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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

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Abstract

Several indigenous groups in northwestern North America used native copper prior to EuroAmerican contact. The Arctic, Subarctic, and Northwest Coast culture areas all have archaeological finds and geological sources of native copper. The copper-rich region of south-central Alaska and southwestern Yukon has often been credited as the source of archaeological native copper found on the Northwest Coast despite the presence of native copper sources further south. This paper presents the results of a pilot study using INAA, ICP-MS, and LA-MC-ICP-MS to assess the potential for native copper provenance research in Alaska and the Yukon Territory. Discrete native copper sources could be distinguished from one another intra-regionally. Difficulties associated with future native copper provenance research in northwestern North America are discussed.

Keywords: Native copper; Geoarchaeology; Alaska; Yukon; Northwest Coast; Athapaskan; Tlingit

1. Introduction

Many indigenous groups in greater northwestern North America used native copper. Within this large area, which includes the Arctic, Subarctic, and Northwest Coast culture areas, are three regions with sources of native copper, and archaeological evidence for its use. These three regions are (1) south-central Alaska and southwestern Yukon Territory, (2) central Arctic and Subarctic, and (3) central and southern Northwest Coast and Plateau (Fig. 1). Native copper provenance research in northwestern North America has been discussed by a number of researchers (e.g., Blake, 2004; Burley, 1981; Franklin et al., 1981; Shinkwin, 1979) and trace element analyses have been performed on both artifacts and geological specimens (e.g., Franklin et al., 1981; Rapp et al., 2000; Veakis, 1979; Wayman et al., 1985; Witthoft and Eyman, 1969). However, not all of these studies had native copper provenance as a goal, and those that did analyzed an insufficient quantity of material to assess the potential value of this type of research in the region.

This paper discusses the results of a study carried out using multiple analytical techniques (INAA, ICP-MS, and LA-MC-ICP-MS) on native copper source material and artifacts from south-central Alaska. This study was initiated in order to determine whether discrete sources of native copper might be differentiated intra-regionally using either trace elements or Pb isotope ratios. This is an initial step toward the differentiation of native copper sources inter-regionally, i.e., between the three regions mentioned above. Trace element analyses of native copper at both the intra- and inter-regional scale may provide additional information not only on the trade and exchange of native copper, but also on the invention and diffusion of native copper metallurgy among hunter-gatherers in northwestern North America.

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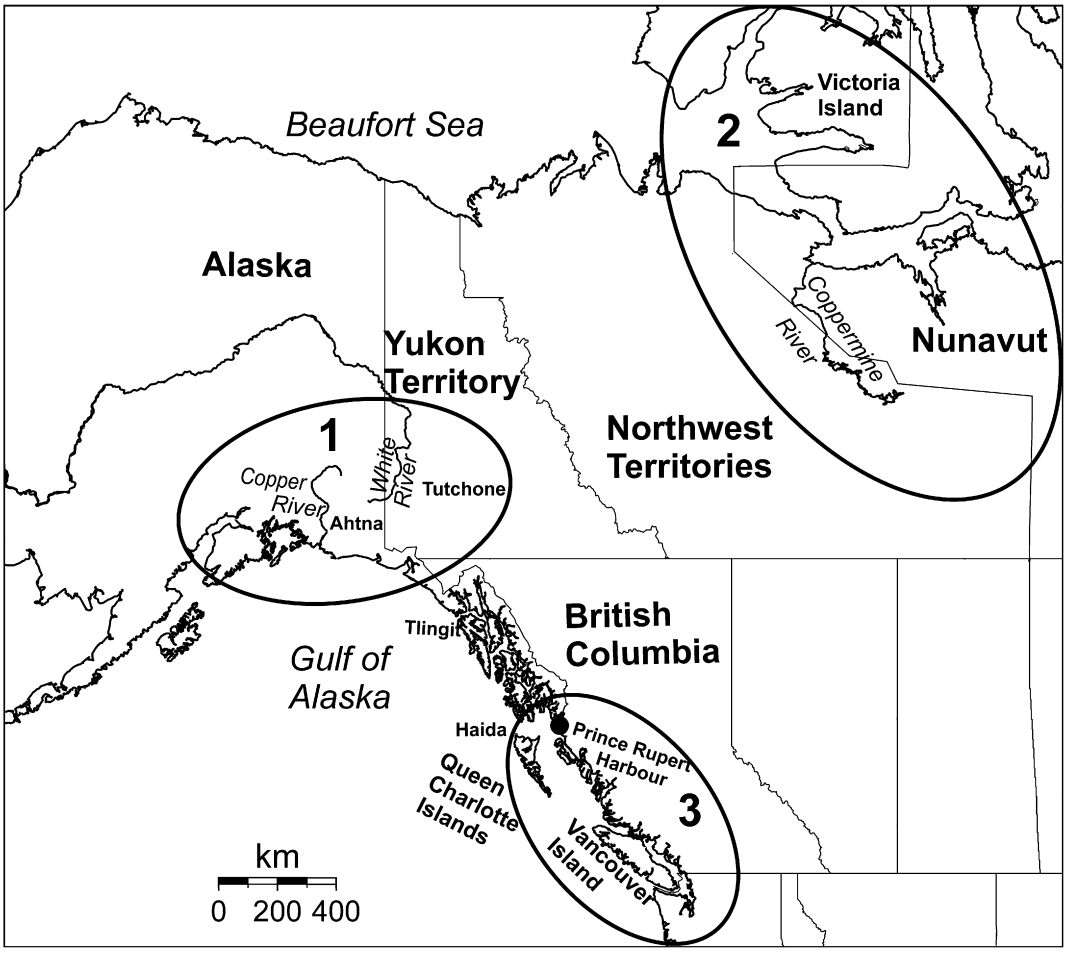

Fig. 1. Northwestern North America showing the three regions noted for both geological sources of native copper and archaeological evidence for its use (1) south-central Alaska and southwestern Yukon Territory, (2) central Arctic and Subarctic, and (3) central and southern Northwest Coast and Plateau.

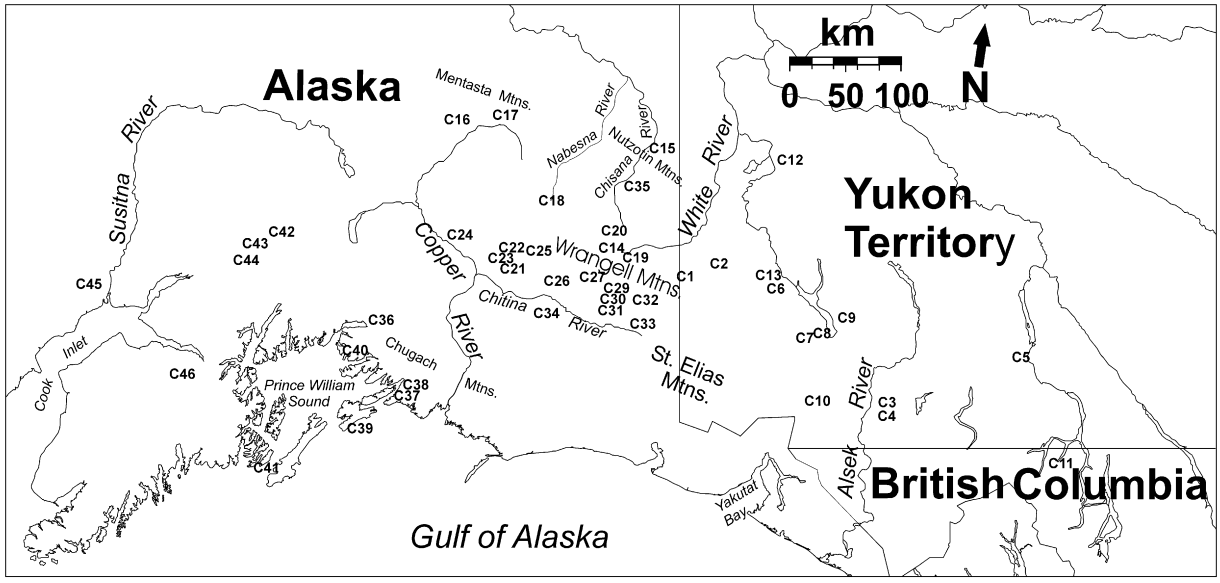

Fig. 2. Potential sources of native copper in southwestern Yukon Territory and south-central Alaska.

2. Prehistoric use of native copper in northwestern North America

Native copper appears in the archaeological record of south-central Alaska and southwestern Yukon Territory in the Late Prehistoric period, ca. 1000 AD. Many native copper sources are located in this region, which corresponds to the traditional territory of the Ahtna and Tutchone Athapaskans (Fig. 1) (Cooper, 2007). According to ethnohistoric sources the northernmost groups in the Northwest Coast culture area, the Yakutat, Chilkat, and Chilkoot Tlingit (Fig. 1), obtained native copper from their Ahtna and Tutchone neighbors in the interior (de Laguna, 1972; de Laguna et al., 1964; Legros, 1984). This native copper was then traded further south along the Northwest Coast in exchange for other prestige goods such as slaves and Haida-built red cedar canoes (Acheson, 2003; Dawson in Brooks, 1900; de Laguna, 1972; Keithahn, 1964).

Athapaskan people collected native copper primarily from stream gravels sometimes with the aid of antler digging tools (Brooks, 1900; Sabina, 1973; Schwatka, 1996). In south-central Alaska and southwestern Yukon native copper was worked through a combination of cold-hammering and annealing. Other than pieces of scrap leftover from the manufacturing process, the most common objects found in south-central Alaska and southwestern Yukon are tools such as awls, knives, and projectile points, though objects of personal adornment are known (Cooper, 2006, 2007). The Ahtna and Tutchone were well known for their control of copper sources and their skill in working native copper (de Laguna, 1972; de Laguna and McClellan, 1981; de Laguna et al., 1964; McClellan, 1975; Reckord, 1983; Von Wrangell in Van Stone, 1970).

Though the copper-rich region of south-central Alaska and southwestern Yukon Territory has been suggested as the source for copper found in archaeological contexts on the Northwest Coast (Acheson, 2003; Ames and Maschner, 1999; Blake, 2004; Burley, 1981), there are several reports of native copper in central and southern British Columbia (e.g., Acheson, 2003; Drucker, 1943; Leaming, 1973; Lincoln, 1981; Rapp et al., 1990; Sanger, 1970), and the state of Washington (e.g., Hayden and Schulting, 1997). An additional problem with assigning all archaeological native copper from the Northwest Coast to a northern source is the timing of the appearance of native copper metallurgy. The Tlingit, who occupied the northernmost portion of the Northwest Coast, attributed the invention of native copper metallurgy to Athapaskans (de Laguna et al., 1964; de Laguna, 1972). However, current archaeological evidence from the Boardwalk site at Prince Rupert Harbour (Fig. 1) indicates that the use of native copper further south on the Northwest Coast may predate its appearance in Alaska and the Yukon Territory by as much as 1000–2000 years (Ames, 2005; Cooper, 2007), suggesting that the development of native copper technology in these two contiguous regions may be unrelated (Cooper, 2006; de Laguna et al., 1964; Workman, 1978).

Table 1
Potential sources of native copper in southwestern Yukon Territory and south-central Alaska

ID #	Name	Reference
C1	Kletsan Creek	Hayes (1892), Brooks (1900) and Moffit and Knopf (1910)
C2	Generc River	Cairnes (1915)
C3	Beloud Creek	Kindle (1953)
C4	Mush Lake	Kindle (1953)
C5	Grafter Mine	Kindle (1964)
C6	Burwash Creek	McConnell (1905)
C7	Bullion Creek	McConnell (1905)
C8	Sheep Creek, YK	McConnell (1905)
C9	Fourth of July Creek	LeBarge (personal communication, 2004)
C10	Kimberley Creek	McConnell (1905)
C11	Windy Arm	McConnell (1906)
C12	Nisling River	Dawson (1899)
C13	Tetamagouche	Muller (1954)
C14	Middle Fork, White River	Brooks (1911) and Moffit and Knopf (1910)
C15	Nutzotin Mountains	Moffit and Wayland (1943)
C16	Chistochina River	Moffit (1954)
C17	Slana River	Moffit (1954)
C18	Nabesna River	Rohn (1900)
C19	Sheep Creek, AK	Capps (1916)
C20	Chisana Glacier	Mendenhall and Schrader (1903) and Moffit and Maddren (1908)
C21	Strelna Creek	Schrader and Spencer (1901)
C22	Kluvesna River/Fall Creek	Mendenhall and Schrader (1903)
C23	Kotsina Drainage	Schrader and Spencer (1901) and Mendenhall and Schrader (1903)
C24	Tsedi Kulaende	Kari (2005)
C25	Nugget Creek	Moffit and Maddren (1909) and Mendenhall and Schrader (1903)
C26	Bear Creek	Mendenhall and Schrader (1903)
C27	Nikolai Mine	Moffit and Maddren (1909)
C28	Chititu Creek	Moffit and Maddren (1909) and Mendenhall and Schrader (1903)
C29	Dan Creek	Moffit and Maddren (1909)
C30	Chititu Creek	Moffit and Maddren (1909)
C31	Young Creek	Rosenkranz (personal communication, 2004)
C32	Glacier Creek	Moffit and Maddren (1909)
C33	Chitina River headwaters	Mendenhall and Schrader (1903)
C34	Hanagita Valley/Chitina River	Mendenhall and Schrader (1903)
C35	Bonanza, Bryan, and Chathenda Creeks	Cobb (1973)
C36	Lowe River	Abercrombie (1900)
C37	Near Cordova	Grant and Higgins (1910) and de Laguna (1956)
C38	NE of Orca	Grant and Higgins (1910), Moffit and Maddren (1908) and de Laguna (1956)
C39	Hinchinbrook Island	de Laguna (1956)
C40	Landlocked Bay	Capps and Johnson (1915) and Grant and Higgins (1910)
C41	Latouche Island	Grant and Higgins (1910) and de Laguna (1956)
C42	Sheep Mountain	Turnbow (2002)
C43	Carpenter Creek	Landes (1927)
C44	Wolverine Creek	Landes (1927)
C45	Mount Susitna	Kari and Fall (2003)
C46	Lynx Creek	Moffit (1904)

Table 2
Trace element data for source material from Alaska (ppm) (Veakis, 1979)

ID	Source	Au	Sb	As	Hg	Ag	Zn	Cr	Fe	Co	Ce	Sc
CU47	Copper River			181	25.3	431	5.23	1.46	29.3	0.69	1.2	
CU48	Copper River		0.979	116	29.3	622	11.5	0.839		6.97	1.09	0.003
CU54	Copper River				2.29	456	5.4	2.21		0.712	1.34	
CU73	Copper River	0.021			1.75	484	10.3	15.9	119	0.152	0.59	0.005
CU74	Copper River	0.017			2.15	414	12.5	9.27	117	0.334	0.606	0.004
CU76	Copper River	0.011			1.25	454	10.9	8.61	393	0.186	0.525	0.03
CU112	Copper River				2.76	423		4.2	62.7	0.243	0.315	0.003
CU35	White River			25	6.024	1210			49	4.95	1.059	
CU40	White River	0.032		31.2	11.4	1150		0.763		0.897	0.591	
CU52	White River				7.95	372	13.7	2.5	25	0.425	1.36	0.01
CU53	White River				7.59	396	7.85	2.24	73.4	0.492	2.23	0.002

3. Native copper geology

3.1. Origin and occurrence

Metallic elements make up a large portion of the earth's crust but occur most often as minerals. Native metals are metallic elements found in their elemental form instead of being chemically combined with other elements as oxides, sulphides, carbonates, etc. Copper, gold, silver, platinum, iron, and lead can all occur in a native state but copper is by far the most abundant native metal worldwide and was the first metal to be used in both the Old and New Worlds (Craddock, 1995; Patterson, 1971; Wayman, 1989).

Native copper occurs primarily in three geologic environments (1) extrusive and intrusive mafic igneous rocks, (2) the oxidized zones of copper sulphide deposits, and (3) as placer deposits in clastic sediments associated with igneous rocks and/or glacial till. Primary native copper deposits are derived from copper mineral bearing hydrothermal solutions associated with mafic igneous rocks. Examples of this type of deposit include those found in the Canadian Arctic, Lake Superior region, and south-central Alaska and southwestern Yukon (Cornwall, 1956; Rapp, 2002; Rapp et al., 2000; Wayman, 1989). Secondary copper deposits are derived from the oxidation of copper sulphides. In the New World most native copper utilized by indigenous peoples originated from primary deposits where it was available at, or near, the earth's surface whereas in the Old World most native copper came from secondary deposits (Rapp et al., 2000; Rapp and Hill, 1998).

Native copper is noted for its purity, which is often greater than 99.9%. Silver and As are the most common and significant impurities associated with native copper. Both can be present in solution with copper up to their respective solubility limits as distinct inclusions. Due to the abundance of Fe in the earth's crust it is also often present in native copper. Silicon, Ca, Al, and Mg can be present in native copper in the form of non-metallic inclusions, most frequently as silicates or oxides (Patterson, 1971; Rapp et al., 2000; Wayman, 1989). Numerous additional elements have been detected in trace amounts during previous analyses of native copper from numerous sources including: Au, Co, Hg, Ni, Se, Sn, Zn (Wayman et al., 1985), Cr, La, Sb, W (Rapp et al., 2000, see page 49 for complete list of elements detected).

3.2. South-central Alaska and southwestern Yukon Territory

Native copper in south-central Alaska and southwestern Yukon Territory occurs as primary deposits in basaltic lavas and interbedded sedimentary rocks where it precipitated out of copper-bearing hydrothermal solutions (Cornwall, 1956; MacKevett et al., 1997; Wayman, 1989). The weathering and erosion of these primary deposits of native copper have

Table 3
Trace element data for artifacts from Alaska (ppm) (Veakis, 1979)

ID	Description	Au	Sb	As	Hg	Ag	Zn	Cr	Fe	Co	Ce	Sc
AR01	Ice pick				1.26	526	14	1.74	58.9	0.265	0.839	
AR02	Ice pick				1.09	508	11.3	1.39	16.3	0.16	0.733	0.009
AR03	Knife blade				44.9	444	17.4	5.92	288	0.405	0.504	
AR04	Knife blade	0.014			27.9	352	23.1	30.9	1040	1.1	0.513	0.003
AR06	Knife blade				2.42	715	28.2	2.54	83.5	2.42	1.13	
AR07	Unworked piece				7.02	831	12.5	2.73	118	0.21	0.675	0.02
AR13	Ice pick				16.3	1250	20.7	0.95		0.275	0.51	
AR37[a]	Projectile point	0.067		45.8	46.4	1460	27.3	7.05	181	0.306	1.16	0.013
AR49[a]	Projectile point			3990	13.7	811	47		30.8	0.162		0.008
AR50	Blade	0.715	27.9	17.1	3.61	167	103	4.09	201	0.875	0.462	0.012
AR51	Bracelet			31.9	27.8	1370	45.1	4.51	160	0.331	8.75	
AR52	Awl				12	1330	81.5	7.16	90	0.319	4.67	0.009

[a] YAK-007 (Old Town).

Table 4
Trace element data for artifacts from the Northwest Territories (and modern day Nunavut) (ppm) (Veakis, 1979)

ID	Description	Au	Sb	As	Hg	Ag	Zn	Cr	Fe	Co	Ce	Sc
AR70	Fragment	0.018		9.78	5.99	827	10.8	2.46	146	0.206	0.6	0.02
AR71	Awl	0.01			74.6	653	18.9	3.19	204	0.194	2.39	0.03
AR72	Fragment	0.036		466	4.34	1040	58.5	8.56	523	0.422	2.71	0.086
AR73	Fragment	0.008		2.38	3.15	496	19	3.58	144	0.169	1.35	0.024
AR74	Awl	24.6	5710	8450	4.94	4480	264	14.9	447	7.66		
AR75	Fragment	0.011		3.2	2.85	524	21.2	3.13	120	0.157	1.43	0.005
AR76	Fragment	0.011	0.554	32.7	2.23	459	24.3	5.64	268	350	28.3	0.035

resulted in the displacement of native copper downslope and downstream where it is found as stream bed placer nuggets that can vary in size from granules to boulder-size pieces weighing 2–3 tons.

Private individuals and government geologists began investigating the mineral wealth of Alaska and Yukon Territory in the latter part of the 19th century, largely as a result of gold discoveries in the region. Interest in the region's economic geology resulted in the documentation of the widespread occurrence of native copper throughout south-central Alaska (e.g., Bateman and McLaughlin, 1920; Capps, 1916; Mendenhall and Schrader, 1903; Moffit and Maddren, 1909; Rohn, 1900; Schrader and Spencer, 1901; Wayland, 1943) and southwestern Yukon Territory (e.g., Kindle, 1953; McConnell, 1905). At least 46 discrete sources of native copper are known for the region (Fig. 2 and Table 1) (Cooper, 2007). Indigenous oral history confirms that some of these sources were exploited prehistorically, but it is highly unlikely that all of these sources were equally important and some may not have been exploited at all.

The major geologic feature in the region where native copper and copper ores are found is the 120 km long contact belt of Nikolai greenstone and Chitistone–Nizina Limestone running southeast from the Chitistone River (south of the White River) to the Kotsina River (near the confluence of the Chitina and Copper Rivers (Cornwall, 1956; Mendenhall and Schrader, 1903; Moffit and Maddren, 1909). Several copper mining operations were in existence in this region in the early part of the 20th century but the largest was the complex of mines at Kennecott where 4,626,000 tons of ore were mined between 1911 and 1938, producing 591,535 tons of copper (Hunt, 1996). The Kennecott-type deposits, which include native copper, are found in the lowermost 100 m of the Upper Triassic Chitistone Limestone, immediately overlying Triassic Nikolai Greenstone. These deposits had an ore grade of 13% copper (Carriere et al., 1981; MacKevett et al., 1997).

Additional copper deposits are found north of the Wrangell Mountains in the upper portions of the Nabesna, Chisana, and White Rivers basins (Schrader and Spencer, 1901; Mendenhall and Schrader, 1903). Native copper in the White River–Kletsan Creek area occurs with chalcocite in "stringers and disseminations in altered Triassic basalt" (Carriere et al., 1981: p. 6). Though these deposits are small, they are associated with a geologic environment similar to the Kennecott deposits of the Wrangell Mountains. Native copper was found in the Mentasta Mountains, near the northeastern end of the Alaskan Range (Brooks, 1900), and the Nutzotin Mountains (Moffit and Wayland, 1943). Though native copper is much more abundant in south-central Alaska and southwestern Yukon Territory its presence has been noted in northern interior Alaska (Cooper, 2007).

4. Previous native copper studies

In addition to the present study, the results of previous analyses of native copper artifacts and source material (Tables 2–7) are presented. These other studies were conducted in a number of different laboratories over several years and, with one exception, these studies do not claim to make determinations of provenance regarding native copper artifacts. The data generated from these studies are not considered to be directly comparable to the present study, but the scarcity of such analyses for the region makes their inclusion worthwhile for the purpose of general comparisons.

In a study of northwestern North American metallurgy Witthoft and Eyman (1969) subjected museum specimens to emission spectroscopy. They ruled out both the Copper River and Coppermine River (eastern Nunavut) regions (Fig. 1) as the

Table 5
Trace element data for geological source material, shown in weight % (Franklin et al., 1981)

Source	As (%)	Sn (%)	Ag (%)	Cu (%)
Victoria Island (central)[a]	n.d. to ≤0.0019	≤0.48 to 0.79(±0.19)	≤0.06 to 0.39(±0.02)	>90
Victoria Island (Shaler Mountains)	Trace	≤0.53	≤0.05	>90
Coppermine River	0.0076(±0.007)	≤0.52 to 0.66(±0.18)	n.d. to ≤0.06	>90
Coppermine River	0.34(±0.003) to 0.37(±0.003)	n.d. to ≤0.5	≤0.05	>90
White River[a]	0.0025(±0.005) to 0.0041(±0.006)	≤0.45 to ≤0.56	≤0.04 to ≤0.06	>90

[a] Range provided for results of two samples, n.d. = not detected.

Table 6
INAA results for artifacts from GUL-077 shown in weight %

ID	As (%)	Ag (%)	Sb	Au	Sn (%)
GUL077/76-33	0.02 ± 0.001	≤0.1	Trace	Trace	≤0.86
GUL077/76-41	≤0.003	≤0.11	Trace	Trace	≤0.94
GUL077/76-55	≤0.003	≤0.08	Trace	Trace	≤0.78
GUL077/76-73	≤0.004	≤0.11	Trace	Trace	≤0.99
GUL077/76-77	0.01 ± 0.001	n.d.	Trace	Trace	≤0.65
GUL077/76-84	n.d.	≤0.09	Trace	Trace	≤0.77
GUL077/76-91	n.d.	≤0.07	Trace	Trace	≤0.58
75AMU-1-447	0.14 ± 0.002	≤0.08	Trace	Trace	≤0.77
75AMU-1-473	n.d.	≤0.08	Trace	Trace	0.85 ± 0.22
75AMU-1-476	0.02 ± 0.001	≤0.07	Trace	Trace	≤0.73
75AMU-1-652	n.d.	≤0.1	Trace	Trace	≤0.82
75AMU-1-1089	n.d.	n.d.	Trace	Trace	≤0.58
75AMU-1-1103	0.08 ± 0.002	n.d.	Trace	Trace	≤0.74
75AMU-1-1357	n.d.	0.17 ± 0.02	Trace	Trace	≤0.63

Copper concentrations exceeded 90% for all samples, n.d. = not detected (Badone, 1980).

source of copper used to make two Tlingit daggers analyzed but presented no analytical results and no information regarding the number or origin of native copper specimens analyzed. Veakis (1979) analyzed native copper geological specimens (Table 2) and artifacts (Tables 3 and 4) from northwestern North America using INAA. The majority of artifacts are of unknown provenience other than state/province or region but two projectile points (AR37 and AR49) are from the Old Town site (YAK-009) (see Fig. 3).

Franklin et al. (1981) subjected 42 artifacts and eight samples of source material (see Table 5 for source material analyses) from Arctic and Subarctic North America to INAA (see Hancock, 1976 for analytical details). Included in the study were 14 artifacts (Table 6) from a Late Prehistoric Ahtna Athapaskan site, GUL-077 (also known as the Ringling or Gulkana site) (Fig. 3). These 14 artifacts were reanalyzed for the present study (see Section 5.1). In their study of Copper Inuit copper metallurgy Wayman et al. (1985) subjected five geologic specimens and four artifacts of native copper from Banks Island to INAA (Table 7) in order to distinguish native from 18th century smelted copper.

Rapp et al. (2000: pp. 110–112) provide INAA trace element results for 52 samples from Chititu Creek (Fig. 3). This source was included in the present study. Rapp et al.'s results were included in a larger study designed to assess the variability of widely separated major source areas. No artifacts from northwestern North America were analyzed and no additional sources from the region were reported on. As a result, no insight was offered regarding the use of native copper in northwestern North America specifically, but it was demonstrated that trace element analysis could (1) source copper artifacts, (2) distinguish most native copper deposits throughout North America from one another, and (3) differentiate between multiple native copper deposits within a single region that were associated with the same geologic occurrence. It was also determined that at minimum, more than 10 samples are required from a source in order to assess within source variability and develop a distinct trace element 'fingerprint' or signature (Rapp et al., 2000).

5. Material analyzed in this study

5.1. The Gulkana site (GUL-077)

The 24 artifacts analyzed in this study are all from the Gulkana site (GUL-077). This large Late Prehistoric Ahtna Athapaskan site was situated along a 1.7 km stretch of bluff above the Gulkana River in the Copper River Valley (Fig. 3). The site was initially excavated in 1975 and 1976 (Workman, 1976), additional testing was conducted by the State of Alaska Office of History and Archaeology in 1986, 1995, and 1996 (Hanson, 1999; Holmes and McMahan, 1986).

The site had numerous cache pits and hearths and has been interpreted as a late winter/early spring campsite. More native copper artifacts ($n = 170$) have been recovered from the Gulkana site than any other site in Alaska, the Yukon Territory, Northwest Territories, or British Columbia. Most of these artifacts were associated with hearth features including 66 that appear to be debris leftover from fabrication processes. The majority of occupation and activity at the site took place between 1150 and 1500 AD based on a recalibration of the radiocarbon dates originally provided by Workman (1976) and Hanson (1999) (Cooper, 2007).

Nineteen of the 24 artifacts subjected to INAA in the present study were analyzed previously. Fourteen were included in the study by Franklin et al. (1981) where the INAA results were summarized. Detailed results of individual specimens provided in Table 6 are from a letter from Ellen Badone (University of Toronto) to Professor William Workman (University of Alaska, Anchorage) (1980). Five additional artifacts from GUL-077

Table 7
Trace element data for geological source material (ppm) (Wayman et al., 1985)

Source	As	Ni	Se	Sb	Ag	Au	Co	Zn	Sn	Hg
Coppermine River NC1A	≤0.9	≤21	≤1.1	≤0.25	333 ± 14	≤0.025	≤1	≤8	163 ± 18	≤0.6
Coppermine River NC1B	≤0.8	≤18	≤0.7	≤0.15	327 ± 14	≤0.020	≤1	≤5	66 ± 10	≤0.4
Coppermine River NC2A	44.9 ± 3.6	≤7	≤0.3	≤1.25	146 ± 6	≤0.180	≤1	≤3	≤10	3.7 ± 0.2
Coppermine River NC2B	11.9 ± 2.6	≤7	≤0.3	≤1.28	172 ± 7	≤0.190	≤1	≤3	≤9	4.5 ± 0.2
Coppermine River NC3A	≤5	≤10	≤0.2	0.31 ± 0.06	183 ± 8	≤0.010	≤1	≤3	103 ± 23	4.9 ± 0.2
Victoria Island NC4A	≤3	≤16	≤0.8	≤0.13	348 ± 13	≤0.010	≤1	≤5	14 ± 5	≤0.4
Victoria Island NC5A	17.8 ± 2.0	≤13	≤0.6	≤0.10	1160 ± 50	≤0.008	≤1	≤4	≤12	≤0.3
Victoria Island NC5B	≤2	≤17	≤0.9	0.36 ± 0.02	662 ± 22	≤0.006	≤1	≤6	≤17	≤0.4

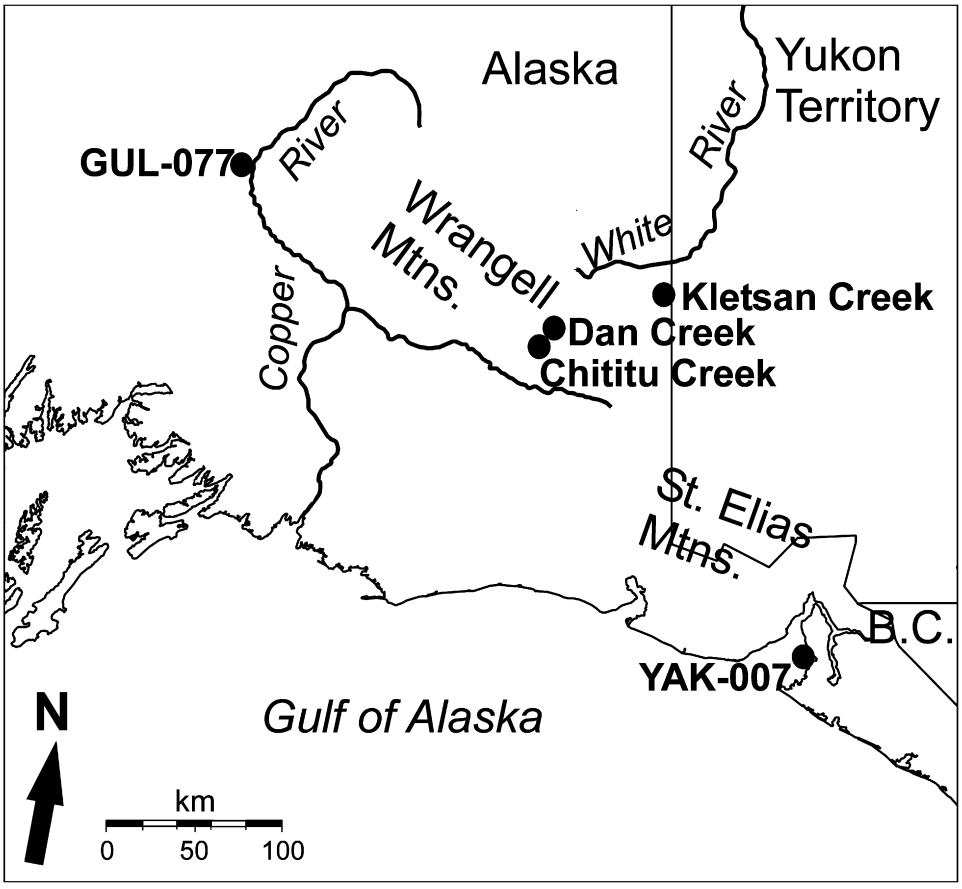

Fig. 3. Archaeological sites and geological sources for which trace element data are provided.

were analyzed by Harritt in the 1990s using scanning electron microscope and electron microprobe analysis but these results have not been published and are not presented or discussed here.

The 19 artifacts analyzed by Franklin et al. (1981) and Harritt were reanalyzed using INAA in the present study as this was considered preferable to damaging as yet unsampled material. An additional five artifacts were selected from material collected during the most recent phase of work at the site in 1995 and 1996 in order to have samples from areas of the site not previously represented. Two of these last five artifacts, a projectile point and large sheet, were selected because it was thought they might be industrial smelted copper. Ten of the 24 artifacts subjected to INAA in the present study were also analyzed using ICP-MS. The artifacts reported on here represent features across both time and space at the site.

The confident assignment of an artifact to a specific geologic source requires establishing that the artifact has not undergone chemical or physical processes that would significantly alter the original trace element pattern (Rapp, 1985; Rapp and Hill, 1998). Experiments by Wayman and Duke (1999) demonstrated that when native copper is melted into a liquid state some Hg is lost and Ag becomes homogenized, but the trace element content is otherwise unaffected. Prehistorically native copper in northwestern North America was not melted but instead worked via annealing, i.e., heated to temperatures as low as around 200–300 °C, far below the 1084 °C melting point of copper (Franklin et al., 1981; Wayman, 1989; Workman, 1976). Though temperatures of 700–800 °C were commonly reached during the annealing process (Schroeder and Ruhl, 1968), the trace element content of native copper artifacts subjected to such conditions should accurately reflect the trace element content of the native copper source material.

5.2. Source material

The source material analyzed in this study comes from three different stream drainages (Dan Creek, Chititu Creek,

Table 8
Selected nuclear data for elements determined by INAA and examined for use in native copper provenance studies

Element	Reaction	Natural abundance (%)	Half-life (d)	Main γ-ray (s) keV (intensity, %)
As	$^{75}As(n,\gamma)^{76}As$	100	1.0778	559.1 (45)
Ag	$^{109}Ag(n,\gamma)^{110m}Ag$	48.161	249.79	657.8 (94.0), 884.7 (72.2)
Se	$^{74}Se(n,\gamma)^{75}Se$	0.89	119.779	264.7 (58.9), 136.0 (58.3), 279.5 (24.99)
Hg	$^{202}Hg(n,\gamma)^{203}Hg$	29.86	46.612	279.2 (81.0)

Table 9
Results of standards analysis (ppm, d.l. = at or below detection limit, n.a. = not analyzed)

Element	SSC-1	INAA	ICP-MS	SSC-2	INAA	ICP-MS	SSC-3	INAA	ICP-MS	ICP-MS DL
Ag	18.8 ± 5.81	19.7	14.61	13.9 ± 3.38	13.5	9.59	16.1 ± 3.59	15.2	10.35	0.04
As	1.16 ± 0.483	d.l.	0.3	1.18 ± 0.612	d.l.	0.176	5.45 ± 1.93	6.45	3.744	0.01
Fe	39.2 ± 7.18	n.a.	43.34	31.9 ± 7.05	n.a.	29.09	40 ± 8.82	n.a.	46.21	0.8
Ni	17.6 ± 3.36	n.a.	9.31	3.17 ± 1.04	n.a.	1.33	48 ± 7.68	n.a.	24.49	0.01
Pb	65.3 ± 7.02	n.a.	58.10	6.12 ± 1.20	n.a.	6.65	4.58 ± 1.51	n.a.	4.66	0.006
Se	7.28 ± 1.61	7.2	3.235	2.58 ± 0.821	2.6	0.968	3.87 ± 0.744	3.95	1.334	0.04
Zn	33.3 ± 7.91	31.6	14.62	16.3 ± 5.15	16.9	5.76	15.3 ± 3.60	15.4	4.55	0.02

The relative standard deviation (2σ) for ICP-MS results is between 5 and 10% for Ag, As, Fe, Ni, Pb, and Zn and between 15 and 20% for Se.

and Kletsan Creek, see Fig. 3) in south-central Alaska. All are located within the boundary of Wrangell-St. Elias National Park and Preserve (WRST-NP/P). These three sources are known to have been important to indigenous peoples at the time of EuroAmerican contact. Dan Creek and Chititu Creek both flow into the Nizina River, which in turn, flows into the Chitina River. Both creeks issue from the same ridge system approximately 10–15 km apart. The Chititu Creek material was collected about 13 km upstream from the confluence with the Nizina River on the north side. The Dan Creek material was provided by a placer miner. Kletsan Creek heads in Alaska crosses over into the Yukon and back into Alaska before entering the White River. The Kletsan Creek samples were collected just upstream from where the creek enters the Yukon Territory along a steep streambank.

In addition to the trace element analyses, Pb isotope analysis was performed on seven geological samples of native copper from: Centennial Mine and White Pine Mine in Michigan, the Coppermine River region of the Northwest Territories, Dan, Chititu, and Kletsan Creeks in WRST-NP/P south-central Alaska, and Burwash Creek in southwestern Yukon Territory.

6. Methods

6.1. INAA

CANMET copper metal rod standards SSC-1, SSC-2 and SSC-3 were used for INAA analyses and the NIST (formerly NBS) Standard 158 (phospho-bronze) and CANMET standard CZN-1 were also used for calibration purposes. Source material samples from Kletsan and Dan Creeks were cut using a jeweler's saw with a steel blade. Samples from Chititu Creek were cut using an electric rotary tool with Dedeco Cut-Off Discs (No. 3031). Artifact samples were cut using either a jeweler's saw or wire cutters. All samples were cleaned in aqua regia for 1 min, rinsed in 2× distilled water, and then rinsed in 95% ethanol. Samples were allowed to air dry before being weighed and packaged for irradiation. Samples were irradiated

Table 10
Results of INAA for GUL-077 artifacts (ppm, d.l. = at or below detection limit)

ID	Feature/unit	Description	Ag	Se	As	Hg
GUL077/76-33	77-3-2	By-product, sheet	157	d.l.	184	2
GUL077/76-41	77-3-2	Bipoint	97	d.l.	d.l.	d.l.
GUL077/76-45	77-3-2	By-product, sheet	178	d.l.	d.l.	19
GUL077/76-55	77-3-2	By-product, sheet	139	d.l.	23	4
GUL077/76-64	77-3-2	Blank	52	d.l.	d.l.	d.l.
GUL077/76-73	77-3-3	By-product, sheet	132	d.l.	14	3
GUL077/76-77	77-3-4	Perforator	171	d.l.	136	2
GUL077/76-84	77-3-5	Rectangle	783	d.l.	8	2
GUL077/76-91	77-6-1	By-product, sheet	210	d.l.	12	6
75AMU-1-447	Pit 29	By-product, sheet	260	d.l.	857	41
75AMU-1-457	Pit 29	Knife	227	d.l.	d.l.	1
75AMU-1-473	Pit 29	By-product, sheet	217	d.l.	d.l.	6
75AMU-1-476	Pit 29	Rectangle	159	d.l.	262	6
75AMU-1-652	Pit 50	By-product, sheet	180	d.l.	49	4
75AMU-1-1088	77-4-LB3	Cone	175	d.l.	19	5
75AMU-1-1089	Pit 29	By-product, sheet	158	d.l.	d.l.	d.l.
75AMU-1-1103	Pit 29	By-product, sheet	67	d.l.	485	3
75AMU-1-1104	Pit 29	Nugget, worked	798	d.l.	d.l.	2
75AMU-1-1357	77-5-1	Single point	745	d.l.	d.l.	d.l.
UA95-65-0208	N225 E698	Blade	191	d.l.	5	2
UA95-65-0261	N102 E653	Rectangle	240	d.l.	d.l.	5
UA96-62-0229	N225 E698	Projectile point	114	d.l.	d.l.	d.l.
UA96-62-0230	MDS #54	By-product, sheet	923	d.l.	8	8
UA96-62-0234	MDS #53	Nugget, worked	142	7	d.l.	d.l.

in the SLOWPOKE reactor at the University of Alberta at a nominal thermal neutron flux of 5×10^{11} $n\ cm^{-2}\ s^{-1}$ for either 4 or 6 h (see Table 8 for selected nuclear data for those elements routinely determined in this study). Following irradiation samples were individually counted twice. An initial count was performed for 15–30 min following a decay period of ~1 week following significant decay of ^{64}Cu ($T_{1/2} = 12.70$ h). A second longer (6–24 h) count was performed following a decay period of ~4 weeks. Gamma-ray measurements were carried out using a 22% relative efficiency Ortec hyperpure Ge detector (FWHM 1.81 keV for 1332.5 keV full energy peak of ^{60}Co) housed in a 10 cm Pb cave. The Ge detector was coupled to an Aptec V.4.3 MCArd PC-based multi-channel analyzer. Elemental quantification was performed using the semi-absolute method of NAA (Bergerioux et al., 1979).

As can be seen from Table 8 the INAA determination of Hg, via the 279.2 keV gamma emission of ^{203}Hg, suffers a potential spectral interference from the 279.5 keV gamma emission of ^{75}Se. Where necessary a correction for this spectral interference was calculated and applied using the ratio of the measured ^{75}Se full energy photopeaks.

INAA detection limits are dependent upon the signal to background ratio (Currie, 1968) and vary with individual sample mass, composition, neutron flux, irradiation and counting times, detector efficiency and counting geometry. In this study the mass of samples analyzed varied by about a factor of two (~80 to ~160 mg), and the long counting times were generally within a factor of two-and-a-half (20,000–50,000 s), though in some instances samples were counted for up to 80,000 s (a factor of four difference in counting time). Consequently, no single detection limit for a specific element can be given that applies to all samples. However, using the most commonly utilized analysis conditions guideline detection limits for a typical analysis of a sample of average mass and counting time are listed in Table 9.

6.2. ICP-MS

CANMET copper metal rod standards SSC-1, SSC-2 and SSC-3 were used for ICP-MS and LA-MC-ICP-MS analyses. Copper samples (weighing between ~50 and ~100 mg) were dissolved in 8 N HNO_3 (~5 mL) using Savillex beakers and placed on a hot plate (100 °C) overnight. Solutions were subsequently diluted to a volume of 90 mL (1% HNO_3). Prior to ICP-MS analysis, an internal standard (indium) was added and sample solutions were diluted (with 1% HNO_3) by a factor of 10. Trace elemental concentrations were determined on a Perkin–Elmer Elan 6000 quadrupole ICP-MS.

Instrumental conditions were as follows: RF power of 1200 W; dual detector mode; blank subtraction applied subsequent internal standard correction; measurement units cps (counts per second); auto lens on; four points calibration curve (0, 0.025, 0.050, and 0.100 ppm for Na; 0, 0.25, 0.50, and 1.00 ppm for Ca, Mg, Fe, and K, respectively; 0, 0.005, 0.010, and 0.020 ppm for rest elements); typical count rate for 10 ppb Pb solution 150,000–200,000 cps. The sample uptake rate was approximately 1 mL/min with 35 sweeps/reading, 1 reading/replicate and 3 replicates. Dwell times were 10–20 ms for all elements with the exception of As and Se (100 ms each). The relative standard deviation (2σ level) for Ag, As, Fe, Ni, Pb, and Zn is between 5 and 10%, whereas that for Se is between 15 and 20%.

6.3. LA-MC-ICP-MS

Seven geological samples of native copper (listed above) and the three CANMET copper rod standards were analyzed for Pb isotopes using LA-MC-ICP-MS. All 10 samples were set in a single epoxy mount and polished for analysis. Laser ablation Pb isotopic analyses were obtained using a Nd:YAG UP213 nm laser system (New Wave Research) coupled to the NuPlasma MC-ICP-MS at the University of Alberta Radiogenic Isotope Facility. Fragments of copper artifacts were

Table 11
INAA results for source material (ppm, d.l. = at or below detection limits)

Source	ID	Ag	Se	As	Hg
Detection limit[a]		*1*	*0.5*	*2*	*0.5*
Kletsan Creek	KC-A-1a	350	2	d.l.	d.l.
Kletsan Creek	KC-A-1b	320	1	d.l.	d.l.
Kletsan Creek	KC-A-2	218	3	d.l.	d.l.
Kletsan Creek	KC-A-3	1063	d.l.	d.l.	d.l.
Kletsan Creek	KC-A-4	179	d.l.	d.l.	d.l.
Kletsan Creek	KC-A-5	190	d.l.	d.l.	d.l.
Kletsan Creek	KC-A-6	119	2	d.l.	d.l.
Kletsan Creek	KC-A-7	534	3	d.l.	d.l.
Kletsan Creek	KC-A-8	205	d.l.	d.l.	d.l.
Kletsan Creek	KC-A-9	94	d.l.	d.l.	d.l.
Kletsan Creek	KC-A-10	180	2	d.l.	d.l.
Kletsan Creek	KC-A-11	87	5	d.l.	d.l.
Kletsan Creek	KC-A-12	103	7	d.l.	d.l.
Kletsan Creek	KC-A-13	179	d.l.	d.l.	d.l.
Kletsan Creek	KC-A-14	114	25	d.l.	d.l.
Kletsan Creek	AE-1	62	d.l.	d.l.	d.l.
Kletsan Creek	AE-3	171	d.l.	d.l.	d.l.
Dan Creek	KC-B-1a	124	d.l.	d.l.	3
Dan Creek	KC-B-1b	107	d.l.	d.l.	1
Dan Creek	KC-B-2	117	d.l.	16	28
Dan Creek	KC-B-3	179	d.l.	127	d.l.
Dan Creek	KC-B-4	186	d.l.	d.l.	d.l.
Dan Creek	KC-B-5	76	d.l.	49	2
Dan Creek	KC-B-6	282	d.l.	d.l.	28
Dan Creek	KC-B-7	211	d.l.	d.l.	2
Dan Creek	KC-B-8	334	d.l.	d.l.	58
Dan Creek	KC-B-9	123	d.l.	4	1
Dan Creek	KC-B-10	100	d.l.	d.l.	1
Dan Creek	KC-B-11	66	d.l.	491	2
Dan Creek	KC-B-12	167	d.l.	d.l.	d.l.
Dan Creek	KC-B-13	98	d.l.	9	1
Dan Creek	KC-B-14	141	d.l.	d.l.	6
Dan Creek	KC-B-15	536	d.l.	d.l.	35
Dan Creek	KC-B-16	161	d.l.	237	253
Chititu Creek	KC-E-1	223	d.l.	d.l.	20
Chititu Creek	KC-E-2	45	d.l.	d.l.	2
Chititu Creek	KC-E-3	346	d.l.	d.l.	1
Chititu Creek	KC-E-4	149	d.l.	d.l.	2
Chititu Creek	KC-E-5	78	d.l.	d.l.	d.l.
Chititu Creek	KC-E-6	184	d.l.	14	5
Chititu Creek	KC-E-7	77	d.l.	16	2

[a] See text for details on INAA detection limit.

Table 12
ICP-MS trace element results for source material and artifacts (ppm, d.l. = at or below detection limits)

Source/site	ID	Cr	Fe	Co	Ni	Zn	As	Se	Ag	Cd	Au
Detection limit		*0.01*	*0.8*	*0.006*	*0.01*	*0.02*	*0.01*	*0.04*	*0.04*	*0.01*	*0.08*
Kletsan Creek	K-1	0.89	72.1	0.009	0.34	2.54	0.20	2.13	250	d.l.	0.19
Kletsan Creek	K-2	0.75	60.5	d.l.	0.49	2.26	1.12	0.21	58.8	d.l.	d.l.
Kletsan Creek	K-3	0.61	45.6	d.l.	0.23	1.79	0.03	2.58	377	d.l.	d.l.
Kletsan Creek	K-4	0.62	53.1	d.l.	0.32	1.66	d.l.	1.10	901	d.l.	d.l.
Kletsan Creek	K-5	0.56	48.2	d.l.	0.34	1.90	0.24	7.81	241	d.l.	d.l.
Kletsan Creek	K-6	0.59	67.0	d.l.	0.47	1.93	1.49	0.20	73.1	d.l.	d.l.
Kletsan Creek	K-7	0.56	50.8	d.l.	0.30	1.56	d.l.	0.15	1627	d.l.	d.l.
Kletsan Creek	K-8	0.46	37.8	d.l.	0.18	1.53	0.18	0.92	217	d.l.	d.l.
Kletsan Creek	K-9	0.60	66.4	0.019	0.37	1.76	25.2	0.31	219	d.l.	d.l.
Kletsan Creek	K-10	0.39	35.6	0.025	18.4	1.85	0.01	0.24	681	d.l.	d.l.
Dan Creek	D-1	0.77	41.4	d.l.	0.23	1.42	194	0.34	188	d.l.	d.l.
Dan Creek	D-2	0.38	38.0	d.l.	0.24	1.41	0.26	0.27	316	d.l.	d.l.
Dan Creek	D-3	0.72	119	0.035	0.31	2.01	46.6	0.42	147	d.l.	d.l.
Dan Creek	D-4	0.55	60.5	0.01	0.63	1.63	18.5	0.49	178	d.l.	d.l.
Dan Creek	D-5	0.45	35.7	d.l.	0.19	1.47	1.03	0.33	370	d.l.	d.l.
Dan Creek	D-6	2.28	718	0.547	3.74	2.63	275	10.2	189	d.l.	d.l.
Chititu Creek	C-1	0.48	39.7	0.006	0.20	3.97	3.69	0.32	503	d.l.	d.l.
Chititu Creek	C-4	0.78	72.4	d.l.	0.31	1.96	1.27	0.43	282	d.l.	d.l.
Chititu Creek	C-5	0.42	37.8	d.l.	0.15	1.41	1.86	0.55	156	d.l.	d.l.
Chititu Creek	C-6	0.52	48.4	d.l.	0.31	1.73	4.24	0.45	368	d.l.	d.l.
GUL-077	GUL077/76-41	0.49	48.0	d.l.	0.19	1.50	0.01	0.40	155	0.011	0.16
GUL-077	GUL077/76-73	0.47	48.2	d.l.	0.24	1.57	14.7	0.40	222	d.l.	d.l.
GUL-077	GUL077/76-77	0.53	51.5	d.l.	0.54	1.54	98.2	0.50	240	d.l.	d.l.
GUL-077	75AMU-1-473	0.37	41.5	0.006	0.22	1.59	0.65	0.40	314	0.025	0.11
GUL-077	75AMU-1-476	0.39	37.8	d.l.	0.17	1.34	223	0.41	262	0.01	0.11
GUL-077	75AMU-1-652	0.99	93.4	0.008	0.94	2.88	47.1	0.71	161	0.014	1.07
GUL-077	75AMU-1-1104	1.78	900.6	1.15	4.75	142	1.63	0.54	1113	0.039	0.27
GUL-077	75AMU-1-1089	0.38	80.7	0.077	0.29	1.52	0.08	0.45	233	d.l.	d.l.
GUL-077	UA95-65-0261	0.56	56.3	d.l.	0.20	1.50	0.42	0.56	356	d.l.	0.13
GUL-077	UA96-62-229	0.36	45.1	d.l.	0.63	1.61	0.07	0.37	149	d.l.	d.l.

Source/site	ID	Sb	Cs	La	Eu	Hf	W	Pb
Detection limit		*0.02*	*0.004*	*0.006*	*0.006*	*0.01*	*0.04*	*0.006*
Kletsan Creek	K-1	0.46	0.012	0.013	d.l.	0.037	0.60	0.155
Kletsan Creek	K-2	0.11	d.l.	0.026	d.l.	0.019	0.23	0.061
Kletsan Creek	K-3	0.04	d.l.	0.008	d.l.	d.l.	0.09	0.056
Kletsan Creek	K-4	0.02	d.l.	0.017	d.l.	d.l.	0.16	0.076
Kletsan Creek	K-5	d.l.	d.l.	0.04	d.l.	d.l.	d.l.	0.082
Kletsan Creek	K-6	d.l.	d.l.	0.029	d.l.	0.015	d.l.	0.061
Kletsan Creek	K-7	d.l.	d.l.	0.02	d.l.	d.l.	d.l.	0.031
Kletsan Creek	K-8	d.l.	d.l.	0.017	d.l.	d.l.	d.l.	0.038
Kletsan Creek	K-9	d.l.	d.l.	0.032	d.l.	d.l.	d.l.	0.062
Kletsan Creek	K-10	0.21	0.005	0.01	d.l.	0.015	0.20	0.086
Dan Creek	D-1	0.06	d.l.	0.012	d.l.	0.016	0.07	0.027
Dan Creek	D-2	0.02	d.l.	0.01	d.l.	d.l.	d.l.	0.022
Dan Creek	D-3	0.04	d.l.	0.017	d.l.	d.l.	0.08	0.047
Dan Creek	D-4	d.l.	d.l.	0.008	d.l.	d.l.	d.l.	0.028
Dan Creek	D-5	d.l.	d.l.	0.008	d.l.	d.l.	d.l.	0.013
Dan Creek	D-6	0.04	0.014	0.038	0.011	0.01	0.04	0.066
Chititu Creek	C-1	0.04	d.l.	0.027	d.l.	d.l.	d.l.	0.07
Chititu Creek	C-4	0.04	d.l.	0.055	d.l.	0.071	d.l.	0.08
Chititu Creek	C-5	0.23	0.004	0.023	d.l.	0.026	0.23	0.028
Chititu Creek	C-6	0.14	d.l.	0.047	d.l.	0.017	0.09	0.042
GUL-077	GUL077/76-41	0.06	d.l.	0.008	d.l.	d.l.	d.l.	0.022
GUL-077	GUL077/76-73	0.09	d.l.	0.008	d.l.	d.l.	d.l.	0.322
GUL-077	GUL077/76-77	0.05	d.l.	0.008	d.l.	d.l.	d.l.	0.102
GUL-077	75AMU-1-473	0.14	d.l.	0.014	d.l.	d.l.	d.l.	0.146
GUL-077	75AMU-1-476	0.07	d.l.	0.014	d.l.	d.l.	d.l.	0.087
GUL-077	75AMU-1-652	0.65	0.007	0.013	d.l.	0.055	0.45	0.088
GUL-077	75AMU-1-1104	0.14	0.007	0.144	0.03	0.046	0.15	0.666
GUL-077	75AMU-1-1089	0.05	d.l.	0.006	d.l.	d.l.	d.l.	0.016
GUL-077	UA95-65-0261	0.60	d.l.	0.011	d.l.	d.l.	0.04	0.118
GUL-077	UA96-62-229	0.06	d.l.	0.013	d.l.	d.l.	d.l.	0.089

Table 13
Pb isotopic data for CANMET copper standards

Standard (run)	Spot size (μm) rep. rate (Hz)	206/204 Ratio	1σ Error	207/204 Ratio	1σ Error	208/204 Ratio	1σ Error	207/206 Ratio	1σ Error	208/206 Ratio	1σ Error	Pb ion signal (V)
SSC-1(1)	160, 5	17.59	0.03	15.47	0.02	37.17	0.05	0.8795	0.0001	2.114	0.0003	0.269
SSC-1(2)	160, 5	17.74	0.02	15.62	0.02	37.50	0.05	0.8804	0.0001	2.114	0.0003	0.264
SSC-2(1)	160, 20	17.24	0.06	15.62	0.06	37.12	0.14	0.9057	0.0003	2.152	0.0005	0.107
SSC-2(2)	160, 20	16.97	0.05	15.35	0.05	36.59	0.11	0.9050	0.0002	2.155	0.0005	0.149
SSC-3(1)	160, 20	17.36	0.11	15.66	0.10	37.34	0.23	0.9016	0.0005	2.151	0.0008	0.072
SSC-3(2)	160, 20	17.48	0.11	15.81	0.11	37.61	0.25	0.9038	0.0004	2.151	0.0008	0.072

ablated in a helium atmosphere (1.0 L/min) using the following parameters: 20–40 s ablation time; 160 μm spot size; 20 Hz repetition rate; ~15 J/cm^2 energy density. The sample-out line from the laser ablation cell was 'y'-connected to the sample-out line from the desolvating nebulizing introduction system (DSN-100 from Nu Instruments) to allow for simultaneous aspiration of a dilute Tl solution. The latter was used to monitor and correct for instrumental mass bias of the measured Pb isotope ratios, similar to the procedure described by Simonetti et al. (2005). The Pb and Tl isotope ion signals were measured simultaneously using six Faraday collectors. The accuracy of the analytical protocol was evaluated by repeated analysis ($n = 10$) of an amazonite feldspar in-house standard from the Broken Hill deposit, Australia. The average Pb isotope values obtained were statistically indistinguishable from those previously obtained by TIMS measurement for the ore from the Broken Hill deposit (Gulson, 1984).

7. Results and statistical analysis

The INAA and ICP-MS analysis of CANMET copper standards show a general overall level of corroboration with the standard deviation of recommended values (Table 9). The relative standard deviation (RSD) for ICP-MS results on Ag, As, Fe, Ni, Pb, and Zn is between 5 and 10%, and for Se is between 15 and 20%. The higher uncertainty associated with Se abundance measurement is due to plasma-based interferences in the mass range for Se (e.g., Ar_2 = mass 80; interferes with the dominant isotope of Se – ^{80}Se) and its relatively low ionization potential compared to other elements.

INAA trace element results are presented in Table 10 (artifacts) and Table 11 (source material) and ICP-MS trace element results are listed in Table 12 (artifacts and source material). Both In and Ir were analyzed using ICP-MS but for all of the samples the results were below their detection limits of 0.006 and 0.008 ppm (μg/g), respectively. As noted in other analyses of native copper, the source material analyzed here is very pure (>99.9% Cu), and Ag is ubiquitous, being present in all of the source material and artifacts analyzed. The trace element analyses also confirmed that all of the artifacts analyzed are made of native copper. Only one (75AMU-1-1104 in Table 12) had significant amounts of a number of trace elements, but is still within the range of what could be expected from native copper. In this study the only trace elements consistently detected using INAA other than Ag were Se, As, and Hg. In a few samples elements such as Sb, Cr, Fe and Zn were quantifiable by INAA. However, these data are not reported here because of the rarity of their detection and quantification in the vast majority of samples rules out their routine use for source discrimination. ICP-MS produced results for several trace elements but only Ag, As, Fe, Se, and Zn were detected in amounts greater than 1 ppm.

The use of LA-MC-ICP-MS to obtain Pb isotopic data on native copper was unsuccessful. Though trace amounts of Pb could provide isotopic data, no Pb isotopic data were obtained on any of the native copper samples analyzed, indicating very low levels of Pb. This was corroborated by ICP-MS analyses which demonstrated that of the 30 native copper samples analyzed, four had Pb in amounts between 0.10 and 0.32 ppm while the remaining 26 samples had Pb in amounts ≤ 0.1 ppm (Table 12). The concentration of Pb present in the three CANMET copper standards (65.3 ± 7.02 (SSC-1), 6.12 ± 1.20 (SSC-2), and 4.58 ± 1.51 (SSC-3) ppm Pb: 1σ uncertainties) was sufficient to generate Pb isotopic data by LA-MC-ICP-MS (Table 13). To our knowledge this is the first time Pb isotopic data for these three CANMET copper standards have been reported and therefore provides data for possible future Pb isotopic studies of native or smelted copper. The absence of Pb isotopic data by LA-MC-ICP-MS does not preclude the use of Pb isotopic analysis in future native copper provenance studies. Pb

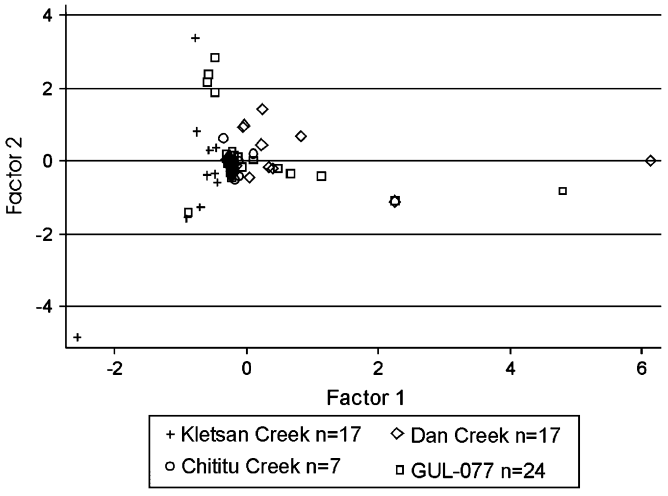

Fig. 4. Principal components factor analysis graph of INAA results using Ag, As, Se, and Hg.

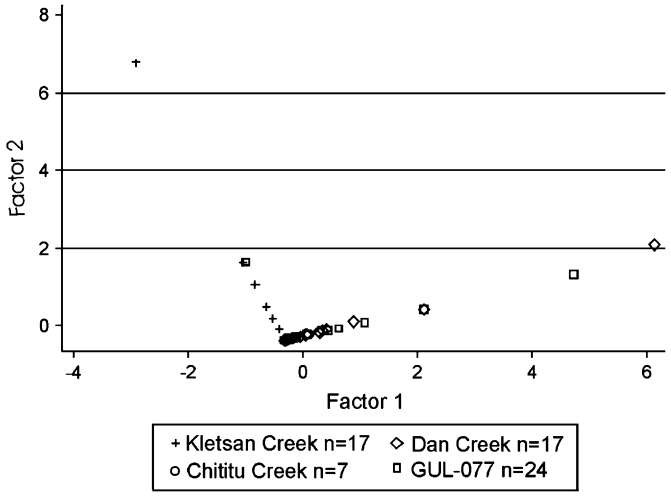

Fig. 5. Principal components factor analysis graph of INAA results using As, Hg, and Se.

isotopic data may potentially be obtained from material with a low abundance of Pb but such analyses will require larger samples (~1 g) and probably require chemical separation of the Pb from other components.

The data analysis program Stata (Intercooled Stata 8.2 for Windows, 2005) was used to perform Principal Components Analysis (PCA). The results of the PCA are plotted in Figs. 4–6. Factor 1 is plotted on the *X*-axis and Factor 2 on the *Y*-axis. Tables 14–16 display the eigenvalues resulting from the PCA.

PCA of the INAA results for Ag, As, Se, and Hg are shown in Fig. 4. Factor 1 has an eigenvalue of 1.30517 (Table 14) and is most heavily influenced by the presence of As and Hg. Factor 2 has an eigenvalue of 1.11504 and is most heavily influenced by the absence of Se and presence of Ag. Fig. 4 reveals the extent to which the four groups under consideration (three sources and the artifacts from GUL-077) overlap, i.e., there is no obvious discernible separation between them.

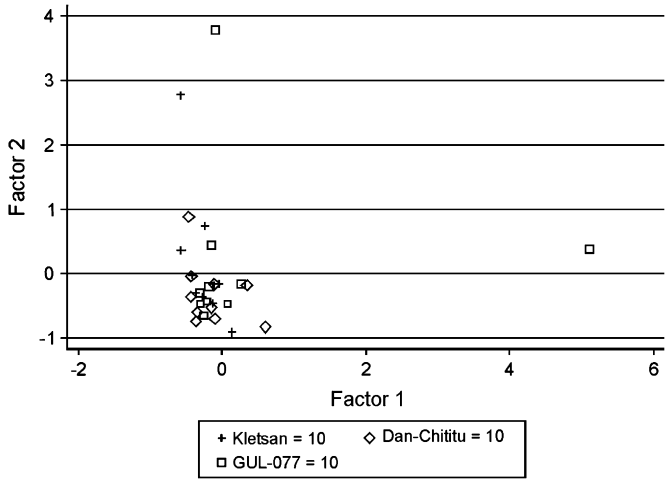

Fig. 6. Principal components factor analysis graph of ICP-MS trace element results.

Because Ag is ubiquitous in native copper, the statistical analysis was performed again using only As, Se, and Hg (Fig. 5). In Fig. 5 Factor 1 has an eigenvalue of 1.28430 (Table 15) and is most heavily influenced by the presence of As and Hg. Factor 2 has an eigenvalue of 0.95361 and is most heavily influenced by the presence of Se. Fig. 5 demonstrates the potential to distinguish the Kletsan Creek material from all of the other samples (Dan and Chititu Creeks and Gulkana artifacts) by applying PCA to INAA data for As, Se, and Hg. Without recourse to statistical analysis an examination of the INAA results (Tables 10 and 11) reveals two groups based on the presence or absence of As and Hg, or Se.

As a result of the geographic proximity and trace element similarity of the Dan and Chititu Creek sources they were treated together as a single source for the PCA of ICP-MS data. Fig. 6 displays the results of PCA using all 19 trace elements for which ICP-MS produced results (Cr, Pb, Au, Ir, W, Hf, Eu, La, Cs, Sb, In, Cd, Ag, Se, As, Zn, Ni, Co, and Fe). Factor 1 has an eigenvalue of 7.64328 (Table 16) and is most heavily influenced by Eu, Co, and Fe and Factor 2 has an eigenvalue of 3.62050 and is most heavily influenced by W and Ir, but as the graph demonstrates, there is no distinct separation of the three defined groups. PCA was performed on two additional sub-sets of the ICP-MS data; one using Fe, Co, Eu, and W and another using As, Fe, and Se. Each of these latter two statistical analyses produced similar results in that each resulted in only a single factor and failed to discriminate between the three defined groups.

8. Discussion

The native copper from Kletsan Creek can be distinguished from Dan and Chititu Creeks on the presence or absence of As, Hg, and Se. The artifacts from GUL-077 more closely resemble the Dan and Chititu Creek material. Due to the large number of unsampled native copper sources in the region encompassing south-central Alaska and southwestern Yukon Territory (Cooper, 2007, see Fig. 2), the assignment of the GUL-077 artifacts to Dan and Chititu Creeks is premature. Kletsan Creek can, however, be ruled out as a likely source for the GUL-077 artifacts. Due to the presence of As and Hg, the two artifacts from the Yakutat Tlingit site of Old Town (YAK-00009) analyzed by Veakis (1979) more closely resemble the Dan and Chititu Creek sources, confirming a trade pattern attested to in ethnohistoric accounts (de Laguna et al., 1964; de Laguna, 1972). However, Veakis reported no data for Se in

Table 14
PCA for INAA corresponds to Fig. 4

Factor	Eigenvalue	Variable loadings			
		Se	Ag	As	Hg
1	1.30517	−0.26763	−0.28771	0.70549	0.58981
2	1.11504	−0.61292	0.73700	−0.13958	0.24834
3	0.90096	0.71146	0.38186	−0.06461	0.58637
4	0.67883	0.21570	0.47774	0.58637	−0.49660

Table 15
PCA for INAA corresponds to Fig. 5

Factor	Eigenvalue	Variable loadings		
		Se	As	Hg
1	1.28430	−0.37755	0.66146	0.64802
2	0.95361	0.92388	0.22189	0.31178
3	0.76209	0.06244	0.71641	−0.69488

his study and there may yet be a source of native copper that has As, Se, and Hg.

According to Franklin et al. (1981), the Gulkana artifacts could be separated into two groups based on the presence ($n = 8$) or absence ($n = 6$) of As, but few geological specimens of native copper were analyzed. Furthermore, citing Broderick (1929), Franklin et al. (1981) cautioned that As concentrations can vary widely within a single native copper deposit. In the present study both INAA and ICP-MS produced results for As for artifacts where none were previously detected (Badone, 1980; Franklin et al., 1981). As a result, the native copper artifacts from GUL-077 constitute a single trace element signature, though there is one potential outlier (UA96-62-0234). The general homogeneity of the native copper artifacts from GUL-077 suggests that they originated from either (1) the Dan/Chititu Creek source, (2) another source with a similar trace element signature, or (3) multiple sources that all share similar trace element signatures.

The origin of native copper found in archaeological contexts on the Northwest Coast has often been attributed to the copper-rich region of the Wrangell and Saint Elias Mountain ranges in south-central Alaska and southwestern Yukon Territory which includes the Chitina and White Rivers. This region corresponds to the traditional territories of the Ahtna and Tutchone Athapaskans, respectively. Ethnohistoric sources describe the movement of native copper from these two Athapaskan groups to people on the coast. However, the extent to which this region has been credited as the source for all native copper found in archaeological contexts throughout the Northwest Coast may be an exaggeration. Native copper was potentially available further south and it appears earlier in the archaeological record of British Columbia than in Alaska or the Yukon Territory.

Table 16
PCA for ICP-MS corresponds to Fig. 6

Factor	1	2	3	4
Eigenvalue	7.64328	3.62050	2.43786	1.36473
Variable loadings				
Cr	0.79355	−0.14993	0.52562	−0.07022
Pb	0.81219	−0.10669	−0.34088	−0.12266
Au	0.36434	0.66522	0.03718	−0.40575
Ir	0.02477	0.80431	−0.10815	0.26264
W	0.34339	0.87603	0.15278	0.06617
Hf	0.51781	0.44708	−0.00977	−0.33430
Eu	0.94510	−0.28227	−0.04903	0.00417
La	0.83977	−0.26565	−0.21549	−0.08158
Cs	0.63048	0.40667	0.56058	0.24345
Sb	0.22545	0.75880	0.07422	−0.28288
In	0.67499	0.49863	−0.17999	0.36632
Cd	0.73101	−0.02897	−0.34155	−0.26460
Ag	0.37393	−0.14636	−0.44595	0.41178
Se	0.24030	−0.19285	0.75881	0.14763
As	0.11974	−0.27844	0.72856	−0.12238
Zn	0.89326	−0.18197	−0.35744	−0.02784
Ni	0.30574	0.13131	0.02905	0.66164
Co	0.93857	−0.30956	0.02435	0.02144
Fe	0.90195	−0.32665	0.23785	−0.00471

The sourcing work of Goad (1980) and Levine (2006, 2007) has proven false the assumption that artifacts of native copper found throughout southeastern and northeastern North America were all derived from Great Lakes sources. The extent to which sources on the southern Northwest Coast were used by indigenous peoples is unknown but Tsimshian oral history attests to the presence of copper on the Skeena and Cassiar Rivers (Boas, 2002). Similar to the situation in eastern North America, the presence of local sources of native copper should discourage the assumption that all archaeological native copper on the Northwest Coast was derived from Alaska and the Yukon Territory.

9. Conclusion

Of the three methods employed in this study INAA proved to be the most useful for discriminating between groups of native copper source material and artifacts. Though ICP-MS obtained results for more trace elements, the inability to analyze for Hg due to its presence in the Ar (plasma) gas precluded the use of an element (Hg) that INAA demonstrated to be useful. An additional important finding of the provenance research was the demonstration that Pb isotopic analysis is unlikely to be of use in discriminating between sources of native copper in Alaska due to the very low levels of Pb ($\leq$0.1 ppm) present. Though Pb as a trace element should not be ruled out in the future for discriminating between sources.

The provenance work reported here has demonstrated the potential to discriminate between different native copper source areas (i.e., stream drainages) intra-regionally based on trace element analysis. Overall, the results of this and earlier studies (Franklin et al., 1981; Veakis, 1979; Wayman et al., 1985) demonstrate the difficulty of native copper provenance work in northwestern North America. Franklin et al. (1981: p. 14) found that both geological specimens and artifacts from the Arctic and Subarctic groups had a ‘‘high degree of uniformity’’ with regard to trace elements. Not all sources of native copper have a unique trace element signature and subsequently, the scale at which native copper provenance studies focus must be geographically realistic (Rapp et al., 2000).

The determination of provenance, or even elimination of sources, for native copper artifacts in northwestern North America will require analyses of additional source material in order to assess the amount of trace element signature variation both intra- and inter-regionally. Analyses of geological specimens of native copper from south-central Alaska, southwestern Yukon, British Columbia, and the central Canadian Arctic and Subarctic, will be necessary to demonstrate the scale at which native copper can be sourced within greater

northwestern North America. Accessing numerous remote sources of native copper in the wider region is a major challenge for further provenance studies (Cooper, 2007); though previously collected material (e.g., Rapp et al., 1990) may be sufficient for assessing intra-regional variability. The ability to differentiate native copper from these three regions would help to address questions concerning the trade and exchange of native copper artifacts and raw material and the invention and/or diffusion of native copper technology in greater northwestern North America.

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