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GeoChemical Sourcing of the LaPrele Mammoth Kill Site

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Introduction

Excavations at the La Prele Mammoth Kill site (48CO1401) in Converse County, Wyoming during the 2015 and 2016 field seasons uncovered a large red ochre stain, approximately 12 meters south of the remains of a juvenile Columbian mammoth. This find is largely unprecedented in North American archaeology. Red ochre is a pigment commonly found in burial, ritual, art and domestic contexts in Paleoindian and Paleolithic complexes (Roper 1992). Red ochre is also known as hematite, a naturally-occurring iron oxide mineral. While red ochre has been found in habitation sites across Russia, Western Europe and the US, red ochre is not common in the context of kill sites (Roper 1992). The function and source of the ochre at this site remain unclear. Within Wyoming, there are two well-known major sources of hematite. One of these, the Powars II site at the Sunrise Mine near Hartville, is well-documented (Stafford 1990; Stafford et al., 2003**).** The other source is the historical Rawlins Paint Mine, just north of the town of Rawlins (see Stafford 1990). The ochre found during excavation at the La Prele Mammoth Kill site may have been derived from one of these two sources. The site sits one mile from the North Platte River and both the Rawlins and Sunrise ochre sources can be easily accessed by travel up- or downstream, respectively. This project analyzes hematite from these sources using ICP-OES and XRD to attempt to determine the geologic source of the ochre found during excavation.

Materials and Methods

A number of methods have been used to successfully differentiate among sources of ochre. These include x-ray diffraction (XRD) (Gil et al., 2007; Cavallo et al., 2015), x-ray fluorescence (XRF) (Gil et al., 2007; Bernatchez, 2008; Popelka-Filcoff et al., 2007), PIXE (Bernatchez, 2008), magnetism (Mooney et al., 2016), neutron activation analysis (INAA) (Popelka-Filcoff et al., 2008; Eiselt et al., 2011; Popelka-Filcoff et al., 2007), infrared spectroscopy (FTIR) and inductively- couple plasma optical emissions spectroscopy (ICP OES) (Moyo et al., 2016)**.** ICP-OES and XRD were used for analysis in this project due to their availability on campus.

Field Sampling

Within Wyoming, there are two well-known major sources of hematite (Sutherland & Cola, 2015). One of these, the Powars II site at Sunrise Mine, is well-documented archaeologically (Stafford 1990; Stafford et al., 2003**).** The other source is the Rawlins Paint Mine, just north of the town of Rawlins (see Stafford 1990). The Rawlins source is 180 km southwest of the La Prele Mammoth site, and the Powars II source is approximately 85 km southeast of the La Prele Mammoth site. Ochre found during excavation at the La Prele Mammoth Kill site may have been derived from one of these two sources, so comparative geological samples were taken from each of these two locations. Samples were collected using a metal trowel to dislodge large chunks of unconsolidated hematite from the surface of each formation. At the Powars II site, some samples collected came from backdirt piles of previous archaeological excavations. To try to capture the range of variability in each source area, sampling occurred at various locations at both sites in places where hematite was visible. Most samples collected were large, hard pieces of hematite and schist.

Table 1. UTM coordinates for sampling locations used in this study

Sample ID	UTM	Easting	Northing

RR1 through RR3	13T	314048	4631423
RR4	13T	313936	4631337
RR5	13T	313924	4631332
RR6 and RR7	13T	313929	4631287
RR8	13T	313841	4631337
RR9	13T	313379	4631344
S1	13T	524115	4686656
S2	13T	524091	4686653
S3	13T	524091	4686653
S4	13T	524098	4686651
S5	13T	524098	4686643
S6	13T	524119	4686640
S7	13T	524089	4686648
S8	13T	524688	4686384
S9	13T	524688	4686384
S10	13T	524538	4686503
S11	13T	524452	4686662
LC1-4	13T	459884	4742495
Excavation Samples	13T	459747	4742530

A third source, iron-rich sandstone cobbles from alluvial gravels of La Prele Creek, was also sampled because of its proximity to the La Prele Mammoth site. Multiple samples were taken from each source in order to compare inter-source variation to intra-source variation. All samples were collected and documented by the researchers during the summer of 2016. A total of 22 samples were collected from the three source locations. Of the samples collected from the three sources, 21 were submitted for ICP-OES analysis and 13 were submitted for XRD analysis.

Over 1200 pieces of ochre were excavated from the La Prele Mammoth Kill site during the summers of 2015 and 2016. Five of these were selected for ICP-OES analysis as part of this study, all from the area of the site known as the "Chopper Block". Three were also submitted for x-ray diffraction. The archaeological samples were selected based on the size of the hematite nodule. The nodule needed to be large enough to provide sufficient hematite for ICP-OES and XRD analysis.

Table 2. Archaeological samples used in the study

Field ID Number	Analyses Used
FS 1849	ICP-OES
FS 2133	ICP-OES, XRD
FS 3786	ICP-OES, XRD
FS 3937	ICP-OES, XRD
FS 4412	ICP-OES

<u>Laboratory Methods</u>

All samples were powdered using an agate mortar and pestle. The ground ochre was then passed through a 125-micron sieve. The resulting fine powder was collected into glass vials and capped. Approximately 15-20 mg of sieved powder were collected from each sample. Working area, sieve, mortar and pestle were cleaned with acetic acid and water between each sample in order to minimize cross contamination of samples. To prep samples for ICP-OES analysis, 2.5 mg of each sample were individually weighed and combined with 25 mL of 12.1 M HCL. The hematite and acid were heated to just below boiling (~80°C) for 30 minutes with continuous stirring using a magnetic stirrer at stir level five. Each sample was spun in a centrifuge at approximately 2200 rpm for five minutes to separate the undissolved hematite from the supernatant. Final samples were prepared by combining 1 mL of concentrated dissolved hematite to 9 mL of purified tap water to create a solution with molarity of 1.2 M HCL and hematite concentration of 100 mg/L for ICP-OES analysis.

In sum, 23 elements were measured using a PerkinElmer Optima 8300 ICP-OES at the University of Wyoming Geochemical Instrumentation Laboratory. Arsenic, chromium, cobalt, nickel, calcium, potassium, magnesium, manganese, sodium, phosphorus, lead, rubidium, selenium, strontium, zinc, sulfur, molybdenum, niobium, silicon, tin, titanium and tungsten were measured to ppb precision. Iron was measured to ppm levels due to high concentration in the samples.

For powder x-ray diffraction, 13 samples were run at the Wyoming Geological Survey. Five were from the Powars II source, four from Rawlins, two from La Prele Creek, and three from the excavation.

Results

Based on the ICP-OES analysis, the Rawlins and Powars II sources are distinguishable based on the presence of titanium and chromium each in relation to iron as well as the presence of aluminum and arsenic each in relation to iron. The La Prele Creek samples are similar to the Powars II samples chemically, but mineralogically the two sources were distinguishable (Figures 1 and 2**)**. The Powars II source samples contained traces of Arsenic, while the Rawlins sources did not. The Rawlins source samples contained traces of Chromium, while the Powars II sources did not. Titanium and Aluminum were present in samples from both sources, but in larger concentrations in the samples from Rawlins. Based on these minerals, excavation samples most closely matched the samples from the Powars II source.

XRD analysis found samples from all sources to contain hematite, quartz and calcite or dolomite in various ratios. Relative mineral abundances were calculated as peak area ratios. Three peaks, hematite (2Θ=33.20°), quartz (2Θ=26.67°), and dolomite (2Θ=31.00°) were used. Ratios of hematite: quartz and hematite: dolomite were calculated to distinguish the sources. The Powars II samples tended to have higher relative concentrations of hematite than the samples from Rawlins, although there is some overlap between the two sources (Figure 3). The samples from the excavation site grouped only with the Powars II samples due to their high concentration of hematite. The La Prele creek gravel samples were primarily composed of quartz and had relatively little hematite, causing this source to be eliminated as a potential source for the ochre found in excavation.

Discussion

The methods of this project proved successful in differentiating hematite sources in Wyoming, which has broad implications for Wyoming archaeology. The methods used in this project demonstrate it is possible to distinguish Wyoming hematite sources by their geochemical signatures, and this can be used to determine the likely source of hematite found during excavation at any given site or in rock art where hematite has been used. This provides insight to the distance Paleoindian groups traveled as well as possible connections between different archaeological sites.

There was not a complete overlap of data between the excavation samples and any source, which could be attributed to exposure and disruption within the historical context of the sampling sources. It is also possible ochre found during excavation came from a source not sampled in this study, as there are many sources of iron within the state of Wyoming (Sutherland & Cola, 2015). Future research analyzing a broader base of sample sources would provide more conclusive results.

Within the sampling locations of this study, Powars is the most likely source of red ochre found at the La Prele Mammoth Kill site. Lithics found during excavation at the La Prele Mammoth Kill Site, including flakes and scraper tools, support this conclusion. Much of the lithic raw material from the excavation site is Hartville Chert, coming from the Hartville uplift, which covers the same vicinity as the Powars II ochre mine. These findings suggest long distance transport of ochre by Clovis people, a novel finding in Wyoming, and possibly North American archaeology.

The long distance transport of ochre demonstrates the significance of ochre usage during Paleoindian times. Ochre may have been used for ritualistic, social or utilitarian reasons. At this point in time, it is difficult to determine the use of the ochre excavated at the La Prele Mammoth Kill Site. However, this discovery links the La Prele Mammoth Kill Site to the Powars II site, which creates contextual information that these two Paleoindian sites did not exist in isolation from one another. The use of ochre at the Powars site may be a clue to the use of ochre at the La Prele Mammoth Kill Site.

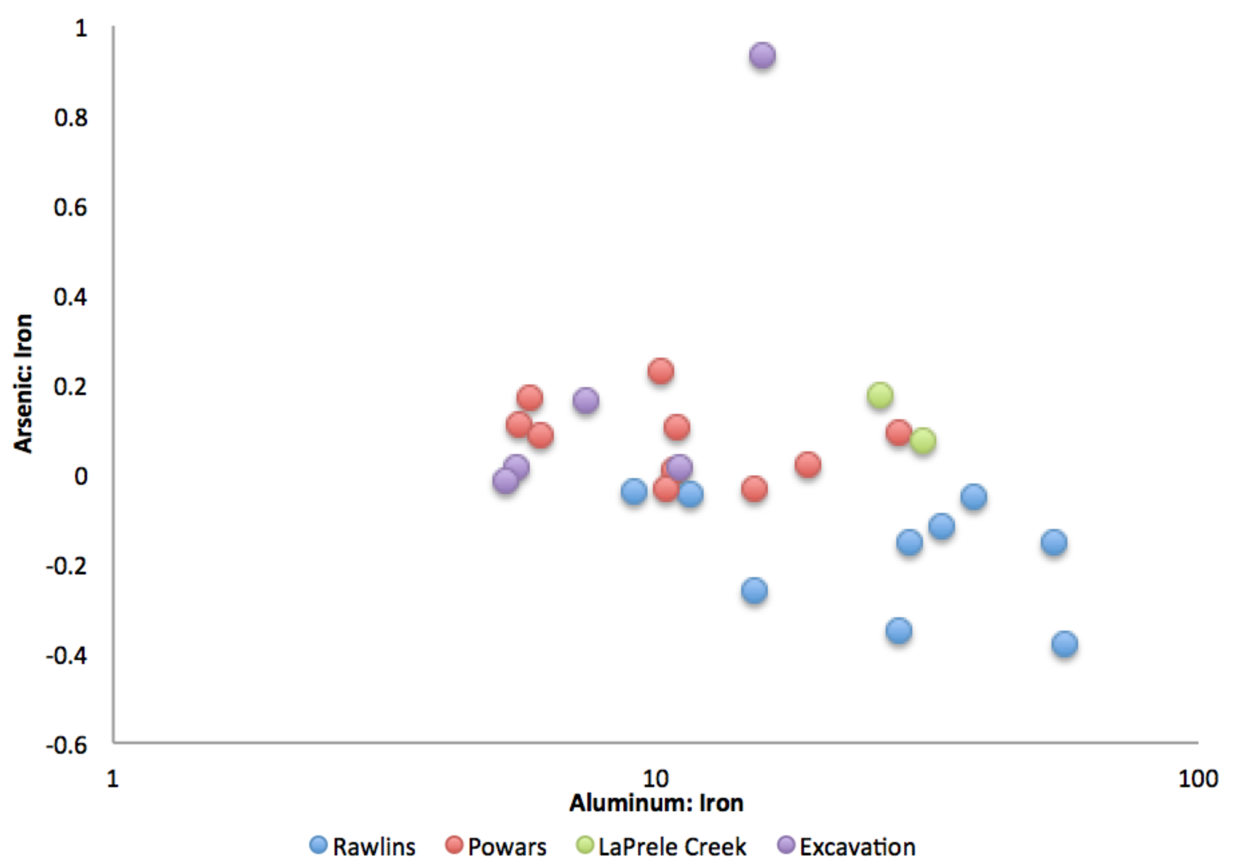


Figure 1 Relative concentrations of Aluminum and Arsenic compared to concentrations of Iron.

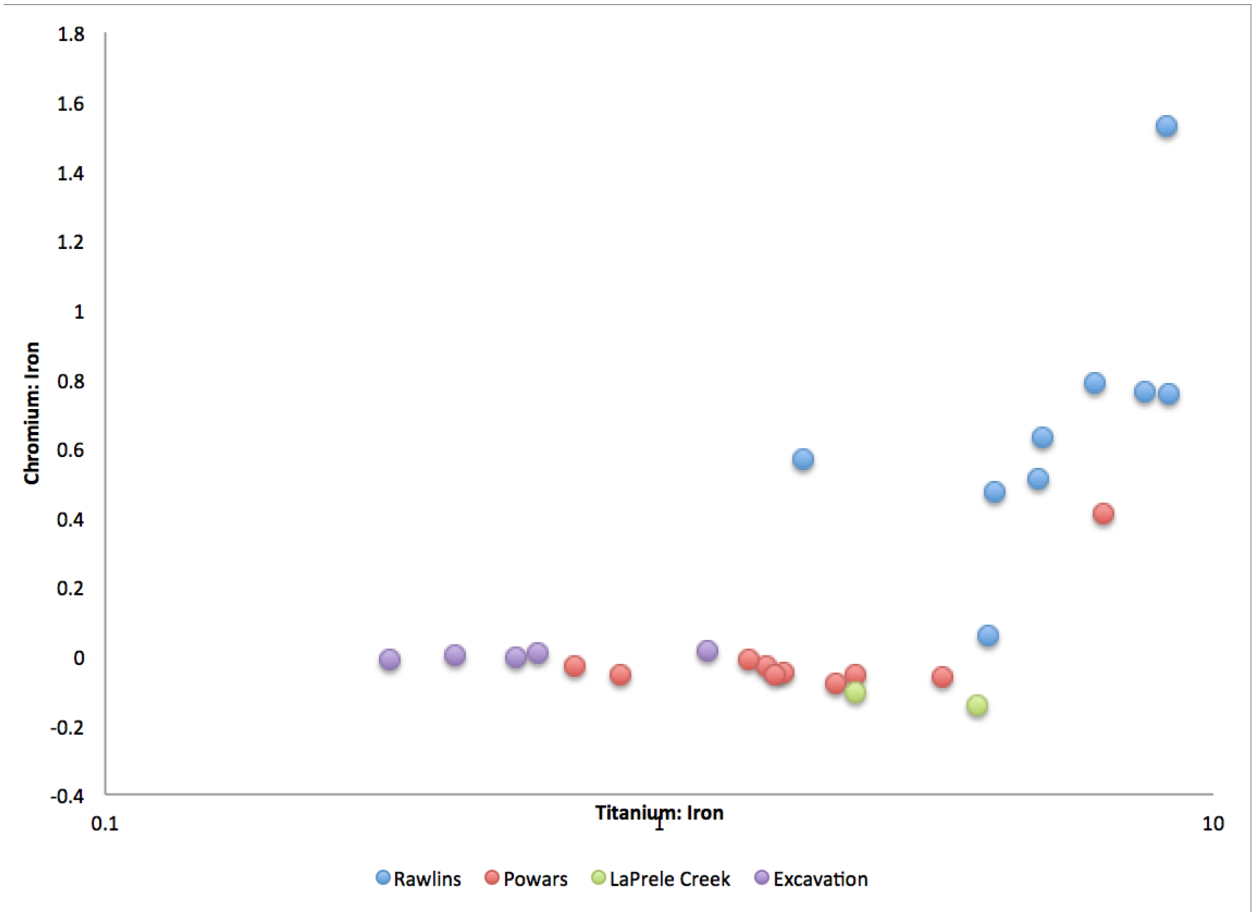
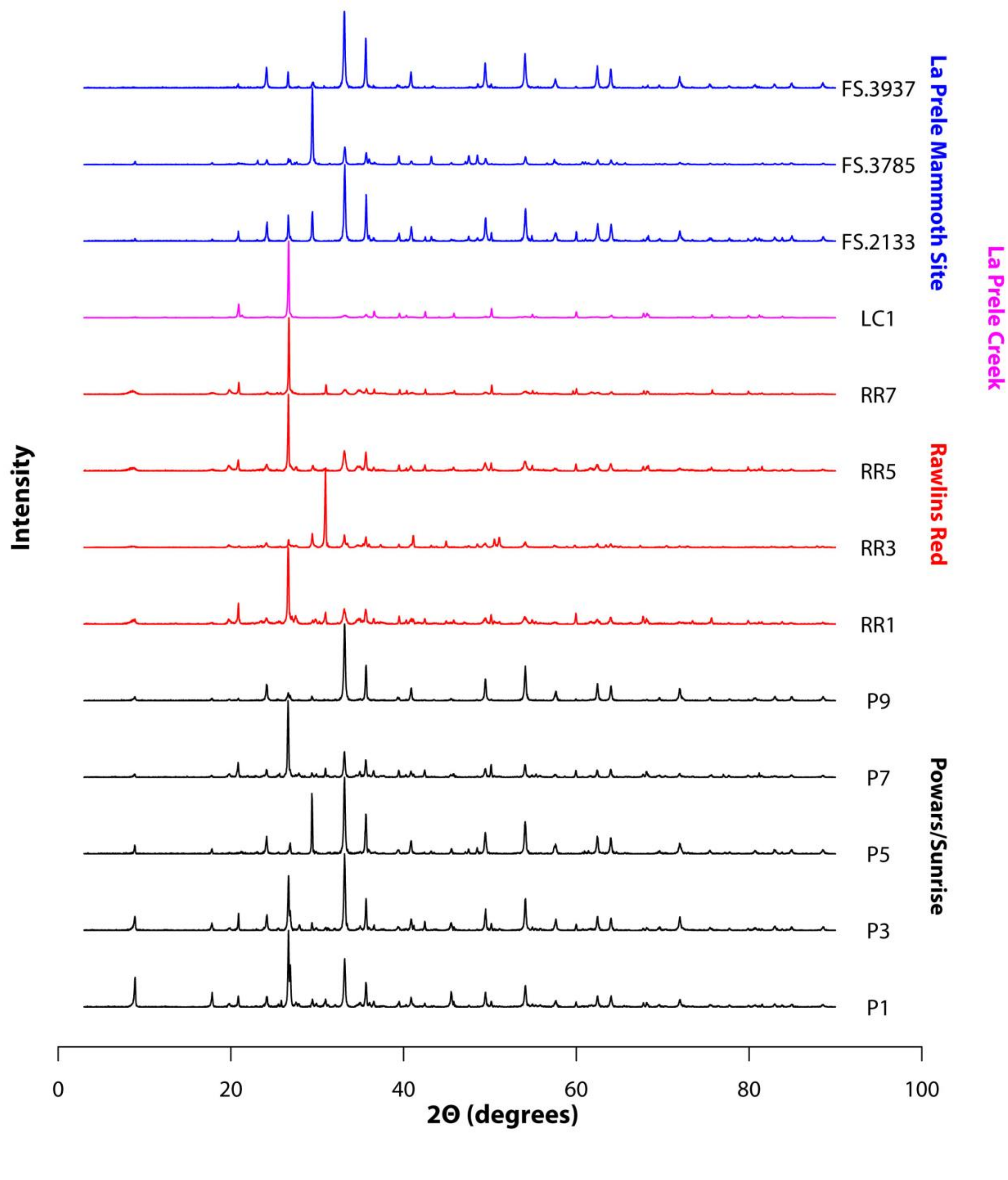


Figure 2 Relative concentrations of Titanium and Chromium each in comparison to Iron

Figure 3


FS.3937
FS.3785
FS.2133
LC1
RR7
RR5
RR3
RR1
P9
P7
P5
P3
P1
La Prele Mammoth Site
La Prele Creek
Rawlins Red
Powars/Sunrise
Intensity
0
20
40
60
80
100
2Θ (degrees)

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