmanson (2004) attempted to use XRF to scientifically confirm the source of Ramah chert lithics found in Newfoundland and on Cape Breton Island to perhaps learn more about migration and trade patterns. The results of the study were inconclusive because the chemical features of rhyolites are similar in many different areas, however, two samples could be positively excluded from the proposed raw material source.

Archaeotec (2012) recently combined visual analysis and pXRF data to attempt to create a catalogue of both visual and chemical characteristics of different raw materials in Quebec. The purpose of the study was to combat inaccuracy caused by visual analysis alone.

Methodology

Initially the project started with the goal of determining the chemical composition of fifteen lithics from the 2010 and 2012 SCENOP excavations and compare the results with the data from the 2012 Archaeotec pXRF project. However, the data is under the ownership of Hydro Quebec and the authorization to release the information could not be obtained. The focus was shifted to determining the chemical composition of the artifacts, locate any trends in the data that could aid sourcing, as well as comparing the data with visual analysis.

A DELTA Premium Dynamic XRF by Innov-X Systems was used to conduct the study, operated by staff at Archaeotec. In order to obtain the most accurate results, each sample was x-rayed three times in different places because chemical composition can vary within the sample

(Archeotec 2012). In order to obtain accurate and useable data, the following criteria were required of each sample, as determined by Archaeotec:

- A flat surface to ensure the x-ray can penetrate the surface. Concave or convex surfaces can cause errors
- Large enough to be scanned in three separate locations. Some flakes under 3mm could not be used because of this criteria
- Have a homogeneous composition (i.e. no cortex that would have a different chemical composition)
- Be composed of multiple elements which can give a distinct chemical signature. (i.e. quartz is usually 99% silica and usually cannot be sourced by chemical analysis)
- Must not have been heated at any point in time because the material will absorb chemicals from the surrounding environment and the chemical signature will change, eliminating the possibility of accurate sourcing

The majority of the lithics from the SCENOP project did not fit all of the criteria, thus minimizing the possibility of creating a pool of samples that were equally distributed across the archaeological sites. Two samples, M5 and M6 were only scanned once because it was determined that they would probably not offer a distinct chemical signature. Furthermore, the pXRF gun broke after nine samples so the geographic dispersal of the samples was limited as well. The data that was successfully collected required substantial cleanup in the form of averaging all the x-ray scans as well as disregarding all the elements that were lower than the level of detection (LOD). Eight elements had levels about the level of detection for all nine samples: silicon, phosphorus, potassium, titanium, vanadium, manganese, iron, and strontium.

SPSS was used to perform principle component analysis, the process of grouping similar variables in order to make the differences more apparent. The two components were used as X and Y variable to create two graphs illustrating the chemical variability between the samples. Finally, the pXRF results are graphed using the results of a visual analysis by Archaeotec which attempted to source the materials strictly using a comparative collection.

Results

The principle component analysis uncovered eight potential components, but only two which showed a significant percent of variability (Fig. 1). Component 1 had a very strong correlation with all the elements except silicon and phosphorus. Component 2 had a strong correlation with phosphorous and a weak correlation with all other elements (Fig 2).

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.016	75.199	75.199	6.016	75.199	75.199
2	1.190	14.871	90.070	1.190	14.871	90.070
3	.575	7.187	97.257			
4	.178	2.222	99.480			
5	.028	.350	99.829			
6	.011	.140	99.970			
7	.002	.030	99.999			
8	6.059E-005	.001	100.000			

Fig. 1 - Principle component analysis of the eight elements.

	Component	
	1	2
Si	-.978	.157
P	-.109	.955
K	.774	.219
Ti	.966	.197
V	.917	.244

Mn	.931	-.209
Fe	.948	.095
Sr	.954	-.233

Fig. 2 - Principal component matrix.

Displayed as a graph, it appears that two samples are distinct outliers and the rest are clustered (Fig 3). The cluster is very interesting because it indicates that the majority of the samples have similar chemical compositions, mostly correlated with component 2 and negatively correlated with component 1. M5 and M6 were only scanned once because they did not show potential as having a distinct chemical signature, but it appears that M5 does have distinct characteristics based on the one scan that was performed. M5 is correlated with both component 1 and 2. M4 negatively correlated with both components, which is very interesting and could be the result of coming from a different source from the other samples.

Although Fig. 3 may appear to display significant variability, both M4 and M5 share a significant similarity with the cluster of the remaining samples, since there are so few samples the difference appear much larger. The lack of chemical variability could mean that all the samples are from a similar source because of the lack of variability, or it could be the case that the raw materials all have a similar composition and sourcing incredibly difficult using pXRF.

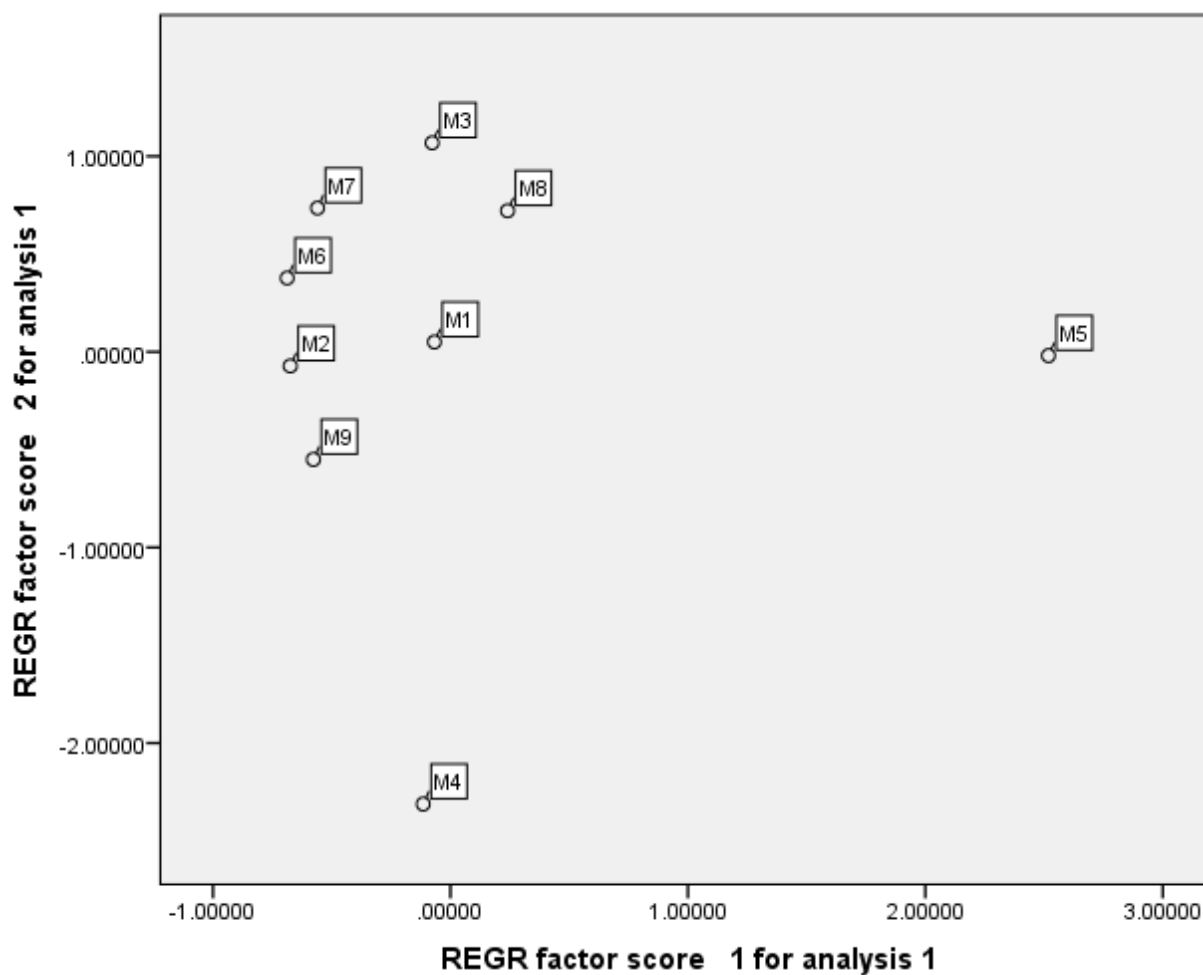


Fig 3. Principle component analysis displayed in a graph

Independently, the pXRF data does not provide any conclusions about potential sources of the raw materials, but combined with visual analysis, the possibility of sourcing the samples was much higher. Archaeologists at Archaeotec provided their professional opinion about each of the samples and made conclusions about potential sources (Fig 4). Combining the principle component analysis with the visual analysis provided some conclusive results, but also created more questions (Fig 5).

Results of visual analysis with Archaeotec		
M#	TP Number	Description
M1	TP143	At first they thought it was chert, but it has a large grain. Could be Nastapoka, but it usually has a more vibrant colour.
M2	TP30NW	It is chert, but has a smaller grain than the comparison artifact. Could be Nastapoka, but missing the characteristic calcareous stripes.
M3	TP147	"Spotty" texture so it's going to have a less homogeneous composition. Could be Abitibi Rhyolite. May be same source as M5.
M4	TP26	May be Abitibi Rhyolite. Heated, so it may have absorbed other elements.
M5	TP147	May have same source as M3. Could be Abitibi Rhyolite. Not sure if flake, interesting material
M6	TP207	Hyaline quartz. Can't be sourced because it is everywhere. Known source of quartz near Wemindji at Lac Duncan(49°28'06" North and 70°23'15" West)
M7	FeGj-1195cm	Probably Nastapoka.
M8	FeGj-1195cm	Maybe Nastapoka
M9	FeGj-1195cm	Maybe Nastapoka
No pXRF data:		
M10	OLF-05-08	Red powder on this flake, could be ochre.
M11	OFL-05-08	Nastapoka
M12	OFL-05-08 TP4	Maybe heated. Cortex. Ardoise?
M13	OFL-05-08 TP4	Nastapoka with the characteristic bands of calcareous stripes
M14	OFL-06-31	Hudson Bay source. Heated.
M15	OFL-07-05	Hudson Bay.

Fig 4. Visual analysis of the samples

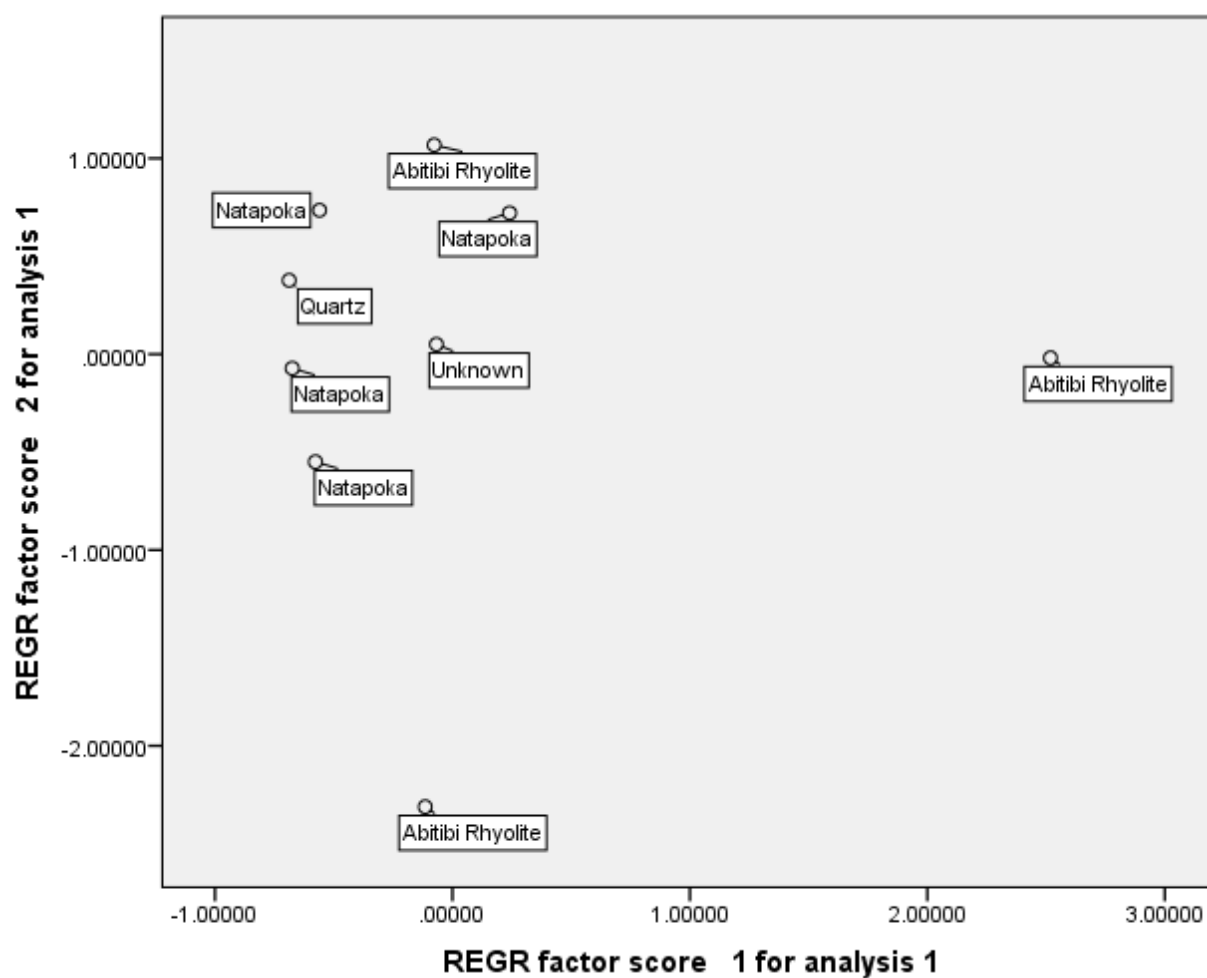


Fig 5. Principle component analysis combined with visual analysis

Fig. 5 demonstrates that there are chemical similarities as well as visual similarities for the samples that were identified as Nastapoka. However, other samples that were identified as

very different sources are clustered very close to all the Nastapoka samples. It is possible that all the samples come from a similar source but were not visually classified correctly, either they could all be of Nastapoka origin, or possibly none of Nastapoka origin, but considering a quartz¹ sample is also in the cluster, it is likely that they have different sources and the chemical signature is not distinct enough to differentiate the sources.

The samples identified as Abitibi Rhyolite are distributed very widely on the graph. It is troubling that one sample of Abitibi Rhyolite is very strongly correlated with component 2 while the other sample is very negatively correlated. Samples from the same source would most likely have similar chemical composition, so the results of this graph can argue that M3 and M4 are not from the same source and the visual analysis can be incorrect. Furthermore, M4 was initially selected as a sample for this study because it matched at the required criteria for pXRF analysis, but was later determined to have been heated, thus the sample may not have an untainted chemical signature.

A third interesting dimension to be considered is the geographical location of where the samples were found. Fig. 6 displays the names of the test sites where the samples were found. The most interesting aspect of this graph is that it also validates that samples M7, M8, and M9 are most likely from the same source. All three were found in the same test pit at Old Factory Lake, visually identified as Nastapoka, and share similar chemical characteristics. This is a strong indication that they are indeed from the same source and prove that there was migration or trade from the Nastapoka area.

¹ Quartz is generally excluded from XRF because it is composed of so few elements (Archaeotec 2012)

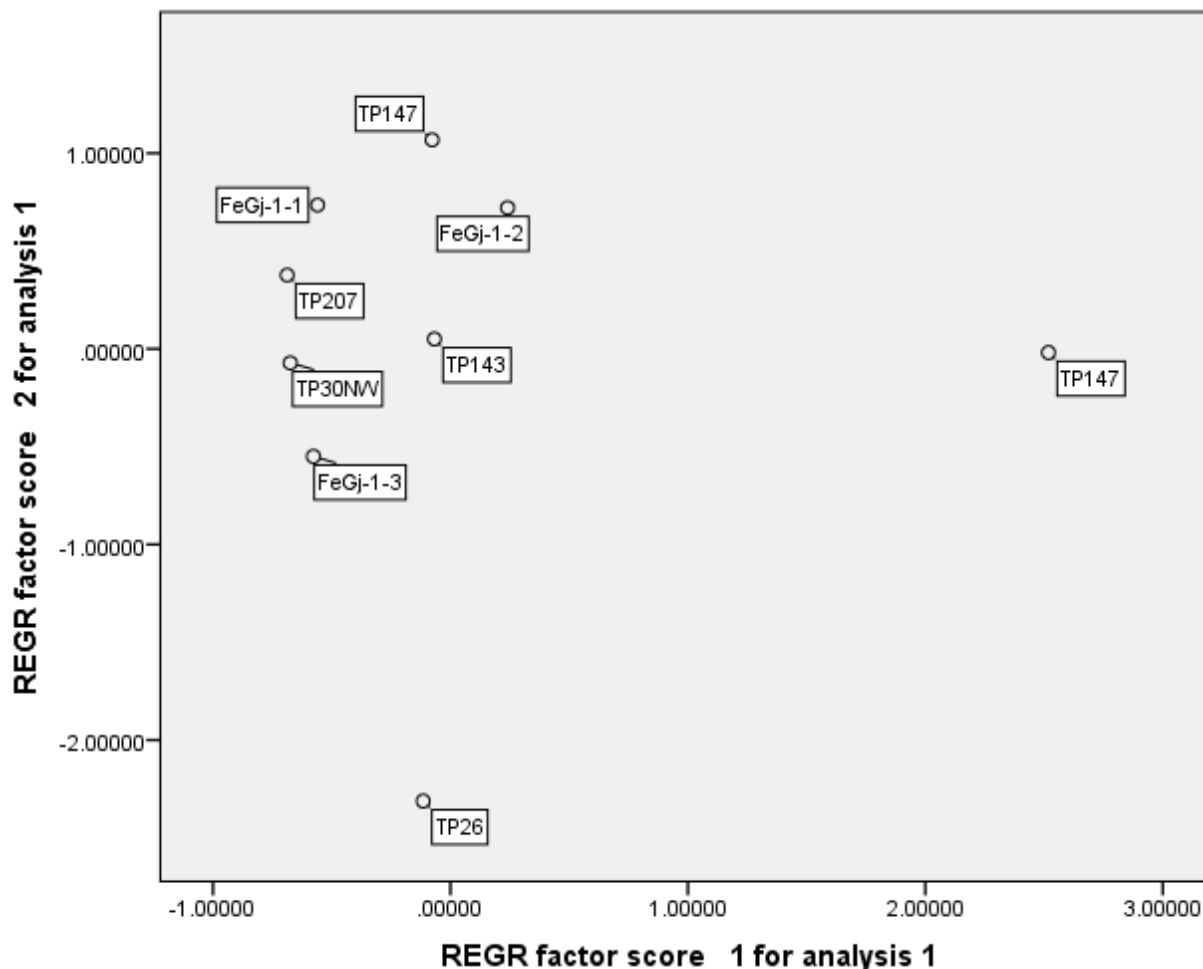


Fig. 6 – Principle component analysis with samples labeled as the sites where they were discovered.

Conclusion

The pXRF is limited when attempting to source raw materials in Quebec, but can be useful when paired with other methods of analysis. Visual analysis is the most common form of sourcing, and combined with the pXRF data provided a strong case that M7, M8, and M9 were from the Nastapoka region. Used together, pXRF and visual analysis can provide a safe guard against misidentification. M3, M4, and M5 were all identified as Abitibi Rhyolite, but the pXRF data raised doubts about the validity of the identification.

Further research should included scanning the remaining six samples, ensuring that there is an even distribution from several different sites. The samples should be thoroughly analyzed

using a comparative collection to avoid misidentification. Finally, the pXRF data collected by Archaeotec on behalf of Hydro Quebec should be obtained in order to get the precise chemical signatures of source raw materials in order to definitive determine sources of the samples from the SCENOP project.

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