Accepted Manuscript

LA-ICP-MS Analysis of Quartzite from the Upper Gunnison Basin, Colorado

Bonnie L. Pitblado, Molly Boeka Cannon, Hector Neff, Carol M. Dehler, Stephen T. Nelson

PII: S0305-4403(12)00510-9

DOI: 10.1016/j.jas.2012.11.016

Reference: YJASC 3504

To appear in: Journal of Archaeological Science

- Received Date: 30 December 2011
- Revised Date: 2 November 2012
- Accepted Date: 26 November 2012

Please cite this article as: Pitblado, B.L., Cannon, M.B., Neff, H., Dehler, C.M., Nelson, S.T., LA-ICP-MS Analysis of Quartzite from the Upper Gunnison Basin, Colorado, *Journal of Archaeological Science* (2013), doi: 10.1016/j.jas.2012.11.016.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Highlights

LA-ICP-MS Analysis of Quartzite from the Upper Gunnison Basin, Colorado (Pitblado et al.)

- 402 samples of quartzite from 48 sources in the Upper Gunnison Basin were systematically sampled in the field and analyzed using LA-ICP-MS to determine the degree to which the sources can be discriminated from one another.
- The long-term goal of discriminating the sources is to use the protocols developed to "source" quartzite tools and debitage by evaluating their degree of similarity vis-à-vis profiled quartzite sources.
- The study assemblage provides a comprehensive and reliable estimate of the range of compositional variability in Upper Gunnison Basin quartzite.
- Results show spatial and geochronological trends in quartzite elemental composition that can be exploited in the future in the Upper Gunnison Basin and perhaps more widely in the world.
- A different methodological approach must be taken to sourcing culturally modified quartzite than is used in traditional and widely applied obsidian sourcing studies.

LA-ICP-MS Analysis of Quartzite from the Upper Gunnison Basin, Colorado

Bonnie L. Pitblado^{a*} Molly Boeka Cannon^b Hector Neff^c Carol M. Dehler^d Stephen T. Nelson^e

^a Anthropology Department, Univ. of Oklahoma, 455 W Lindsey, Dale Hall Tower 521, Norman, OK 73019, USA
^b Anthropology Program, Utah State University, 0730 Old Main Hill, Logan, UT 84322, USA
^c Institute for Integrated Research in Materials, Environments and Society, California State University, Long Beach, 1250 Bellflower Blvd., Long Beach, CA 90840-1003, USA
^d Geology Department, Utah State University, 4505 Old Main Hill, Logan, UT 84322, USA
^e Geology Department, Brigham Young University, S-389 ESC, Provo, UT 84642

Abstract

We report the results of LA-ICP-MS analysis of 402 quartzite samples representing 48 collection loci in the Upper Gunnison Basin (UGB), Colorado and determine the extent to which the sources can be geochemically discriminated from one another using this non-destructive technique. The ability to differentiate among the sources would open the door to provenance studies of the quartzite chipped-stone tools and debitage that constitute 95% or more of most of the 3,000-plus prehistoric site assemblages documented in the UGB. Our samples represent prehistorically quarried and non-quarried quartzite sources, including outcrop (primary) and gravel (secondary) deposits. The results reveal spatial and chronological trends in quartzite elemental composition that can be exploited for provenance determinations of quartzite artifacts from UGB sites, albeit using an assemblage-based sourcing strategy that differs from the familiar approach of "matching" obsidian artifacts to its statistically likeliest geological source. We offer a preliminary version of a sourcing protocol for UGB quartzite.

Keywords: Laser ablation; ICP-MS; Quartzite; Gunnison Basin, Colorado; Artifact sourcing; Provenance

1. Introduction

^{*} Corresponding author. Tel.: +1 405 325 2490. Fax: +1 405 325 7386. *E-mail addresses*: <u>bonnie.pitblado@ou.edu</u> (B.L. Pitblado), <u>molly.cannon@usu.edu</u> (M.B. Cannon), <u>hneff@csulb.edu</u> (H. Neff), <u>carol.dehler@usu.edu</u> (C.M. Dehler), <u>steve_nelson@byu.edu</u> (S.T. Nelson)

Archaeologists working around the world use stone-sourcing data to reconstruct how humans and tool-making hominids moved across the landscape (e.g., Odell, 2000, 2004). Investigators invoke the movement of stone from geologic source to archaeological site as a proxy for the movement of the people who handled it. However, such studies have traditionally focused on volcanic and microcrystalline materials to the virtual exclusion of one of the most commonly used rock types everywhere: quartzite. As we have reported elsewhere (Pitblado et al., 2008), the number of researchers who have published attempts to differentiate one source of quartzite from another using any method is in the single digits (e.g., Church, 1996; Elbright, 1987; Julig, Pavlish and Hancock, 1987; Schneider, 2006; Stross, 1988).

In this paper, we report the results of LA-ICP-MS analysis of 402 samples of quartzite from 48 collection loci in the Upper Gunnison Basin (UGB), Colorado (Fig. 1). A pilot study of 20 culturally modified quartzite samples (Pitblado et al., 2008) previously suggested that some degree of geochemical discrimination among UGB quartzite sources would be possible, a finding with important archaeological implications locally and world-wide. The study reported here constitutes the logical next step to the pilot study results: determining the degree to which geochemical variation in UGB quartzite units show sufficient patterning to permit assessments of where quartzite used by prehistoric UGB occupants could (and could not) have been procured.

1.1. Archaeology of the Upper Gunnison Basin

More than 3,000 prehistoric sites have been recorded in the $11,000 \text{ km}^2 \text{ UGB}$, spanning the time from Folsom, 10,500 - 10,000 radiocarbon years before present (rcybp), through the protohistoric Ute era. Because the UGB is a high-altitude Rocky Mountain basin with elevations ranging from 2200 - 4300 m and a very short growing season, the region has always been the purview of mobile hunter-gatherers. On the other hand, UGB geography (e.g., limited entry points for game and people) and environmental diversity rewarded foragers with many economically useful floral and faunal resources that varied with elevation, season, and climate.

Because the prehistory of the UGB is a story of shifting but always mobile land use, archaeologists require a tool kit that permits them to track the movement of people who left behind little but chipped stone tools and debitage. Recent Utes occasionally made pottery, but like all who preceded them in the Basin, their sites are dominated by chipped-stone artifacts.

The assemblages of UGB occupants throughout prehistory consist of quartzite tools and debitage in percentages often exceeding 95% (Pitblado 2002; Stiger 2001, 2006). This poses a challenge to archaeologists attempting to reconstruct land use strategies across time and space in the UGB: the lack of a geochemical (or any) sourcing strategy to support affiliating culturally modified quartzite recovered at archaeological sites with one of the Basin's many sources of quartzite.

Great Basin archaeologists and others working in regions where obsidian dominates forager assemblages have long exploited geochemical sourcing to develop and substantiate detailed interpretations of prehistoric mobility (e.g., Arkush and Pitblado, 2000; Beck and Jones 1990, 2010; Hughes, 1992; Shackley, 1995). Where this has occurred, sophisticated questions about hunter-gatherer behavioral change across time and space have been effectively addressed (e.g., Beck et al., 2002; Jones et al., 2003). Not so in in the UGB. As a result, archaeological reconstructions of Basin prehistory to date can be fairly critiqued as rudimentary (e.g., Stiger, 2001), despite evidence for more than 10,000 years of intensive and dynamic prehistoric use (Lipe and Pitblado, 1999; Reed and Metcalf, 1999; Stiger, 2006).

1.2. Pilot study of the potential to discriminate among Upper Gunnison Basin quartzite sources

Recently (Pitblado et al., 2006, 2007, 2008), we conducted a small-scale study to assess the potential for discriminating one source of quartzite from another in the UGB. We analyzed 20 total quartzite samples, 8 from a Middle Archaic level at the multi-component Chance Gulch site (e.g., Pitblado, 2002; Stamm et al., 2004) and 12 from geological quartzite sources located both within one km of the Chance Gulch site and hundreds of km away.

We divided each of the samples into 6 sub-samples and analyzed the sub-samples using petrography, ultraviolet fluorescence, instrumental neutron activation analysis (INAA), wavelength-dispersive x-ray fluorescence, acid digestion inductively coupled mass spectrometry (AD-ICP-MS) and laser ablation ICP-MS (LA-ICP-MS). Although the sample was small (n = 120 tests), INAA, AD-ICP-MS, and LA-ICP-MS successfully discriminated rocks from different sources and hinted at affiliations between Chance Gulch flakes and nearby quartzite sources. Because a goal of the Gunnison Basin archaeological research program is to lay the groundwork for sourcing culturally modified quartzite found across the UGB landscape, the fact that LA-ICP-MS is essentially non-destructive gives it a distinct advantage over AD-ICP-MS and INAA (see

Giusanni et al., 2009; Neff, 2012; Resano et al., 2010, 2012; and Speakman and Neff, 2005 for examples and summaries of other recent applications of LA-ICP-MS). That is the reason we applied the LA-ICP-MS method to the larger study reported here.

Quartzite is a granular sedimentary or metamorphic rock that sometimes fractures conchoidally and can thus be suitable for production of chipped stone tools (Howard, 2005; Pitblado et al., 2008; Rapp, 2002). It occurs commonly in the mountains as bedrock outcrops and in drainages that move the material downstream, and it has long been economically important to people throughout the Rocky Mountains (e.g., Black, 1991; Brunswig and Pitblado 2007; Church, 1996; Pitblado, 1993, 1998, 1999, 2000, 2003). Although quartzite is generally considered to consist of nearly pure silica, our pilot study showed UGB quartzite to be considerably "dirtier" (i.e., higher in constituents other than silica) than microcrystalline silicates such as chert, flint and chalcedony (Luedtke, 1978, 1979; Pitblado et al., 2008).

Enrichment of components other than silica arises from incorporation of grains other than quartz (e.g., feldspars) and from the siliceous cement that binds the quartz grains together. Because of its variable mineralogy, Pitblado et al., (2008) concluded that petrography may offer a complement to geochemical techniques for quartzite source discrimination. To determine the degree to which this is the case in the UGB, petrographic analysis continues for a subset of the 402 samples sourced using LA-ICP-MS, and we will present those results in a separate paper. We focus here on UGB quartzite geochemistry, because for those pursuing archaeological provenance studies, any non-destructive technique—if its data alone provide adequate source-discrimination power—is preferable to a technique that inflicts sample damage, as petrography does. That said, Section 5.1 offers a glimpse as to how petrographic analyses can yield data capable of cross-checking and refining geochemical results.

2. Methodology

2.1. Field collection methods

The collection area covers most of the UGB and is centrally located (Fig. 1). The project area is within Gunnison County, with the exception of the headwaters of Chance Gulch, which is in Saguache County. Major geographic features in the study region include West Elk Peak, West

and East Elk Creeks, Tenderfoot ("W") Mountain, Flat Top Mesa, Fossil Ridge, Chance Gulch, Blue Mesa Reservoir, Taylor Park Reservoir, Huntsman Mesa, Tomichi Creek, and the Gunnison River. We sampled bedrock outcrop (primary) and gravel (secondary) quartzite exposures in and around these features (Fig. 1), focusing on three landscapes in particular (while still sampling widely throughout the UGB): Chance Gulch (e.g., Pitblado, 2002; Stamm et al., 2004); quartzite quarry 5GN1 (Stiger, 2001) west of Gunnison; and the Parlin region east of Gunnison.

We targeted outcrop and gravel source areas for several reasons. First, prehistoric residents of the UGB quarried both source types equally. An effective method for associating artifacts with sources must account for the presence of both. Second, the gravel deposits provide a natural means to sample a robust range of quartzite in the UGB, past and present, because the gravels traveled to their current locations from various upstream locales through time. In the case of ancient (e.g., older Tertiary) gravel deposits, for example, we can sample quartzite that once cropped out in the UGB high country, but due to tectonic, volcanic or erosional change in this geologically active region no longer does. Finally, we could reasonably expect from the outset—and test during analysis—that trace-element signatures for the two source types will differ in nature, because UGB gravels typically derived from multiple quartzite outcrops as they formed, whereas primary outcrops are discrete geologic units. Gravels are therefore expected to show greater trace-element diversity as depositional units than any quartzite outcrop, a point with implications for archaeological provenance studies.

We located quarried outcrops through a Colorado State Historic Preservation Office (SHPO) site records search and non-quarried (or non-recorded) outcrops using geologic maps of the UGB. The maps indicated the following quartzite-bearing units in the UGB: Precambrian metaquartzite (DeWitt et al., 1985; Hedlund and Olson, 1974; Olson 1976 a, b; Zech, 1988); Cambrian Saguache orthoquartzite (DeWitt et al., 1985, 2002; Streufert, 1999; Zech, 1988); Jurassic Junction Creek locally quartzitic sandstone and Cretaceous Morrison Dakota formation orthoquartzite (DeWitt et al., 1985, 2002; Streufert, 1999; Zech, 1988); Jurassic Morrison and Cretaceous Burro Canyon, Dakota and Mesa Verde formation conglomerates with quartzite clasts (Gaskill, 1977; Gaskill et al., 1987, 1988; Hedlund and Olson, 1974; Olson, 1976a; Streufert, 1999); Cambrian Peerless formation contact-metamorphosed orthoquartzite (DeWitt et al., 1985, 2002; Zech, 1988); and gravels, discussed below.

The team located at least one exposure, and often several exposures of each of the aforementioned quartzite-bearing units (Table 1). We used a Jacob's staff to measure an outcrop in prescribed vertical increments, collecting fist-sized samples at each increment. We then transected exposures laterally, intending and sometimes managing to systematically sample at fixed horizontal spacing. However, many outcrops proved so laterally variable—grading from friable sandstone to well cemented quartzite and back—that we collected quartzite wherever it occurred within a given outcrop (although always controlling our vertical sampling interval).

To locate cobbles in secondary settings such as alluvial fans and glacial moraines, we used SHPO records to identify previously recorded quarries and geologic maps identifying Tertiary and Quaternary gravels or gravel-bearing features (DeWitt et al., 1985, 2002; Gaskill et al., 1987; Olson, 1976a; Streufert, 1999; Tweto, 1987; Zech, 1999). The mostly stream-laid (but occasionally glacial) cobbles required a different sampling strategy than outcrops. Upon locating a quartzite-bearing gravel deposit, we laid a 30-m tape along an east-west or north-south axis. At 1-m intervals, we tested the cobble under or nearest the tape (looking right and then left up to 10 cm) and recorded it as metamorphic, igneous, non-quartzitic sandstone, quartzite, or absent. If quartzite, we removed a fist-sized sample; 10 per transect (Table 1).

When we collected 10 samples before reaching the 30-m mark, we continued recording rock-type data to 30 m for later evaluation of intra- and inter-gravel deposit variability in UGB gravel quarries. If we did not encounter 10 quartzite samples within 30 m, we continued along the same axis for another 30 m, and occasionally, yet another 30 m. In no case did we need more than 90 m to collect 10 quartzite samples from gravels, and in each instance we recorded rock type at every meter along the complete transect length.

Table 1

Study sources, geologic settings, numbers of samples/locus (# analyzed), and locations

Collection Locality	Geologic Context	No. Samples Collected	UTM Easting	UTM Northing					
	OUTCROP SOURCES								
SC09-4	Precambrian Black Canyon schist (p E bh)	3	307911	4251680					

Collection Locality	Geologic Context	No. Samples Collected	UTM Easting	UTM Northing				
BP09-5	Paleoproterozoic	2	336915	4264148				
SC09-27-Xqt	Paleoproterozoic quartzite (Xqt) dikes	9	324484	4260309				
SC09-23	Cambrian Saguache (E s)	10	359918	4282250				
BF09-7	Jurassic Junction Creek (Jj)	3	313980	4260326				
SC09-1	Jurassic Junction Creek (Jj)	7	314982	4259746				
SC09-10	Jurassic Junction Creek (Jj)	14	320669	4239062				
SC09-25	Jurassic Junction Creek (Jj)	6	310597	4258868				
SC09-26	Jurassic Junction Creek (Jj)	4	317625	4260356				
SC09-11	Jurassic Entrada (Je)	9	338846	4298849				
SC09-5	SC09-5 Jurassic Junction Creek (Jj)		314163	4259679				
SC09-7	SC09-7 Jurassic Junction Creek (Jj)		315084	4260106				
SC09-18	209-18 Jurassic Junction Creek (Jj)		343240	4256751				
SC09-21	C09-21 Jurassic Entrada (Je)		336826	4306411				
SC09-20	Jurassic Morrison (Jm)	7	336737	4307122				
SC09-19	SC09-19 Cretaceous Dakota/Burro Canyon (Kdb)/ Jurassic Morrison (Jm)		358241	4260577				
BP09-1	Cretaceous Dakota/Burro Canyon (Kdb)	5	348774	4265520				
CD09-3	Cretaceous Dakota/Burro Canyon (Kdb)	9	349293	4265522				
CD09-4	Cretaceous Dakota/Burro Canyon (Kdb)	4	348387	4264728				
CD09-5	Cretaceous Dakota/Burro Canyon (Kdb)	3	348212	4264921				
COBBLE SOURCES								
5GN1982	Gravel deposit, age unknown	10	340332	4263394				
5GN2269	5GN2269 Gravel deposit, age unknown		323834	4267568				
5GN3510	Gravel deposit, age unknown	10	323549	4267736				
5GN840	Tertiary gravel deposit (Tg)	10	335672	4265014				

Collection Locality	Geologic Context	No. Samples Collected	UTM Easting	UTM Northing
5GN850-1	Gravel deposit, age unknown	10	336833	4264861
5GN850-2	Gravel deposit, age unknown	10	336473	4265764
5GN850-3	Gravel deposit, age unknown	10	336207	4265019
5GN850-4	Gravel deposit, age unknown	10	336565	4264266
5GN852	Gravel deposit, age unknown	10 (9)	337057	4264422
5GN852-2	Gravel deposit, age unknown	10 (9)	337309	4264144
5GN901	Gravel deposit, age unknown	10	337551	4264410
BF09-4	Tertiary gravel deposit (Tg)	10	328108	4264371
BP09-2	Quaternary fan (Qf) gravels	10	318634	4238765
BP09-4	Gravel deposit, age unknown	10	323691	4269384
BP09-6	Gravel deposit, age unknown	10	345670	4287319
BP09-8	Quaternary (lf) gravels	10	335348	4305043
CD09-2	Gravel deposit, age unknown	10	350394	4265573
MP09-1	Tertiary gravel (Tg) deposit	10 (9)	308360	4244741
SC09-12	Quaternary (Qg3/Bull Lake) gravels	10	336383	4296888
SC09-13	Quaternary alluvium (Qa) gravels	10	336212	4296760
SC09-2	Tertiary (Tw) gravels	10	335542	4269157
SC09-22	Modern River Gravels	10	336515	4306335
SC09-24	Quaternary debris flow (Qdb) gravels	10	340310	4282031
SC09-3	Quaternary fan gravels	10	316690	4252721
SC09-6	Gravel deposit, age unknown	10	315020	4260051
SC09-8	Tertiary gravel and Tw deposit	11	337270	4273843
SC09-9	Tertiary gravel and Tw deposit	10	340894	4274238
VW09-1	Contemporary Taylor River gravel	3	364265	4299840

We conclude our discussion of project methodology with a note on quartzite identification. In theory, quartzite looks nothing like other major rock types such as obsidian or chert, and archaeologists routinely characterize artifacts as quartzite on site forms. In practice, however, we learned that when closely scrutinizing samples for their eligibility for a study of "quartzite" variability per se, attribution of rock type can be less straightforward. One person's well indurated sandstone is another's quartzite, and missing a crystalline grain in a fresh exposure can introduce a grainy igneous rock into a quartzite database. Additionally, there is the issue of how prehistoric people evaluated potential lithic raw materials: it is unlikely that they contemplated the origin and taphonomic history of a durable ("grainy") core candidate; they either could or could not control how it fractured and knapped materials accordingly.

Predictably, our field collection database therefore includes samples that upon closer examination in the lab fell outside the spectrum of geologic "quartzite." We left such samples *in* the database, but we indicated their "closer-look" status in a distinct data column. We did this because while our goal is indeed to discriminate among "quartzite" sources, our field identifications likely best approximate a *behavioral* definition of quartzite, and it is, after all, human behavior that we aim to better understand by developing a sourcing protocol. However, it also made sense for some analyses to restrict our database to samples that qualified as quartzite from a geologic perspective. Part I of our analysis (Section 3.1) included the complete "behaviorally—looks like it/acts like it—quartzite" database (n = 402 samples), while Part II (Section 3.2) used the more conservative subset of "geological quartzite" samples (n = 355) for reasons that will become clear.

2.2. Laboratory methods

When we returned from the field, we divided each individual fist-sized sample into three smaller samples, one each for LA-ICP-MS analysis, petrographic evaluation, and an archive for future research. Co-author Dehler assumed control of the petrographic samples, having them thin-sectioned and proceeding on to petrographic analysis. We will touch on preliminary petrographic data, as noted, in Section 5.2 and report full results in a future paper. We submitted samples for LA-ICP-MS to co-author Neff of the Institute for Integrated Research on Materials, Environment and Society (IIRMES), at California State University, Long Beach.

IIRMES personnel tallied and created individual, unique sample IDs by combining the USU site designation and sample ID. IIRMES found a few cases of improper or unclear labeling, and they removed these samples from the database. Lab technicians prepared each quartzite sample for LA-ICP-MS analysis by removing two pieces and mounting each one separately on microscope slides, with a fresh break exposed for analysis. Each individual piece underwent analysis three separate times, for a total of six analyses per sample.

LA-ICP-MS analysis was undertaken on the IIRMES GBC Optimass TOF ICP-MS instrument. Duwe and Neff (2007) and Neff (2010, 2012) have described TOF technology and its advantages for LA-ICP-MS in archaeology. As a microprobe, the basic advantage of the TOF over conventional ICP-MS instruments is that the speed of data acquisition—30,000 full spectra collected per second in the GBC Optimass—permits high-sensitivity, high-precision analysis of even small particles, which would be consumed by the ablation with the longer data acquisition times required for quadrupole or magnetic-sector instruments (e.g., Neff and Sheets, 2005).

In this study, IIRMES staffers ablated samples in a helium atmosphere with a New Wave UP213 laser ablation system. Spots 75 microns in diameter were ablated with the laser set at 60% power and firing ten times per second. Signal intensities were averaged over five two-second integrations measured by the TOF during each ablation.

The LA-ICP-MS intensity data were calibrated to parts per million using NIST glass standards SRM614, SRM612, and SRM610 along with Little Glass Buttes obsidian. The NIST glasses are appropriate for the rare earth elements and many other trace elements, and the obsidian extends the range of concentration values for magnesium, potassium, manganese, iron, and barium in order to achieve more accurate values for these elements.

Neff (2010) has described the basic IIRMES approach to data calibration, a variation of one developed by Gratuze (1999). It involves fitting standardized concentrations (ratios to silicon, monitored at mass 30) in the standards to standardized counts (ratios of raw counts to raw silicon counts in the standard). That is, is the standardized signal for element y (subscript "is" indicates internal standard) is:

$$SS_{y} = \frac{Signal_{y}}{Signal_{is}}$$

And the standardized concentration for element y is:

$$SC_y = \frac{Conc_y}{Conc_{is}}$$

Using the external standards, regression of SC_y on SS_y for each element yields parameters (slope, *K* and intercept) for calculating the standardized concentrations, SC_y , in the unknowns. In principle, the regression line should pass through zero, and experience has shown that forcing the regression through zero yields the best results. With the intercept constrained to be zero, the slope, *K*, can now be used to calculate SC_y in the unknowns by:

$$SC_y = K(SS_y)$$

And, since SC_y is defined as the actual concentration divided by the internal standard concentration, the internal concentration of each analyte can be determined by dividing through by the internal standard concentration:

$$Conc_y = K_y(SS_y)Conc_{is}$$

Further, one can ratio each side of the above equation to the total of all *m* elements measured in the sample, as follows:

$$\frac{Conc_{y}}{\sum Conc_{i}} = \frac{K_{y}(SS_{y})Conc_{is}}{\sum_{i=1}^{m} K_{i}(SS_{i})Conc_{is}}$$

Gratuze (1999) recognized that in geological materials the elements that form rocks and minerals occur as oxides, so if it can be assumed that all of the constituents of the rock or mineral have been analyzed, the denominator on the left must equal 100% once the concentrations are converted to oxides. The concentration of the internal standard also drops out, giving:

$$Conc_{yox} = \frac{O_{y}K_{y}(SS_{y})}{\sum_{i=1}^{m}O_{i}K_{i}(SS_{i})} 100\%$$

where the O_is represent the element-specific oxide conversion factors. If concentrations are in ppm, as in this case, the multiplication is by 1 million rather than 100%. The resulting oxide concentrations can also be divided by the O_is in order to express the data as ppm-element rather than ppm-oxide.

IIRMES lab personnel ran standards after every 25 unknown samples (approximately every 45 minutes) to account for instrument drift. Each batch of 25 unknowns was then calibrated using average standardized signal (*SS_i*) values obtained from bracketing sets of standards. Background was removed by collecting a blank along with every set of standards, then subtracting the average of bracketing blank values from signal intensities for both the unknowns and standards. All four external standards were used to calculate the *Ky* values for the elements Li, Be, Na, Mg, Al, Si, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, R, Au, Tl, Pb, Bi, Th, and U.

A total of 2464 valid analyses were obtained on the 402 samples. In a number of cases, one of the six replicate analyses was invalid, and averages were calculated on fewer than six analyses. Microsoft Excel data files catalog separate tabulations for the 2464 analyses; the averages from each separate piece from each rock; and the average from all six analyses of each rock. The latter worksheet is digitally archived at (insert URL for data archive) for other researchers to access. With some exceptions early in the sequence, the six analyses for each rock have suffixes A1 through A3 and B1 through B3 for the two pieces.

The essential question addressed in our study is whether geochemical variation in UGB quartzite shows sufficient patterning to permit an assessment of where the quartzite used prehistorically to manufacture artifacts may have been procured. Geographical patterning can be evaluated directly by monitoring the extent to which elemental concentrations or dimensions derived from them (e.g., principal components) correlate with spatial variables, such as site designation, geological formation, or UTM coordinates. Alternatively, pattern recognition techniques coupled with other statistical approaches can identify subgroup structure in the data, and the subgroups can be evaluated according to whether they show non-random distributions in space. We used both approaches, and each yielded evidence of meaningful structure in the data.

3. Results and Discussion

3.1 Evaluation of sources by trace-elements and dimensions derived therefrom

Our evaluation of elemental concentrations in the UGB sources took as its basic unit of analysis averaged trace-element concentrations for the 48 locales and approached them first collectively and then as two distinct data sets consisting of outcrop (n = 20) and cobble (n = 28) sources respectively. For each data set, we conducted principal components analyses (PCA) to determine how much inter-source geochemical variability the trace elements measured could explain. Although we conclude from the results of all three analyses that geochemical signatures are not unique to individual quartzite sources in the UGB, we can also conclude that the UGB quartzite data are structured in ways that point to potential for archaeological sourcing.

In our first pass through the data, we focused on the complete 48-source data set, again with trace-element values averaged for each source. Our PCA showed that 10 components account for 92% of the variability among all sources, with PC1 accounting for the majority (46%) of that total. PC2, for reference, accounted for 12% of variability. A cluster analysis of all sources based on the PCA (Fig. 2) revealed a separation between outcrop and cobble sources, with the latter nearly all captured by the largest cluster. Although 7 outcrop sources cluster with the 28 cobble sources, the distinction between the two source types is nonetheless relatively sharp. The anomalies represent samples that can be explored in the future at finer scales of analysis and also through petrographic evidence.

The reason the two kinds of quartzite sources divide as clearly as they do becomes apparent through an examination of a biplot derived from the principal components of the entire (non-averaged) data set (Fig. 3). The plot shows that PC1 expresses correlated enrichment of many trace elements. Fig. 4 shows that scores on this component are patterned geographically in the UGB, with the central and northern regions characterized by higher scores and the east- and west-central areas characterized by lower scores. Cobble sources, by virtue of their multipleoutcrop-source origins, show enriched trace-element variability when sampled as an assemblage and with trace-element composition averaged across the assemblage. Bedrock sources show depleted trace-element signatures relative to the gravels, due to their more homogenous nature.

Having demonstrated that outcrop and cobble sources show distinctly different traceelement compositions even when they can look alike, we next evaluated the two databases

independently to establish whether and how sources within each group can be discriminated from one another. We began with outcrop sources, which showed depleted trace-element signatures compared to cobble sources. As with the complete database, we ran a PCA of the outcrop data averaged by source and then performed a cluster analysis of those data. The PCA indicates that six components account for 100% of the geochemical variability in the sample, with PC1 and PC2 accounting for 46% and 21% of variability, respectively, and PC6 for 3%. A complete-linkage dendrogram shows ordering, and in one case true clustering, of outcrop sources by geological age: Precambrian versus Jurassic versus Cretaceous (Fig. 5).

The grouping is imperfect, with two Cretaceous-aged sources (CD09-3 and CD09-5) aligning with the Jurassic-aged sources; however, geologic age undeniably plays a role in structuring the geochemical signatures of UGB quartzite outcrops. Figure 4 shows the 20 sampled UGB outcrop sources (the blue "O"s on the map) labeled by geologic age. The clustering within the Jurassic samples (Fig. 5), suggests that future, more in-depth analysis may permit additional discrimination among sources, possibly again by age (within the Jurassic period), or perhaps according to the differential induration that forms the localized quartzitic expressions of what is predominantly sandstone.

The final step in our holistic evaluation of trace-element data focused on the cobblesource data set. A PCA indicated that eight components account for 99% of geochemical composition variability in UGB cobble sources (compared to six components for the more homogenous outcrop sources—an indicator itself of the greater trace-element diversity of cobble deposits), with PC1 accounting for 31% of variability, PC2 24%, and PC8 3%.

Complete-linkage dendrograms of cobble sources based on all components and upon PC1, respectively, suggest two distinct geographic trends. Figure 6, based on all components, shows a major division between sources 5GN850-2 and 5GN2269 (marked for reference by a hatched dividing line). Samples below that division are most likely to occur to the southeast of the center of the project area, conceived of for this discussion as the town of Gunnison (see Fig. 6 compass-diagram inset and map Fig. 1). This geographic tendency is driven by cobble sources sampled in the vicinity of the Chance Gulch site (see cross-hatching of Chance Gulch cobbles sources on the y-axis of Fig. 6). The four other sources below the major dendrogram dividing line occur in other directions vis-à-vis Gunnison. On the other hand, cobble sources that fall

above that line show a propensity to occur to the southwest, north, or northeast of Gunnison (Fig. 6 compass-diagram inset). We further note a subset of four samples, represented by the cross-hatched arm of the upper compass plot, which fall in the bottom half of the upper cluster. These samples, like those below the cluster divisor, derive from the Chance Gulch area.

This outcome suggests that while cobble sources in the vicinity of Chance Gulch (and just southeast of Gunnison) do not tidily cluster together on the basis of their overall traceelement signatures, about half of them are statistically different from other sources in the UGB assemblage. Nearly the entire other half of the Chance Gulch sources occur near each other stepwise in the cluster analysis and therefore order-wise in the dendrogram, suggesting more similarity from Chance Gulch source to Chance Gulch source than, for example, from Chance Gulch sources within that group to those occurring in the top third of the dendrogram. The relative positioning of all the Chance Gulch sources near one-another in Fig. 6 suggests that future analysis should target these data to try to characterize and account for the variability (or similarity) in trace element signatures among gravels from the Chance Gulch portion of the UGB, as well as how those signatures compare to those from sources in other parts of the Basin.

The Fig. 7 dendrogram reveals a second geographic tendency in the cobble-source data set, involving distance of the sources from the center of the project area. Figure 7 organizes the cobble PC1 data set, in contrast to the complete cobble trace-element data of Fig. 6. Focusing again on one major cluster division, all those sources (except VW09-1) falling below the break in the dendrogram are located geographically near the center of the project area. Excluding the outlier, which is 46 km from Gunnison, all others in this group occur just 4 - 9 km from Gunnison, with a mean distance from Gunnison-to-source in this cluster of cobble sources of 7 km. As with directionality, the short mean distance of these sources from Gunnison is driven in part, but not exclusively, by the five Chance Gulch samples in this subsample (Chance Gulch is 7 km from Gunnison). Three of the four non-Chance Gulch sources below the dendrogram divisor (VW09-1 is again the exception), are located 7 - 9 km from the project's center.

As was the case with Fig. 6, the large grouping of sources that fall above the major cluster division show an intriguing two-part character with respect to their distance from Gunnison, with sources from the same general area, Chance Gulch, again responsible for the outcome. All but one sample (SC09-2) in the upper two-thirds of the group occur at a much

greater distance from Gunnison than from the samples that cluster apart from them (discussed above) and from the lower one-third of samples within their group (with again, one exception, source BP09-8). Excluding outlier SC09-2, which is located just 5 km from Chance Gulch, the upper two-thirds of sources occur at a range of 12 to 38 km from Gunnison (with a mean of 24 km from Gunnison). The lower third, excluding BP09-8 (37 km from study-area center), occur at ranges from 4 - 7 km, and a mean of 6 km from Gunnison. As with the sources below the major cluster division, this mid-range set of sources is being influenced by nearby Chance Gulch, with four of the sources from that area; however, two of the three others are not from Chance Gulch, but are still located near the center of the project area.

Together, Figs. 6 and 7 suggest that cobble sources located at the center of the UGB and immediately southeast of Gunnison have a different geochemical character than cobble sources located farther afield, primarily to the north-northeast, but also to the southwest. This reveals meaningful geographic patterning in the geochemical signatures even of UGB cobble sources; patterning surely rooted in the geologic history of the Basin. This in turn suggests that it will be possible to assign source-location parameters even to archaeological quartzite assemblages that derive from inherently heterogeneous cobble sources; and that further "peeling of the data-set onion" should permit more refined discrimination among cobble sources. Although such peeling is beyond the scope of this paper, we note that UGB cobble-source diversity appears to be related to UGB drainage size, order, and position relative to major stream confluences.

3.2 Quartzite subgroup identification and analysis

Another way to examine geochemical patterning in the data set is to search for relatively homogenous subgroups that can then be evaluated in terms of UGB geography. We defined subgroups via pattern-recognition and statistical group evaluation techniques (Neff, 2002), an approach similar to that used with artifacts (unknowns) whose subgroup structure must be identified before projecting the groups against a source-sample database.

For defining subgroups, only specimens identified after closer scrutiny with a 10 X handlens as quartzite were used to avoid defining spurious groups influenced by non-quartzite rocks. This reduced the working sample set from 402 to 355. We identified subgroups by inspecting dendrograms from cluster analyses, principal components analyses, and by examining bivariate

elemental-concentration plots (Figs. 8a-c). We carried out multivariate comparisons using Mahalanobis distances as well, but large differences in group size and large ranges of variation for some elements within some of the groups complicated such comparisons because of the need to select different subsets of elements depending on which groups were being comparing.

We identified six groups in the quartzite data, designated Q1, Q2a, Q2b, Q2c, Q3 and Q4. Group Q1 differs from the rest of the data in its high and very consistent sodium and aluminum values (Fig. 8a). Gallium and thallium, which have valence electron configurations identical to aluminum, are also high in Group Q1. Groups Q3 and Q4, meanwhile, are both high in calcium, while Q3 is also high in magnesium relative to the remaining data (Fig. 8b). Groups Q2b and Q2c are similar in composition to Group 2a and were initially included in that group; however, on plots of aluminum versus rubidium (Fig. 8c) and aluminum versus potassium, Q2b and Q2c lie along correlation lines distinct from Q2a. Q2b has relatively high concentrations of aluminum and Q2c has relatively high rubidium and potassium. Fourteen samples were not assigned to any of the six groups, explaining the Table 2 sample grand total of 341, and not 355.

The six quartzite groups are distributed non-randomly among all the sources (Table 2), and outcrop versus cobble sources show distinctly different group distributions. Most obviously, cobble sources comprise significantly more quartzite groups than most outcrop sources—yet another indicator of their greater heterogeneity vis-à-vis bedrock. Precambrian outcrop sources are the exception, reflecting more quartzite groups than sources in younger formations.

Table 2

Geological Unit	Collection Location	Q1	Q2a	Q2b	Q2c	Q3	Q4	Grand Total
OUTCROP SOURCES								
Kdb	BP09-1		5					5
Kdb	CD09-3		9					9
Kdb	CD09-4		4					4
Kdb	CD09-5		2					2

Frequencies of six compositional groups across the sampled sources

				Subg	roup			
Geological Unit	Collection Location	Q1	Q2a	Q2b	Q2c	Q3	Q4	Grand Total
Kdb/Jm	SC09-19		4		2			6
Jm	SC09-20		4	2	1			7
Jj/Jm	SC09-26		3				1	4
Jj	SC09-1		7					7
Jj	SC09-10		7	5			1	13
Jj	SC09-18	1	7					8
Jj	BF09-7		3					3
Jj	SC09-25		6					6
Jj	SC09-7		4				Y	4
Jj	SC09-5		10		1			11
Je	SC09-11		2	1		5		8
Je	SC09-21		5					5
Xqt	SC09-27-Xqt		1	3	1	1	1	7
р Є	SC09-4		1	Y				2
E	SC09-23	2	3				5	10
		COI	BBLE S	SOUR	CES			
Cobble	5GN1982		7	1				8
Cobble	5GN2269	2	4	2				8
Cobble	5GN3510	1	7	1	1			10
Cobble	5GN840	1	5					6
Cobble	5GN850-1	1	5		2			8
Cobble	5GN850-2	2	5					7
Cobble	5GN850-3	1	8					9
Cobble	5GN850-4	4	4	1	1			10
Cobble	5GN852	2	4					6
Cobble	5GN852-2	3	5				1	9
Cobble	5GN901	2	4	1	1			8
Cobble	BF09-4		8	1				9

			Subgroup					
Geological Unit	Collection Location	Q1	Q2a	Q2b	Q2c	Q3	Q4	Grand Total
Cobble	BP09-2		5	4			1	10
Cobble	BP09-4	1	5	1				7
Cobble	BP09-6	1	4	2		3		10
Cobble	BP09-8		2	1	3	1	2	9
Cobble	CD09-2	1	7	1				9
Cobble	MP09-1		5	4				9
Cobble	SC09-12	2	2		2	2		8
Cobble	SC09-13	2	3		2			7
Cobble	SC09-2	4	1	1			~	6
Cobble	SC09-22	2	1		1		3	7
Cobble	SC09-24	2	3	4		1		10
Cobble	SC09-6		10					10
Cobble	SC09-3		2	5			2	9
Cobble	SC09-8	4		Y			2	6
Cobble	SC09-9	1					1	2
Cobble	VW09-1	$\langle \rangle$	3					3
	Total	44	204	42	18	13	20	341

To explore further the spatial patterning in the occurrence of the groups, we transformed the data in Table 2 to percentages of the whole sample, and carried out multivariate analysis similar to those run previously on elemental concentration on the six-variable group-frequency data set. A PCA of the group-percentage data shows that the major dimension of variance is a continuum from high values Q1 and Q4 (low PC1 score) to high Q2a, while high percentages of Q2b and Q3 drive PC2 scores down (Fig. 9). These patterns are also expressed in a completelinkage cluster analysis (Fig. 10), which places collections dominated by Group Q2a to the near (but not entire) exclusion of other groups in the upper portion of the dendrogram, while collections dominated by Q2b and Q3 occur at the very bottom.

To visually express these data, we placed each quartzite sample on a project area map, coded with a unique color representing each quartzite group. Some quartzite samples, 14 of 355, do not fall into any of the six defined groups and thus do not appear on the map and are not included in counts. Figure 11 shows all outcrop samples (n = 121) coded by group membership. Figure 12 shows the same data for all cobble sources (n = 220 samples). Even the quickest of glances at the two maps side-by-side conveys that in the UGB, outcrop sources are far more homogenous in terms of group membership (reflected by groupings of the colors representing the groups) than cobble sources, and they are overwhelmingly dominated by the group Q2a (coded in black). With few exceptions, outcrop sources that show quartzite group variability are of Precambrian age (SC09-4, SC09-23, and SC09-27-Xqt).

The cobble sources are heterogeneous with respect to quartzite group membership, such that samples from a single cobble locus are coded with many colors in Fig. 12. Seventeen of the cobble sources contain quartzite representing three or more of the six groups (and eight of those sources represent four or five of the six groups). Only two cobble sources reflect a single quartzite group: VW09-1 and SC09-6. The former does not appear in Fig. 12 because it is located in the very high country bounding the UGB to the west and just off the map. That collection locus is Taylor Park Reservoir, elevation 2895 m. We hypothesize that the VW09-1 cobbles did not travel far from their highest possible point of origin and likely all derived from a single nearby outcrop of group Q2a. SC09-6 is a cobble source located at the site of well-known outcrop quarry 5GN1. Given its group homogeneity, and the fact that it matches the group of the also-homogenous surrounding outcrop sources (Q2a), we conclude that this particular gravel deposit was more locally derived than other gravel deposits sampled.

4. Archaeological Implications

Our results show that UGB quartzite sources, outcrops and gravel deposits alike, express geochemical signatures with meaningful structure and patterning. This bodes well for archaeological sourcing efforts for quartzite artifacts from sites in the UGB and perhaps elsewhere. However, we must approach archaeological sourcing of quartzite differently than the routinely invoked approach scientists take to sourcing volcanic rocks (e.g., obsidian) with discrete geologic origins. Rather than attempting a "match-the-artifact-to-the-geologic-source"

protocol (although see Shackley [1998] for a reminder that even obsidian sourcing establishes only a statistical probability that an obsidian sample derived from a particular geologic source), we conclude that with UGB quartzite, an assemblage-based approach will be more fruitful. We illustrate how this protocol would work using the case of the multi-component Chance Gulch site that ultimately spawned the proof-of-concept research reported in this manuscript.

Chance Gulch (Section 1.2), is a multi-component site located southeast of the town of Gunnison, Colorado. Human occupations date to the late Paleoindian, Middle Archaic, and late Prehistoric periods, and the lithic assemblages for each, like nearly all sites in the UGB, consist overwhelmingly of quartzite. Within 0.5 km of the site, numerous quartzite-rich gravel deposits occur, and many of these show evidence for prehistoric quarrying. Manuscripts to date (e.g., Pitblado, 2002; Pitblado and Camp, 2003; Pitblado et al., 2001; Stamm et al., 2004) have therefore reported the inference that the quartzite recovered from the site originated in one or more of those local cobble sources, and that the cobble sources may in fact have drawn prehistoric people repeatedly to the Chance Gulch site.

We cannot choose any single artifact from among the Chance Gulch assemblage, develop its geochemical profile, and expect to convincingly match it to a single UGB quartzite source. We propose instead an assemblage-based approach that entails treating the chipped stone debitage from each prehistoric occupation level as a unit, referred to hereafter as a "subassemblage." We can add a fourth Chance Gulch sub-assemblage to the mix: late Paleoindian projectile points from the site surface and excavation. Prehistoric people typically curated these formal tools longer than other artifacts, and they therefore often represent more distant raw material sources (e.g., Binford, 1979; Keeley, 1982; Pitblado, 2011). We can then select 10 pieces of debitage per sub-assemblage, just as we sampled 10 quartzite cobbles per gravel source, and subject them to the LA-ICP-MS analysis performed on samples in the source dataset.

Figure 13 shows in flow-chart form how interpretation of the results of those analyses would proceed, the sorts of questions we should ask and can reasonably expect to answer at various junctures, and the nature of archaeological conclusions we could draw and anticipate supporting with evidence. We have not yet performed this study and do not wish to include such an analysis in this manuscript because like so many logical "next steps," it exceeds the scope of

what we aim to convey here. However, Fig. 13 outlines the methodology and general inferential process for a follow-up study that is in progress.

Implementing an "if-then" approach to each Chance Gulch sub-assemblage can help quickly establish whether a sub-assemblage more likely derived from an outcrop or cobble source. Then, whichever the answer for each sub-assemblage, we can draw increasingly specific conclusions about the nature and possible geographic location(s) of source candidates. In so doing, we can establish probabilistic parameters for where lithic raw material could and could not have been quarried by Chance Gulch occupants. This opens the door to testing hypotheses about mobility strategies that yielded a particular sub-assemblage result, and also to comparing the sub-assemblages to evaluate if and how use of chipped stone changed diachronically (and perhaps in the case of the projectile points, with respect to function) at the locality.

5. Conclusions and Future Research Directions

5.1 Conclusions

This paper has aimed to ascertain, via a first-pass through a robust data set, the minimum degree to which we can expect to discriminate among quartzite sources in the UGB using data generated through LA-ICP-MS. We determined that UGB quartzite sources can be fruitfully characterized in two complementary ways: through the holistic evaluation of the complete trace-element database and by identifying quartzite groups that reflect particular combinations of trace elements and their concentrations. Both approaches support the following conclusions:

- 1. UGB quartzite from outcrop and cobble sources can be distinguished from one another accurately, although not perfectly.
- 2. Outcrop sources are geochemically more homogeneous than cobble sources and are comparatively depleted in trace-elements relative to their gravel counterparts.
- 3. Outcrop sources can be discriminated accurately, although again not perfectly, according to their geologic age (Precambrian versus Jurassic versus Cretaceous).
- Despite the heterogeneity of most cobble sources, they are still distributed across the UGB in discernible patterns. These patterns suggest that further discrimination among even UGB cobble sources will be possible.

5. By adopting an assemblage-based, rather than artifact-based approach to geochemically characterizing modified quartzite at UGB sites, we can expect to obtain results that permit us to rule out some potential UGB sources of the material, and to ascertain the degree of consistency of the results with the geochemical signatures of sources not eliminated from consideration.

5.2 The role of petrography in geochemical studies of UGB quartzite sources

We (Pitblado et al., 2008) have elsewhere discussed the differing character types of UGB quartzite, a function of their variable geneses (also see Section 2.1, this paper). For example and most basically, the UGB assemblage contains both orthoquartzite (sedimentary) and metaquartzite (metamorphosed orthoquartzite or quartz sandstone). Although both types of quartzite are quartz-rich, their variable and sometimes unpredictable origins may not be captured by geochemical analysis alone. Both types of quartzite could in theory yield similar elemental signatures, yet have distinctive textures, grain composition, and cement (Fig. 14). Petrographic analysis of thin sections of samples, however, captures the latter variables, allowing an independent evaluation as to whether samples likely represent the same or different sources (e.g., Fig. 15). Petrography can also be used to cross-check any subset of geochemical results.

As reported in this paper, for example, exploratory cluster analyses (Figs. 2, 5, 6, 7, and 10) revealed a few quartzite samples that do not conform to the general patterns that emerged. Petrographic analysis can help in two ways: by independently confirming that the patterned data points do not include samples have similar geochemical signatures but actually represent different sources; and by illuminating why a given sample does not group with others known to be from the same or a nearby source. From an archaeological perspective, we hope that petrographic analysis need not be a regular part of the protocol for archaeological sourcing studies, because it is destructive, whereas LA-ICP-MS is not. However, its potential as a tool for evaluating individual samples as needed is significant and worth the effort of further study.

5.3 Future research directions

Having completed a first-pass analysis of the geochemistry of geological quartzite sources in the UGB, many future research directions present themselves. These range from exploring variability in the quartzite assemblage addressed in this paper, but at higher-resolution scales than the assemblage as a whole; to determining whether and how quarried sources differ geochemically from those not prehistorically worked; to evaluating the Chance Gulch site quartzite assemblage (by level) as a test of the sourcing protocol presented in Section 4; to identifying, sampling and developing geochemical signatures for additional UGB sources.

Opportunities to expand this preliminary research outside the UGB abound as well. For our own research, we will sample geologic sources of quartzite immediately outside the UGB, which could yet be part of the sourcing universe exploited by prehistoric occupants of the Basin (see Black, 1991 and Baker, 2008 for relevant land-use hypotheses). Beyond our own research domain, we note that quartzite is commonly exposed around the world, and humans and their pre-human ancestors used it to manufacture everything from Olduvai choppers to colossal Egyptian statues. If the archaeological sourcing protocol we have proposed here can be refined and more broadly applied, many archaeologists, and for that matter, earth scientists, will benefit.

Acknowledgments

We gratefully acknowledge funding for the field component of our research from the National Science Foundation (BCS-0728664) and the Bureau of Land Management (Gunnison Field Office). Without the energy of the 2009 USU archaeological field school staff, students, volunteers, and visiting colleagues, who "climbed every mountain" to collect UGB quartzite, the research reported here could not have occurred. We are likewise grateful to federal scientists Elizabeth Francisco and Dan Haas (BLM Gunnison and Colorado, respectively); Forest Frost, Bill Commins, and Ken Stahlnecker (National Park Service, Black Canyon of the Gunnison and Curecanti National Recreations Areas); and Justin Lawrence (U.S. Forest Service—Gunnison National Forest) for facilitating quartzite sample collections on the lands they manage. We thank Scott Bigney and Richard George for their careful work preparing samples for and executing LA-ICP-MS analysis. Funding for the laboratory analysis came from the National Science Foundation (BCS-0917702). Finally, we thank Vance Holliday and an anonymous reviewer for extremely helpful reviews that contributed to an improved paper.

References

- Arkush, B.S., Pitblado, B.L., 2000. Paleoarchaic surface assemblages in the Great Salt Lake desert, northwestern Utah. Journal of California and Great Basin Anthropology 22:12-42.
- Baker, S.G., 2008. Trails, trade, and west-central Colorado's Gateway Tradition: ethnohistorical observations. Southwestern Lore 74:1-37.
- Beck, C., Jones, G.T., 1990. Toolstone selection and lithic technology in early Great Basin prehistory. Journal of Field Archaeology 17:283-299.
- Beck, C., Jones, G.T., 2010. Clovis and Western Stemmed: population migration and the meeting of two technologies in the Intermountain West. American Antiquity 75, 81-116.
- Beck, C., Taylore, A.K., Jones, G.T., Fadem, C.M., Cook, C.R., Millward, S.A., 2002. Rocks are heavy: transport costs and Paleoarchaic quarry behavior in the Great Basin. Journal of Anthropological Archaeology 21, 481-507.
- Binford, L.R., 1979. Organization and formation processes: looking at curated technologies. Journal of Anthropological Research 35, 255-272.
- Black, K.D., 1991. Archaic continuity in the Colorado Rockies: the Mountain Tradition. Plains Anthropologist 36:1-29.
- Brunswig, R.H., Pitblado, B.L. (Eds.), 2007. Frontiers in Colorado Paleoindian Archaeology: From the Dent Site to the Rocky Mountains. University Press of Colorado, Niwot.
- Cackler, P., Glascock, M.D., Neff, H., Iceland, H., Pyburn, K.A., Hudler, D. Hester, T.R., Chiarulli, B. M., 1999. Chipped stone artifacts, source areas, and provenance studies of the northern Belize chert-bearing zone. Journal of Archaeological Science 26, 389-397.
- Church, T., 1996. Lithic resources of the Bearlodge Mountains, Wyoming: description, distribution and implications. Plains Anthropologist 41, 135-164.
- DeWitt, E., Stoneman, R.J., Clark, R., 1985. Mineral Resource Potential Map of the Fossil Ridge Wilderness Study Area, Gunnison County, Colorado, Map MF-1629-A.
- DeWitt, E., Zech, R.S., Chase, C.G., Zartmann, R.E., Kucks, R.P., Bartelson, B., Rosenlund, G.C., Early, D., 2002. Geologic and Aeromagnetic Maps of the Fossil Ridge Area and Vicinity, Gunnison county, Colorado, Map I-2738, scale 1:30,000.
- Dudgeon, J.V., Neff, H., Saint, A., Balsanek, W., 2007. Evaluating the precision requirements for isotope ratio determination of archaeological materials using LA-TOF-ICP-MS: increasing ratio precision, in: Glascock, M.D., Speakman, R.J., Popelka-Filcoff, R.S., (Eds.), Archaeological Chemistry: Analytical Techniques and Archaeological Interpretation. Oxford University Press, New York, pp. 297-310.
- Duwe, S., Neff, H., 2007. Glaze and slip pigment analysis of Pueblo IV ceramics from eastcentral Arizona using Time of Flight-Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (TOF-LA-ICP-MS). Journal of Archaeological Science 34, 403-414.
- Elbright, C.A., 1987. Quartzite petrography and its implications for prehistoric use and archaeological analysis. Archaeology of Eastern North America 15, 29-45.
- Gaskill, D.L., 1977. Chapter 1: geology of the West Elk Wilderness and vicinity, Delta and Gunnison counties, Colorado. USGS Open File Report 77-751, 4-31.

- Gaskill, D.L., Colman, S.M., DeLong, J.E., Jr., Robinson, C.H., 1986. Geological Map of the Crested Butte Quadrangle, Gunnison county, Colorado, Map GQ-1580, 1:24,000 scale.
- Gaskill, D.L., DeLong, J.E., Cochran, D.M., 1987. Geologic Map of the Mount Axtell Quadrangle, Gunnison County, Colorado, Map GQ-1604, 1:24,000 scale.
- Giussani, B., Monticelli, D., Rampazzi, L., 2009. Role of laser ablation-inductively coupled plasma-mass spectrometry in cultural heritage research: a review. Analytica Chimica Acta 635, 6-21.
- Gratuze, B., 1999. Obsidian characterization by LA-ICP-MS and its application to prehistoric trade in the Mediterranean and the Near East: sources and distribution of obsidian within the Aegean and Anatolia. Journal of Archaeological Science 26, 869-881.
- Hedlund, D.C., Olson, J.C., 1974. Geologic Map of the Iris NW Quadrangle, Gunnison and Saguache Counties, Colorado, Map GQ-1134, 1:24,000 scale.
- Howard, J.L., 2005. The quartzite problem revisited. The Journal of Geology 113, 707-713.
- Hughes, R.E., 1992. Another look at Hopewell obsidian studies. American Antiquity 57:515-523.
- Hunter, J.F., 1925. Precambrian rocks of the Gunnison River, Colorado. USGS Bulletin 777, 1-77.
- Jones, G.T., Beck, C., Jones, E.E., Hughes, R.E., 2003. Lithic source use and Paleoarchaic foraging territories in the Great Basin. American Antiquity 68, 5-38.
- Julig, P.J., Pavlish, L.A., Hancock, R.G.V., 1987. Instrumental neutron activation analysis of archaeological quartzite from the Cummins site, Thunder Bay: determination of geological source. Current Research in the Pleistocene 4, 59-61.
- Keeley, L.H., 1982. Hafting and retooling: effects on the archaeological record. American Antiquity 47:798-809.
- Lipe, W.D., Pitblado, B.L., 1999. Paleoindian and Archaic periods, in: Lipe, W.D., Varien, M.D., Wilshusen, R.H. (Eds.), Colorado Prehistory: A Context for the Southern Colorado River Basin. Colorado Council of Professional Archaeologists, Denver, pp. 95-131.
- Luedtke, B.E., 1978. Chert sources and trace-element analysis. American Antiquity 43, 413-423.
- Luedtke, B.E., 1979. The identification of sources of chert artifacts. American Antiquity 44, 744-756.
- Neff, H., 1994. RQ-mode principal components analysis of ceramic compositional data. Archaeometry 36, 115-130.
- Neff, H., 2002. Quantitative techniques for analyzing ceramic compositional data, in: Glowacki, M., Neff, H., (Eds.), Ceramic Production and Circulation in the Greater Southwest: Source Determination by INAA and Complementary Mineralogical Investigations, Monograph 44. The Cotsen Institute of Archaeology at UCLA, Los Angeles, pp. 15-36.
- Neff, H., 2010. LA-ICP-MS analysis of quartzite from the Gunnison Basin, Colorado. Prepared for and on file with project Principal Investigator, Bonnie Pitblado, Department of Anthropology, University of Oklahoma, Norman.

- Neff, H., 2012. Laser ablation-ICP-MS in archaeology, in: Lee, M.S., (Ed.), Applied Handbook of Mass Spectrometry, Wiley, New Jersey, USA, pp. 829-844.
- Neff, H., Sheets, P., 2005. Archaeological applications of tephra analysis by LA-ICP-MS, in: Speakman, R.J., Neff, H., (Eds.), Laser Ablation ICP-MS in Archaeological Research. University of New Mexico Press, Albuquerque, pp. 117-123.
- Peterson, J., Mitchell, D.R., Shackley, M.S., 1997. The social and economic contexts of lithic procurement: obsidian from Classic-Period Hohokam sites. American Antiquity 62, 231-259.
- Odell, G.H., 2000. Stone tool research at the end of the millennium: procurement and technology. Journal of Archaeological Research 8, 269-331.
- Odell, G.H., 2004. Lithic Analysis. Kluwer Academic/Plenum Publishers, New York, USA.
- Olson, J.C., 1976a. Geologic Map of the Iris Quadrangle, Gunnison and Saguache Counties, Colorado, Map GQ-1287, 1:24,000.
- Olson, J.C., 1976b. Geologic Map of the Houston Gulch Quadrangle, Gunnison and Saguache Counties, Colorado, Map GQ-1287, 1:24,000.
- Pitblado, B.L., 1993. Paleoindian Occupation of Southwest Colorado. Unpublished master's thesis, Department of Anthropology, University of Arizona, Tucson.
- Pitblado, B.L., 1998. Peak to peak in Paleoindian time: occupation of southwest Colorado. Plains Anthropologist 43, 333-348.
- Pitblado, B.L., 1999. Late Paleoindian Occupation of the Southern Rocky Mountains. University of Michigan, Ann Arbor.
- Pitblado, B.L., 2000. Living the high life in Colorado: late Paleoindian occupation of the Caribou Lake site, in: Cassells, E.S. (Ed.), This Land of Shining Mountains: Archaeological Studies in Colorado's Indian Peaks Wilderness Area, Research Report 8. Center for Mountain Archeology, Ward, CO, pp. 124-158.
- Pitblado, B.L., 2002. The Chance Gulch Paleoindian site, Gunnison Basin, Colorado. Current Research in the Pleistocene 19, 74-76.
- Pitblado, B.L., 2003. Late Paleoindian Occupation of the Southern Rocky Mountains. University Press of Colorado, Niwot.
- Pitblado, B.L., 2007. Angostura, Jimmy Allen, Foothills-Mountain: clarifying terminology for late Paleoindian southern Rocky Mountain spear points, in: Brunswig, R.H., Pitblado, B.L., (Eds.), Frontiers in Colorado Paleoindian Archaeology: From the Dent Site to the Rocky Mountains. University Press of Colorado, Niwot, pp. 311-337.
- Pitblado, B.L., 2011. A tale of two migrations: reconciling biological and archaeological evidence for the Pleistocene peopling of the Americas. Journal of Archaeological Research 19:327-375.
- Pitblado, B.L., Camp, B.A., 2003. Final Report: 2001-2002 Excavations at the Chance Gulch Site (56N817). Prepared for and on file at the Bureau of Land Management, Gunnison Field Office & Colorado Historical Society Office of Archaeology and Historic Preservation, Denver.

- Pitblado, B.L., Camp, B.A., Stamm, J., 2001. Final Report: 2000 Test Excavations at the Chance Gulch Site (5GN817). Prepared for and on file at the Bureau of Land Management, Gunnison Field Office & Colorado Historical Society Office of Archaeology and Historic Preservation, Denver.
- Pitblado, B.L., Dehler, C.M., Neff, H., Nelson, S.T., 2008. Pilot study experiments sourcing quartzite, Gunnison Basin, Colorado. Geoarchaeology 23, 742-778.
- Pitblado, B.L., Dehler, C.M., Nelson, S.T., 2006. Sourcing quartzites from the late Holocene Chance Gulch site, Gunnison Basin, Colorado: a pilot study. Current Research in the Pleistocene 23, 135-138.
- Pitblado, B.L., Neff, H., Nelson, S.T., Dehler, C.M., 2007. AD-ICP-MS vs. LA-ICP-MS analysis of quartzite sources, Gunnison Basin, Colorado. Current Research in the Pleistocene 24, 133-136.
- Rapp, G.R., 2002. Archaeomineralogy. Springer-Verlag, Berlin.
- Reed, A.D., Metcalf, M.D., 1999. Colorado Prehistory: A Context for the Northern Colorado River Basin. Colorado Council of Professional Archaeologists, Denver.
- Resano, M., Garcia-Ruiz, E., Vanhaecke, F., 2010. Laser ablation-inductively coupled plasma mass spectrometry in archaeometric research. Mass Spectrometry Reviews 29, 55-78.
- Resano, M., Garcia-Ruiz, E., Vanhaecke, F., 2012. Laser ablation-inductively coupled plasma mass spectrometry for the investigation of archeological sample, in: Lee, M.S. (Ed.), Applied Handbook of Mass Spectrometry, Wiley, New Jersey, USA, pp. 859-884.
- Schneider, E., 2006. Rock 'n radiation: X-ray fluorescence analysis of lithic materials from the Bear Lodge Mountains, Crook County, Wyoming. Report prepared by TRC Mariah Associations (Laramie, WY) for the Wyoming Department of Transportation.
- Shackley, M.S., 1995. Sources of archaeological obsidian in the greater American Southwest: an update and quantitative analysis. American Antiquity 60:531-551.
- Shackley, M.S., 1998. Gamma rays, x-rays and stone tools: some recent advances in archaeological geochemistry. Journal of Archaeological Science 25:259-270.
- Speakman, R.J. and Neff, H. (Eds.), 2005. Laser Ablation ICP-MS in Archaeological Research. University of New Mexico Press, Albuquerque.
- Speakman, R.J., Neff. H., 2005. The application of laser ablation ICP-MS to the study of archaeological materials – an introduction, in: Speakman, R.J., Neff, H., (Eds.), Laser Ablation ICP-MS in Archaeological Research. University of New Mexico Press, Albuquerque, pp. 1-15.
- Stamm, J.F., Pitblado, B.L., Camp, B.A., 2004. The geology and soils of the Chance Gulch archaeological site near Gunnison, Colorado. The Mountain Geologist 41:63-74.
- Stiger, M., 2001. Hunter-gatherer archaeology of the Colorado high country. University Press of Colorado, Niwot.
- Stiger, M., 2006. A Folsom structure in the Colorado mountains. American Antiquity 71, 321-351.

- Streufert, R.K., 1999. Geology and mineral resources of Gunnison county, Colorado. Colorado Geological Survey, Resource Series 37, 1:150,000-scale map, 76 pp.
- Stross, F.H., Hay, R.L., Asaro, F., Bowman, H.R., Michel, H.V., 1988. Sources of the quartzite of some ancient Egyptian sculptures. Archaeometry 30, 109-119.
- Tweto, O., 1987. Rock units of the Precambrian Basement in Colorado. USGS Professional Paper 1321-A, 54 pp.
- Zech, R.S., 1988. Geologic Map of the Fossil Ridge Area, Gunnison County, Colorado, Map I-1883, 1:24,000.

CER MAN

Pitblado et al., LA-ICP-MS Analysis of Upper Gunnison Basin Quartzite

Figure Captions

- 1. Location of all project area and all UGB quartzite sources sampled in this study, with primary bedrock outcrop sources distinguished from secondary cobble (gravel) sources.
- Dendrogram produced by complete-linkage cluster analysis of averaged trace-element signatures for 48 source localities sampled in the UGB. Dendrogram based on a principal components analysis (PCA) of the data set. Note the general separation of cobble and outcrop sources.
- 3. Biplot (i.e., simultaneous plot of variables and objects) derived from PCA of the correlation matrix of the complete quartzite data set. Vectors connect variable coordinates with the origin to depict inter-elemental correlations. Principal Component 1 subsumes approximately 46% of total variance in the data, and Principal Component 2 subsumes approximately 12% of total variance.
- 4. Map showing geographic distribution of outcrop and cobble samples with high and low PC1 values respectively, with high PC1 values indicating overall trace-element enrichments of a source and low PC1 values indicating trace-element depletion in a source. Map also shows geologic ages of outcrop sources.
- Dendrogram produced by complete-linkage cluster analysis of averaged trace-element signatures for bedrock outcrop sources only, showing ordering of results by geologic age. Asterisks denote non-Jurassic sources that clustered with others representing the Jurassic.
- 6. Dendrogram produced by complete-linkage cluster analysis of averaged trace-element signatures of UGB cobble sources. Inset compass plots show the predominant direction (from a central project-area origin defined as the town of Gunnison) of sources within each of the two major clusters. Chance Gulch cobble sources are cross-hatched.
- 7. Dendrogram produced by complete-linkage cluster analysis of cobble-source PC1 data. Insets are another form of compass plot that shows the direction and distance of each cobble-source in each major cluster from Gunnison. Chance Gulch samples have been highlighted and shown in bold on the upper compass plot.

- 8. Bivariate plots of element concentrations in samples, with ellipses representing 90% confidence level for membership in source groups: (a) aluminum and sodium concentrations in all quartzite samples analyzed in this study; (b) magnesium and calcium concentrations in quartzite samples assigned to groups Q1, Q2a, Q3, and Q4; (c) aluminum and rubidium concentrations in quartzite samples assigned to groups Q1, Q2a, Q3, and Q4; Q2b, and Q2c.
- Biplot derived from PCA of the group frequency data. Data points are sources listed in Tables 1 and 2. Proximity to the end of each vector indicates the extent to which the site collection is dominated by the group the vector represents.
- 10. Dendrogram of all sources (outcrops and cobbles) derived from complete-linkage cluster analysis of the quartzite group frequency data of Table 2. Group Q2a dominates the upper portion of the dendrogram; the other groups occur primarily nearly the bottom.
- 11. Map showing the distribution of quartzite groups for every sample from every outcrop source included in this study. In contrast to the cobble-source pattern shown in Fig. 12, note the homogenous colors among specimens removed from outcrop sampling loci.
- 12. Map showing the distribution of quartzite groups for every sample from every cobble source included in this study. In contrast to the outcrop pattern shown in Fig. 11, note the heterogeneous colors among specimens removed from cobble sampling loci.
- 13. Flow chart illustrating how interpretation of quartzite assemblages from UGB sites can proceed and the nature of potential source parameters we can expect to establish for a given assemblage. Note that this sourcing process differs in kind from the procedure used to "source" obsidian artifacts, whereby a geochemist compares the signature of an obsidian artifact against the signatures of possible geologic sources and identifies (or fails to identify) a statistically probable match.
- 14. Photomicrographs of UGB quartzite samples representing three of the six geochemically defined groups discussed in Section 3.2: (a) SC09-23A—Feldspathic sandstone from the Cambrian Sawatch Formation (geochemical group Q4). Note the partially weathered feldspar grain in the middle of the photomicrographs and associated quartz grains and small pockets of calcite cement. Left photo plane light, right photo cross-polars, magnification 20X; (b) 5GN850-4B—Biotite-bearing quartz sandstone from a cobble source (group Q1). The larger angular quartz grains are heavily fractured. The presence

of a significant amount of detrital biotite could explain why this sample falls into a different geochemical group. Left photo plane light, right photo cross-polars, mag. 10X; (c) MP09-1A—Feldspathic sandstone from a cobble source (group Q2A). Note well developed quartz overgrowths and weathered feldspar (yellow-stained grain). Left photo plane light, right photo cross-polars, mag. 20X; (d) SC09-19C—Well-cemented lithic- and quartz-rich sandstone from the Dakota Formation (group Q2A). The "dirty grains" in photo on right are volcanic rock fragments. All other grains are quartz. The grains are cemented by zebraic chalcedony (another form of quartz). Left photo plane light, right photo cross-polars, mag. 10X; (e) SC09-27-xqt—Precambrian metamorphic quartzite (group Q4). Note sutured boundaries between quartz grains. The other light brown mineral is likely staurolite or andalusite, metamorphic minerals with complex chemical signatures that would make this rock type stand out with respect to other samples. Cross-polars, mag. 10X. Of the specimens illustrated here, only "d" showcases quartzite from an archaeological quarry, demonstrating that prehistoric UGB tool-makers did not avoid quartzite that deviates from the classic geologically defined version of the rock.

15. Petrographically determined composition of the six geochemically defined groups in the UGB assemblage. Compositional groups determined by using standard point-counting methods (100 point counts per sample). N = 2 per category, except for SC09-27xqt (N =1). Q = quartz; F = feldspar; L = lithic (i.e., a rock fragment). The pink outlier (SCO9-27xqt) is actually a metamorphic rock, but we kept it in to illustrate that it is quartz-poor relative to the other samples. Note that the samples of each of the other geochemical groups pair together, yet there is some overlap between the groups. The Dakota formation (again, a source that was prehistorically quarried) and Sawatch samples appear to be geochemically and mineralogically different enough from each other and the other groups that they could be recognized as distinct quartzite bedrock sources in the Gunnison Basin. Last, note that all but 2 of the samples do *not* lie within the compositional field for geologically defined quartzite.



6	CD09-4			
2	BP09-1			
5	SC09-19			
9	▲ SC09-27-XQT			
8	▲ SC09-4			
13	BP09-5			
	▲ SC09-23			
	▲ SC09-25			
0	▲ BF09-7			
50	▲ SC09-21			
2	SC09-20			
	CD09-3			
E)	▲ SC09-26			
-	5GN840			
_	5GN850-4			-
_	5GN852-1			
_	VW09-1			
	CD09-5			
	SC09-1			2
	SC09-7			0
	SC09-5			
_	BP09-6		1	
_	BP09-8			
_	MP09-1			
_	SC09-12			
_	SC09-13	2		
_	SC09-3			
_	SC09-6			
_	SC09-22			
_	SC09-24			
_	SC09-2			
	BP09-4			
_	CD09-2			
_	5GN852-2			
_	5GN901			
	BF09-4			
-	BP09-2			
_	SC09-9			
_	5GN850-1			
	5GN850-2			
_	5GN2269			
	5GN850-3			
	SC09-10			
	5GN3510			
	SC09-18			
_	- 5GN1982			
	– SC09-8		J	
	SC09-11			
1	5009-11			



Principal Component 1

ncipal Componen



	0	5	10	15	20	Fig. 5 ²⁵
	BP09-1	Cretaceous				
	SC09-19	(Kdb)	Ì	1	i	I.
	CD09-4	145-65 MYA				
SCO	09-27-XQT		I	1	I	1
	BP09-5	Precambrian	1			
	SC09-4	(E) 4600 542 MVA	1		1	1
	SC09-23	4000-542 1017	i		1	1
	BF09-7	1	1		1	
	SC09-21		1		1	1
	SC09-20		i		1	
	CD09-3*				1	
	SC09-26					
	SC09-1	- ·	1		1	
	CD09-5*	Jurassic	1		1	
	SC09-5	(50, 511, 55)	i		i	
	SC09-18	199-145 MYA	1		1	
	SC09-10		i i		i	
	SC09-7					
	SC09-25		1	1	1	
						i
	SC09-11		1			1



Chance Gulch Locations





Aluminum (log-base 10 ppm)



Magnesium (log-base 10 ppm)



ubidium (log-base 10 p

ıminum (log-base 10 ppm



Principal Component 1

Principal Component

Dominate		0 5	10	15	20 Fig. 10 25
Subgroup	DE00.7		1	i i	i i
	BF09-7	1		l l	Subgroup
	VW09-1		1		O Q1
	CD09-5		1	1	🗖 Q2a
	SC09-26				Q2b
	SC09-4		1		∆ Q2c
	5GN850-1				▲ Q3
	SC09-19		1		x Q4
	SC09-13		i I	i.	
	CD09-4			1	
	SC09-7		1	i I	
	BP09-1				
	SC09-21				
	5GN840				
	BP09-4		1		
	SC09-20				
	5GN2269		1	1	
	5GN901			i	
	5GN850-2		1		
	5GN852				
	5GN852-2				
$\circ\Box$	5GN850-4				
Δ	BP09-8	 			
	SC09-12	1	1		
	CD09-3		1		
	SC09-6		l I		
	SC09-5				
	SC09-1		i I		
	SC09-18		 		
	SC09-25		1		
	5GN3510		1		
	CD09-2		1	-	
	5GN1982		1		
	BF09-4		1		
	5GN850-3				
	BP09-2				
	MP09-1		1	1	
	SC09-10				
	SC09-27-Xqt	1	<u> </u>		
	SC09-3				
	BP09-6				
	SC09-24				
×	SC09-22			1	
×	SC09-23			I I	1
0	SC09-9			1	
			1	1	
0	SC09-2				
0	SC09-8				
	SC09-11		I	1	
		1	I	1	1



Fig. 11















d





e

