

Article

Lead Isotope Analysis of Geological Native Copper: Implications for Archaeological Provenance Research in the North American Arctic and Subarctic

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Abstract: The Indigenous inhabitants of Arctic and Subarctic North America had been using native copper for several centuries prior to sustained interaction with Europeans beginning in the 18th century. The connection, if any, between the use of copper in these two adjacent regions is, at present, unclear. The ability to determine the source of native copper artifacts found in greater northwestern North America would inform on the movement of copper via trade and exchange between, and aid in understanding the innovation and diffusion of native copper metallurgy among, ancestral Dene and Inuit People. This paper provides the results of a Lead Isotope Analysis (LIA) pilot study examining Pb isotope ratios of native copper samples from multiple locations in the northern regions of North America. The results from this preliminary study indicate some overlap in Pb isotope ratios between Arctic and Subarctic sources of native copper, and these nonetheless record distinct isotope signatures relative to those associated with other North American native Cu deposits.

Keywords: native copper; lead isotope analysis; provenance; arctic; subarctic; archaeometallurgy



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1. Introduction

The Archaeological evidence indicates native copper was used by Indigenous cultures at least 1000 years ago in the Western Subarctic and as early as 2000 years ago in the Central Canadian Arctic. The use of native copper by Inuit and Dene people in these regions was noted by some of the earliest Europeans to visit these places, e.g., [1–3] and documented in some of the earliest archaeological research in the region, e.g., [4–7]. Native copper, i.e., naturally occurring pure copper [8,9] in these two regions was used primarily for tools such as awls, projectile points, fishhooks, and various types of knives [10–13]. Franklin et al.'s (1981) volume *An Examination of Prehistoric Copper Technology and Copper Sources in Western Arctic and Subarctic North America* provided the first inventory of both archaeological examples and sources of copper and other metals for this large region. The question they raised then, which remains, is whether the copper-working traditions in these two adjacent but widely separated regions, which have a temporal and cultural (Dene) overlap, are related. An approach to examining the distribution of archaeological copper without relying on provenance data has been offered [13], but questions remain regarding the utility of provenance research in answering questions about the trade, exchange, diffusion, and innovation of copper in the far north. However, the ability to distinguish native copper deposits from the western Subarctic (Alaska and Yukon) from those in the Central Canadian Arctic and Subarctic (Nunavut and Northwest Territories) using Pb isotope ratios would provide the potential for examining the extent to which native copper metallurgy in one region may have influenced the other. Additionally, this might allow for provenance determination for native copper artifacts found between, but at great distance from, both source areas.

2. Native Copper Geology and Provenance in the Far North

Provenance studies are based on the hypothesis that an artifact's physical and chemical properties will be reflective of the original geological deposit from which the raw material was derived. Two techniques commonly used to determine the geological source, or provenance, of archaeological materials are isotope values and patterns of trace element concentrations [14]. While provenance research in archaeology has been successful in answering such questions by analyzing other materials such as obsidian or ceramics, determining the source of artifact copper is more difficult. Compared to other materials analyzed in archaeological provenance research, native copper is very pure, resulting in a great deal of similarity in the composition of native copper from one source to another [8]. A minimum of 10 samples has been recommended to chemically characterize a source [8], but no further work has been conducted to determine whether this minimum number of samples is actually enough to properly capture the variation within a single source.

An additional difficulty with native copper provenance research is the past use of native copper from glacial till. As a result, native copper samples distant from each other may have the same trace element signature, which can make reconstructing trade routes and mechanisms difficult [15]. This makes it difficult to determine the source of native copper for Indigenous inhabitants in the past. Native copper provenance studies, in far northwest North America specifically, are hampered by: the existence of numerous possible sources, an apparent lack of an existing library of geological samples of native copper available for analysis, and the potential cost in both time and money of attempting to collect the necessary samples from the field [16].

An earlier pilot study [16] found that two sources within south-central Alaska could be distinguished from each other based on the presence or absence of two elements, Se and Hg. However, as noted then, these two sources represent only a fraction of those known in the region. Fifty-four discrete sources of native copper are reported for Alaska and Yukon, most of these are found in southwestern Yukon and south-central Alaska in the Wrangell and St. Elias Mountain ranges [11,16]. Many distinct sources of native copper have also been reported for the central Canadian Arctic and Subarctic concentrated along the lower portion of the Coppermine River, the southern part of Victoria Island, and Bathurst Inlet [2,11,17].

The earlier study [16] attempted lead isotope analysis (LIA) using Laser Ablation Multi-Collector Inductively Coupled Mass Spectrometry (LA-MC-ICP-MS). Pb was detected, but in amounts considerably less than 1 ppm, which resulted in ratios associated with extremely large uncertainties. It was noted at the time that processing larger sample sizes (involving acid digestion) followed by solution-mode (SM)-MC-ICP-MS analyses may yield more precise and accurate results [16]. A recent review [18] discussed the value and limitations of LIA in investigations of archaeometallurgical provenance in Europe, the circum-Mediterranean, Central and South America, Asia, and Africa. This review focused on pre-Modern smelting technology and, as a result, North America was not included as smelting of metal from ores did not occur in this region prior to the arrival of Europeans. Consequently, there is very little work to reference with respect to LIA of native copper. Additionally, though the most up-to-date provenance research involves the combined use of LIA with trace element data for both geological samples and artifacts [19], our study focuses solely on LIA of geological native copper. This pilot study analyzed 25 native copper samples from Alaska, Yukon, Nunavut, and Michigan (Table 1, Figure 1) by SM-MC-ICP-MS in an effort to test the efficacy of LIA for differentiating between native copper from different regions and geological formations.

Table 1. Results of Native Copper LIA.

Sample Name	$^{206}\text{Pb}/^{204}\text{Pb}$	2s Error	$^{207}\text{Pb}/^{204}\text{Pb}$	2s Error	$^{208}\text{Pb}/^{204}\text{Pb}$	2s Error	$^{208}\text{Pb}/^{206}\text{Pb}$	2s Error	$^{207}\text{Pb}/^{206}\text{Pb}$	2s Error	Total Beam (V)
Standards											
NBS 981 + Tl 25/6.25 ppb-1	16.936	0.001	15.488	0.001	36.688	0.002	2.16624	0.00005	0.91448	0.00002	6.33
NBS 981 + Tl 25/6.25 ppb-2	16.936	0.001	15.489	0.001	36.691	0.001	2.16644	0.00003	0.91456	0.00001	10.4
NBS 981 + Tl 25/6.25 ppb-3	16.934	0.001	15.488	0.001	36.687	0.002	2.16643	0.00003	0.91456	0.00001	13.4
Yukon											
Steep Creek Mayo	18.632	0.002	15.633	0.002	38.222	0.005	2.0514	0.0001	0.83904	0.00003	6.19
Burwash Creek Nugget 1	17.750	0.004	15.511	0.004	37.466	0.011	2.1112	0.0001	0.87396	0.00003	1.50
Burwash Creek	18.345	0.008	15.583	0.006	38.160	0.016	2.0800	0.0002	0.84938	0.00004	1.25
12 Fourth of July Creek Nugget 1	17.764	0.001	15.550	0.001	37.490	0.002	2.1104	0.0001	0.87533	0.00001	5.24
Coppermine River											
Nunavut1	18.068	0.009	15.563	0.007	37.788	0.018	2.0912	0.0002	0.86129	0.00009	1.00
Nunavut2	17.609	0.001	15.543	0.001	37.464	0.004	2.1275	0.0001	0.88266	0.00002	13.8
Nunavut3	17.205	0.001	15.510	0.002	36.910	0.005	2.1455	0.0002	0.90152	0.00004	7.15
Michigan											
23 MI	20.819	0.001	15.864	0.002	39.650	0.006	1.9045	0.00014	0.76196	0.00003	67.1
24 MI	17.629	0.085	15.377	0.082	39.120	0.188	2.2188	0.00090	0.87097	0.00056	0.09
25 MI	20.791	0.001	15.857	0.001	39.622	0.005	1.9057	0.00012	0.76271	0.00003	78.1

Table 1. Cont.

Sample Name	$^{206}\text{Pb}/^{204}\text{Pb}$	2s Error	$^{207}\text{Pb}/^{204}\text{Pb}$	2s Error	$^{208}\text{Pb}/^{204}\text{Pb}$	2s Error	$^{208}\text{Pb}/^{206}\text{Pb}$	2s Error	$^{207}\text{Pb}/^{206}\text{Pb}$	2s Error	Total Beam (V)
Alaska											
Chititu Creek 30-21-27BV	19.246	0.154	15.660	0.121	38.612	0.306	2.0065	0.0019	0.81383	0.00081	0.03
Chititu Creek 30-21-27BU	18.200	0.020	15.605	0.019	37.860	0.042	2.0806	0.0001	0.85725	0.00007	0.29
Chititu Creek 30-21-27BT	17.902	0.012	15.535	0.011	37.541	0.030	2.0971	0.0003	0.86783	0.00006	0.66
Chititu Creek 30-21-27AX	18.664	0.021	15.608	0.008	38.284	0.022	2.0512	0.0001	0.83622	0.00005	0.27
Chititu Creek 30-21-27AZ	18.912	0.012	15.609	0.012	38.438	0.033	2.0318	0.0002	0.82526	0.00009	0.72
13 Dan Creek	18.857	0.058	15.530	0.046	38.219	0.106	2.0265	0.0006	0.82342	0.00024	0.10
14 Dan Creek	18.975	0.032	15.607	0.013	38.389	0.032	2.0231	0.0001	0.82247	0.00005	0.24
15 Dan Creek	18.554	0.218	15.806	0.093	38.435	0.224	2.0712	0.0009	0.85182	0.00052	0.02
16 Dan Creek	18.958	0.017	15.640	0.008	38.428	0.018	2.0271	0.0001	0.82506	0.00009	0.38
17 Dan Creek	18.636	0.015	15.624	0.007	38.234	0.018	2.0511	0.0001	0.83845	0.00008	0.32
18 Kletsan	19.650	0.134	15.989	0.058	39.481	0.137	2.0099	0.0007	0.81316	0.00041	0.03
19 Kletsan	18.344	0.171	15.417	0.144	37.633	0.350	2.0516	0.0014	0.84008	0.00076	0.03
20 Kletsan	18.521	0.094	15.401	0.079	37.762	0.193	2.0387	0.0009	0.83161	0.00034	0.06
21 Kletsan	18.925	0.280	15.752	0.230	38.631	0.570	2.0412	0.0018	0.83272	0.00102	0.03
22 Kletsan	18.342	0.310	15.211	0.250	37.448	0.638	2.0427	0.0026	0.83297	0.00148	0.02



Figure 1. Map showing copper-bearing formations (red areas) associated with native copper sources. Dots correspond to location of samples used in this study.

3. Pb Isotope Analysis of Native Copper

Primordial lead refers to lead present since the formation of Earth approximately 4.56 billion years ago. Lead contains four isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb ; the amount of ^{204}Pb has remained constant since the time of Earth's formation, whereas the present-day contents of the latter three isotopes consist of their primordial abundances in addition to amounts accrued over geologic time from the radiogenic decay of their parent radionuclides ^{238}U , ^{235}U and ^{232}Th , respectively. Consequently, lead isotope ratios (e.g., $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) have increased over time and are a function of their U/Pb and Th/Pb ratios, and these can be used to determine the age and source of lead for provenance purposes [20]. As it pertains to this study and as described below, the provenance or metallogenesis of the native copper deposits within the northern regions of North America are intimately linked to regional tectonic events and associated magmatic activity. Hence, this study provides the opportunity to compare the Pb isotope signatures for the native copper samples relative to those for igneous rocks within pertinent tectonic terranes, if such data are available.

4. Geological Background

The Nikolai Greenstone (basalt formation) and Chitistone Limestone are copper-bearing geological formations associated with the Wrangell and St. Elias Mountain ranges, which stretch northwest to southeast across the Alaska–Yukon border. The Nikolai Greenstone was formed in the Triassic, 237–201 million years ago. The copper ores of the Kennecott-type deposits, which correspond to the lower member of the Chitistone Limestone (Triassic), were formed by orogenic processes that occurred 100 million years later in the Late Jurassic [21,22]. Copper mineralization is extensive throughout the Coppermine River Group in Nunavut and Northwest Territories and is derived from basalts formed in the late Precambrian [23]—more specifically, the Mesoproterozoic [24]. Potassium-argon dating of copper-bearing basalts in this region ranged from 735 million years ago to a little

over 1 billion years ago [25]. The Copper Creek Formation basalts within the Coppermine River Group are attributed to the 1.27 billion years old Mackenzie magmatic activity [24].

5. Materials and Methods

Twenty-five samples of native copper were analyzed: four from southwestern Yukon, three from the Coppermine River region in Nunavut, three from upper Michigan, and fifteen from Alaska within Wrangell–St. Elias National Park, which abuts the Yukon border. The samples weighed between 90 and 110 mg and were carefully selected to be inclusion-free. Samples were digested in “aqua regia” (1:1 concentrated HNO₃/Nitric Acid:HCl/Hydrochloric Acid), followed by Pb separation via ion exchange chromatography in a class 1000 clean room environment. Pb isotope compositions were analyzed using a Nu Plasma II multicollector-inductively coupled plasma mass spectrometer (MC-ICP-MS) instrument (Nu Instruments Ltd., Wrexham, UK) at the Midwest Isotope and Trace Element Research Analytical Center (MITERAC) ICP-MS facility, University of Notre Dame, and a brief outline of the procedure [26] is provided here. At the start of the analytical session, the instrument operating conditions and parameters were tuned and optimized using a Pb elemental standard solution. Subsequently, repeated measurements ($n = 3$) of a mixed solution containing the NIST SRM 981 Pb isotope (25 ppb) and NIST SRM 997 Tl isotope standards (6.25 ppb) were conducted (Table 1), and the results are in agreement with recommended values [27]. The same Tl isotope standard solution was added to each sample aliquot prior to aspiration in dry plasma mode using a DSN-100 desolvating nebulizing system (Nu Instruments, Ltd., Wrexham, UK). Pb, Tl and ²⁰²Hg ion signals were simultaneously acquired using seven Faraday cups, and the ²⁰⁵Tl/²⁰³Tl ratio was measured for monitoring the instrumental mass bias (exponential law; ²⁰⁵Tl/²⁰³Tl = 2.3887). The ²⁰²Hg ion signal was used to determine the ²⁰⁴Hg interference correction on ²⁰⁴Pb, which was negligible. Instrument ion signal baseline levels (gas and acid blank) were determined with a 30 s “on-peak-zero” measurement prior to sample introduction. Total procedural blanks were typically <10 picograms (10^{−12} g/g) and, therefore, considered negligible relative to the total amount of sample Pb processed.

6. Results

The Pb isotope results for the native copper artefacts investigated here are listed in Table 1 and shown in Figures 2–4. These three figures compare our results to the temporal evolution trends for the Pb isotope compositions of several major terrestrial reservoirs, i.e., mantle, orogene, and upper and lower crust [28], and to the Pb isotope compositions for basalts from the Wrangellia tectonic terrane [29]. Moreover, Figure 4 illustrates the Pb isotope results obtained here (Table 1) using the ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁶Pb isotope ratios, which are more precise measurements and, therefore, are slightly more advantageous for interpretative (provenance) purposes compared to the remaining ²⁰⁴Pb-normalized ratios; the latter are associated with larger uncertainties given that these involve measurement of the significantly lower ²⁰⁴Pb ion signal intensities.

The Pb isotope data for the 3 Coppermine samples are clearly distinct compared to the remaining samples as these are characterized by less radiogenic values, and overlap with recent (last ~500 million years) isotope compositions for mantle and orogene reservoirs. The three native copper samples from Coppermine define a linear regression with a slope that corresponds to a secondary Pb–Pb isochron age of ~1115 Ma and intercept the two-stage Stacey and Kramers Pb evolution curve at ~1200 Ma [30]; both results are consistent with the range of ages reported for volcanic/magmatic activity within the region (i.e., Mackenzie dyke swarm, Muskox intrusion), and the depositional age for the Huskey Creek Formation, which is host to Cu mineralization in the region [24].

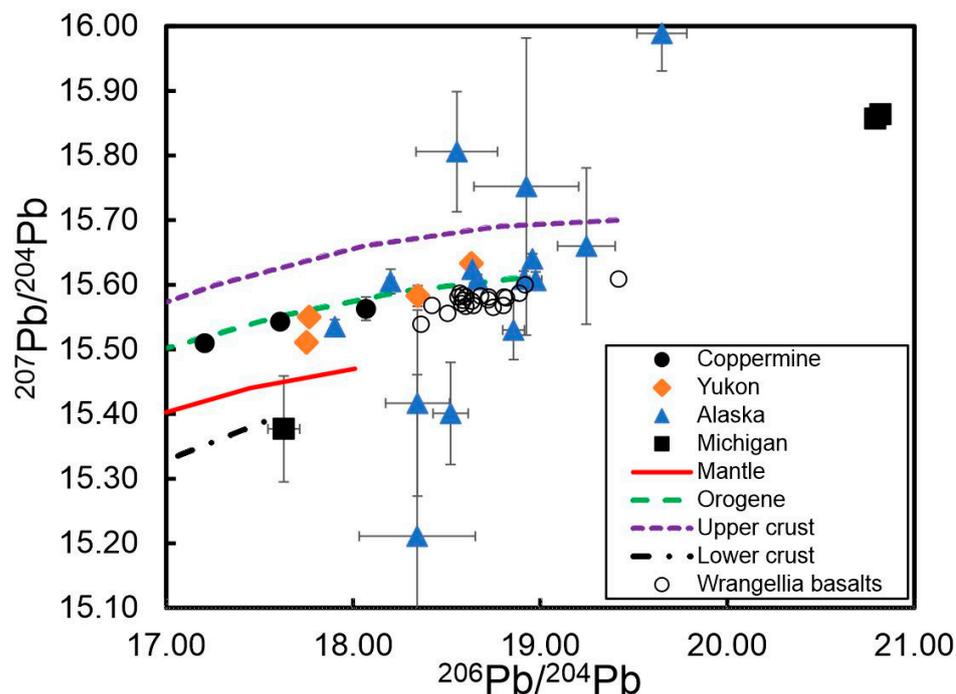


Figure 2. Plot of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for native Cu samples investigated here. Pb isotope data for mantle, orogene, and lower and upper crust evolution curves are taken from [28], whereas Pb isotope compositions for Wrangellia basalts are from [29]. Error bars represent associated 2s level uncertainty and are not shown if these are within the size of the symbol.

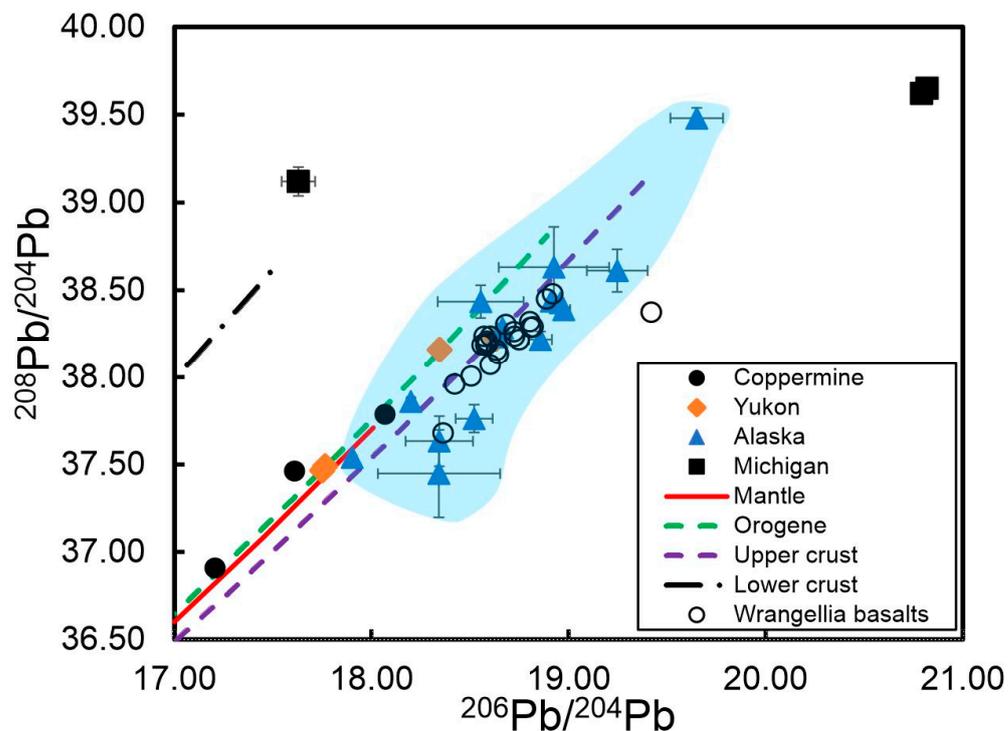


Figure 3. Diagram illustrating $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for native Cu samples investigated here. Pb isotope data for mantle, orogene, and lower and upper crust evolution curves are taken from [28], whereas Pb isotope compositions for Wrangellia basalts are from [29]. Blue field denotes range of compositions for Alaskan native Cu samples. Error bars represent associated 2s level uncertainty and are not shown if these are within the size of the symbol.

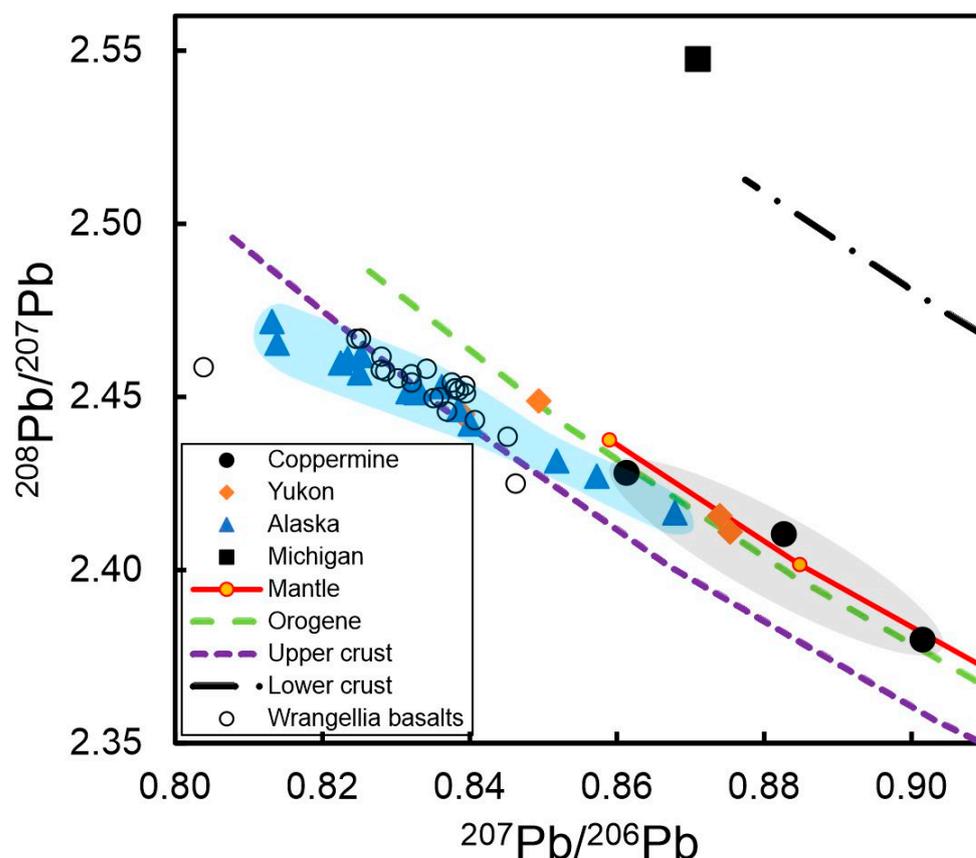


Figure 4. Plot illustrating $^{208}\text{Pb}/^{207}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for native Cu samples investigated here. Pb isotope data for mantle, orogene, and lower and upper crust evolution curves are taken from [28], whereas Pb isotope compositions for Wrangellia basalts are from [29]. Blue field denotes range of compositions for Alaskan native Cu samples; gray field outlines range of compositions for samples from Coppermine region. Error bars are within the size of the symbol.

The native Cu samples from Michigan also exhibit a significant variation in Pb isotope compositions; two samples record the most radiogenic values, whereas one sample plots consistently close to the present-day composition for a lower crustal reservoir (Figures 2–4). The slope of the linear regression defined by the $^{207}\text{Pb}/^{206}\text{Pb}$ compositions for the three Michigan samples corresponds to an age of ~2400 million years. In Michigan, this age equates to that for Paleoproterozoic rocks referred to as the Marquette Range Supergroup and the Kona Dolomite, which are hosts to a sub-economic concentration of copper [31].

In contrast, the native Cu samples from Alaska and Yukon are characterized overall by more radiogenic Pb isotope compositions (with the exception of two samples from Michigan) and exhibit some overlap (Figures 2–4). This is perhaps not surprising given that the Nikolai Greenstone and Kennecott type ores are not spatially distinct within this region, and samples were collected in areas downstream from these bedrock formations; thus, copper from each formation could be found in the same stream drainage. Despite some overlap between the Alaska and Yukon samples, those from Alaska record significant variation in their Pb isotope compositions, and do not define a well-constrained secondary Pb–Pb isochron. Of particular note is their overlap with the Pb isotope composition for an upper crustal reservoir ([28]; Figures 3 and 4) and they are characterized by more thorogenic ratios, i.e., higher $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ signatures relative to their corresponding $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ compositions compared to the remaining samples (Figures 3 and 4), including Yukon. Additionally, comparison of the Alaska and Yukon data relative to Pb isotope compositions for basalts along the Alaska–Yukon border [29] demonstrates remarkable consistency with our results, confirming that copper mineraliza-

tion in this region is most likely of magmatic origin, and linked with the emplacement of the basaltic flows 230 million years ago.

7. Conclusions

This is the first set of highly accurate lead isotope measurements for native copper from this region. Trace element results for a small number of geological and archaeological native copper from Alaska were previously obtained using both LA-MC-ICP-MS and Instrumental Neutron Activation Analysis [16]. The size of the earlier dataset and location of samples precludes meaningful comparisons between this earlier study and the current one. As noted in this earlier study, the logistics involved with obtaining geological samples of native copper in Alaska, and neighboring parts of northwestern Canada, are costly in terms of both time and money, and there are currently no plans for additional provenance analyses. Similar to the earlier study, the relatively small number of samples analyzed for this pilot study only allows for a preliminary assessment regarding the usefulness of LIA for native copper provenance research in the North America Arctic and Subarctic, but as expected, copper from geological formations of different ages does have distinct Pb isotope signatures. Native copper artifacts from all four regions sampled in this study can be differentiated from each other, though there is some overlap in the Alaska and Yukon samples. This means archaeological artifacts of native copper from Alaska and Yukon could be differentiated from those made using copper from Nunavut. Additionally, our results for the Alaska and Yukon native copper results exhibit remarkable overlap with the Pb isotope data collected previously for basalts from the Wrangellia tectonic terrane [29].

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References

1. Grinev, A.V. On the Banks of the Copper River: The Ahtna Indians and the Russians, 1783–1867. *Arctic. Anthropol.* **1993**, *30*, 54–66.
2. Hearne, S. *A Journey from Prince of Wales's Fort in Hudson's Bay to the Northern Ocean, 1769, 1770, 1771, 1772*; McMillan: Toronto, ON, Canada, 1958.
3. Pratt, K. Copper, Trade, and Tradition among the Lower Ahtna of the Chitina River Basin: The Nicolai Era, 1884–1900. *Arctic. Anthropol.* **1998**, *35*, 77–98.
4. de Laguna, F. *Archaeology of Cook Inlet*; The University Museum, University of Pennsylvania Press: Philadelphia, PA, USA, 1934.
5. McGhee, R. *Copper Eskimo Prehistory*; Publications in Archaeology, No. 2; National Museums of Canada: Ottawa, ON, Canada, 1972.
6. Rainey, F.G. Archaeology in Central Alaska. *Anthropol. Pap. Am. Mus. Nat. Hist.* **1939**, *36*, 353–405.
7. Taylor, W.E., Jr. Summary of Archaeological Field Work on Banks and Victoria Islands, Arctic Canada, 1965. *Arctic. Anthropol.* **1967**, *4*, 221–243.
8. Rapp, G.; Allert, J.; Vitali, V.; Jing, Z.; Henrickson, E. *Determining Geologic Sources of Artifact Copper: Source Characterization Using Trace Element Patterns*; University Press of America: Lanhan, MD, USA, 2000.
9. Wayman, M.L. Native Copper: Humanity's Introduction to Metallurgy? In *All That Glitters: Readings in Historical Metallurgy*; Wayman, M.L., Ed.; Canadian Institute of Mining and Metallurgy: Montreal, QC, Canada, 1989; pp. 3–6.

10. Cooper, H.K. Innovation and Prestige among Northern Hunter-Gatherers: Late Prehistoric Native Use in Alaska and Yukon. *Am. Antiq.* **2012**, *77*, 565–590. [[CrossRef](#)]
11. Franklin, U.M.; Badone, E.; Gotthardt, R.; Yorga, B. *An Examination of Prehistoric Copper Technology and Copper Sources in Western Arctic and Subarctic North America*; National Museums of Man: Ottawa, ON, Canada, 1981.
12. Pike, M. Continuity and Change in Indigenous Copper Technologies of the Arctic and Central Subarctic. Ph.D. Thesis, Purdue University, West Lafayette, IN, USA, August 2020.
13. Pike, M.; Cooper, H.K.; Hunt, G. Defining a 'reasonable geographic framework': Path Distance as native copper provenance in the Arctic, Subarctic, and Northwest Coast. *JAS* **2019**, *26*, 101903. [[CrossRef](#)]
14. Rapp, G., Jr.; Hill, C. *Geoarchaeology: The Earth Science Approach to Archaeological Interpretation*; Yale University Press: New Haven, CT, USA, 1998.
15. Halsey, J. Copper from the Drift. In Proceedings of the Joint 50th Midwest Archaeological Conference and the 61st Annual Meeting of the Southeastern Archaeological Conference, St. Louis, MO, USA, 21 October 2004.
16. Cooper, H.K.; Duke, M.J.M.; Simonetti, A.; Chen, G. Trace element and Pb isotope provenance analyses of native copper in northwestern North America: Results of a recent pilot study using INAA, ICP-MS, and LA-MC-ICP-MS. *J. Archaeol. Sci.* **2008**, *35*, 1732–1747. [[CrossRef](#)]
17. Rapp, G., Jr.; Henrickson, E.; Allert, J. Native copper sources of artifact copper in pre-Columbian North America. In *Archaeological Geology of North America*; Lasca, N., Donahue, J., Eds.; Geological Society of America: Boulder, CO, USA, 1990; pp. 479–498.
18. Killick, D.; Stephens, J.A.; Fenn, T.R. Geological Constraints on the use of Lead Isotopes for Provenance in Archaeometallurgy. *Archaeometry* **2020**, *62*, 86–105. [[CrossRef](#)]
19. Artioli, G.; Canovaro, C.; Nimis, P.; Angelini, I. LIA of Prehistoric Metals in the Central Mediterranean Area: A Review. *Archaeometry* **2020**, *62*, 53–85. [[CrossRef](#)]
20. Faure, G.; Mensing, T.M. *Isotope Principle and Applications*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 2005.
21. MacKevett, E.M., Jr.; Cox, D.P.; Potter, R.W.I.; Silberman, M.L. Kennecott-type Deposits in the Wrangell Mountains, Alaska: High-Grade Copper Ores Near a Basalt-Limestone Contact. *Econ. Geo.* **1997**, *9*, 66–89.
22. Price, J.B.; Hitzman, M.W.; Nelson, E.P.; Humphrey, J.D.; Johnson, C.A. Wall-Rock Alteration, Structural Control, and Stable Isotope Systematics of the High-Grade Copper Orebodies of the Kennecott District, Alaska. *Econ. Geo.* **2014**, *109*, 581–620. [[CrossRef](#)]
23. Kindle, E.D. *Classification and Description of Copper Deposits, Coppermine River Area, District of Mackenzie, Bulletin 214*; Geological Survey of Canada: Ottawa, ON, Canada, 1972.
24. Skulski, T.; Rainbird, R.H.; Turner, E.C.; Meek, R.; Ielpi, A.; Halverson, G.P.; Davis, W.J.; Mercadier, J.; Girard, E.; Loron, C.C. *Bedrock Geology of the Dismal Lakes-Lower Coppermine River Area, Nunavut and Northwest Territories: GEM-@ Coppermine River Transect*; Report of Activities 2017–2018; Geological Survey of Canada: Ottawa, ON, Canada, 2018.
25. Wanless, R.K.; Stevens, R.D.; Lachance, G.R.; Rimsaite, J.Y.J. *Age Determinations and Geological Studies*; Technical Report for Geological Survey of Canada: Ottawa, ON, Canada, 1965; p. 64.
26. Simonetti, A.; Gariépy, C.; Banic, C.; Tanabe, R.; Wong, H.K. Pb Isotopic Investigation of Aircraft-Sampled Emissions from the Horne Smelter (Rouyn, Québec): Implications for Atmospheric Pollution in Northeastern North America. *Geochim. Cosmochim. Acta* **2004**, *68*, 3285–3294. [[CrossRef](#)]
27. Baker, J.; Peate, D.; Waight, T.; Meyzen, C. Pb isotopic analysis of standards and samples using a 207Pb–204Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chem. Geol.* **2004**, *211*, 275–303. [[CrossRef](#)]
28. Zartman, R.E.; Doe, B.R. Plumbotectonics—The Model. *Tectonophysics* **1981**, *75*, 135–162. [[CrossRef](#)]
29. Greene, A.R.; Scoates, J.S.; Weis, D. Wrangellia flood basalts in Alaska: A record of plume-lithosphere interaction in a Late Triassic accreted oceanic plateau. *Geochim. Geophys. Geosys.* **2008**, *9*, 1–34. [[CrossRef](#)]
30. Stacey, J.S.; Kramers, J.D. Approximation of Terrestrial Lead Isotope Evolution by a Two-Stage Model. *Earth Planet. Sci. Lett.* **1975**, *26*, 207–221. [[CrossRef](#)]
31. Bornhorst, T.J.; Barron, R.J. Copper Deposits of the Western Upper Peninsula Michigan. In *Geological Society of America Field Guide*; Miller, J.D., Hudak, G.J., Wittkop, C., McLaughlin, P.I., Eds.; The Geological Society of America: Boulder, CO, USA, 2011; Volume 24, pp. 83–99. [[CrossRef](#)]