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Iron isotope analysis of red and black pigments on pottery in Nasca, Peru

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Abstract The Nasca culture of the south coast of Peru developed during the first millennium AD and is known internationally for its elaborately decorated polychrome pots. Despite decades of iconographic analysis, little is known about the more technological aspects of Nasca pigment production and application. We present results from a pilot study on iron isotopes as a potential line of inquiry into the differences between red and black pigments in Nasca pigments. As well, we conduct a small firing experiment to examine potential changes in isotope composition. Our analyses show three significant results. First, firing does not change the isotopic ratios of Fe in pigments. Second, red and black pigments show differences in their iron isotope composition, which relate to differences in the minerals used to make the different colors. Third, naturally available hematite samples show greater isotopic variation than pigment samples, suggesting that people selected a limited range of iron oxides to produce pigments.

Keywords Isotope analysis · Nasca · Hematite · Red and black pigments · Iron oxides

Introduction

Iron oxides are common in geological deposits around the world and were incorporated by ancient peoples into a range of technologies. Of course, iron oxides were an integral part of the sweeping changes in metallurgy during the Iron Age in Eurasia (ca. 1200BC; Gullapalli 2009; Wells 1990) and Africa (Holl 2009). Older still is the role that iron oxides played in pigmenting technologies. The vivid red and black colors of different oxides and oxyhydroxides made them especially attractive as coloring agents, and iron oxides are known from a number of Pleistocene sites. For example, scored pieces of red ochre from Middle Stone Age sites in Southern Africa have recently been cited as among the earliest evidence for dramatic changes in symbolic behavior among our human ancestors (Henshilwood et al. 2011; Mackay and Welz 2008; Marean et al. 2007).

As in other regions, iron oxides were also widely used in the ancient Andean world. Smelting of iron ores is unknown in pre-Columbian times, but their use has been documented as part of offerings in graves (e.g., Lagostera et al. 2000) and to the sea where they were combined with white corn flour (Petersen 2010). More important, however, is the widespread use of iron oxides as pigmenting agents, including in wall murals (Scott et al. 1998), pottery (Petersen 2010: p. 9; Vaughn et al. 2005; Yacovleff and Muelle 1934), and textiles (Bonavia 1959, 1985; Phipps 1989; Yacovleff and Muelle 1934).

Surprisingly, other than simply documenting their presence in pigments, the study of iron oxides in Andean archaeological contexts has been minimal. We know that these minerals were mined on a fairly large scale (Salazar et al. 2011; Salinas and Salazar 2008; Vaughn et al. 2007, 2013), yet, little archaeometric research has focused on characterizing iron oxides. This is quite unlike the growing archaeometric literature on iron oxides in other regions (e.g., Erlandson et al. 1999; Degryse et al. 2009; Kiehn et al. 2007; Mooney et al. 2003; Popelka-Filcoff et al.

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2007, 2008; Smith and Pell 1997; Weinstein-Evron and Ilani 1994).

In this paper, we explore the potential of Fe isotopes in Nasca ceramic pigments to inform on ancient ore exploration, pigment manufacture, and pottery production. We examine variation in Fe isotopes in three types of materials: red pigments, black pigments, and a small sample of unmodified hematite samples. As well, we initiate a small set of experiments to show that iron isotope ratios in pigments do not change when fired. We follow the lead of other recent studies exploring the stable isotope ratios of tin and lead in ancient weapons, coins, and sacred objects such as the Gundestrup cauldron (Gale and Stos-Gale 1982; Gale et al. 1999; Nielsen et al. 2005; Haustein et al. 2010; Klein et al. 2010). These methods use the significant natural variations in isotopes observed in ore minerals. In cases where the isotopic compositions of the ancient metal objects were not significantly altered during smelting (e.g., Cui and Wu 2011; Gale and Stos-Gale 1982; Gale et al. 1999; Stos-Gale and Gale 2009), stable isotope ratios have been used to trace potential ore sources to workshops and finally to artifacts. For example, Habicht-Mauche et al. (2000) examined thirteenth century glassy pigments on pottery in the American Southwest and conclude that the Pb isotopic composition of ore minerals added as flux to pigments remains unchanged during production. They ultimately use that information to trace pigments to lead ores mined at Cerillos Hills, New Mexico.

Three complementary studies were conducted here. First, we undertook experiments to determine the influence of firing in oxidizing and reducing atmospheres, respectively, on Fe isotopic compositions in iron-rich pigments. This was done to monitor possible disturbances in iron isotope compositions of pigments during ancient firing. Second, we measured iron isotopes in red and black pigments from Nasca sherds to determine if these differed for the two colors. Iron isotopic compositions of three ceramic pastes underlying pigments were also measured to monitor the potential of isotopic exchange between clay and pigment during ancient firing. Third, we analyzed a small number of iron oxide samples from one ancient and several modern mines. Our goal here was to examine the potential range of Fe-isotope ratios in possible pigment sources and compare that to variation in the actual pigments.

Background

Iron isotopes

Iron is an abundant element in the earth's crust (~5 wt% on average). It often initially occurs in silicate minerals as

ferrous iron (Fe^{2+}), but is oxidized in some environments to form a range of ferric (Fe^{3+}) or mixed ($\text{Fe}^{2+}/\text{Fe}^{3+}$) oxide and oxyhydroxide minerals. Table 1 presents some common oxide and hydroxide minerals that are found in pigments (see Eastaugh et al. 2008), including those found in the Nasca artifacts discussed below. When included as part of pigment mixtures, color can vary depending on the texture (i.e., how fine the mineral is ground in a pigment) and the presence of impurities (i.e., elements that substitute for iron).

Iron has four naturally occurring stable isotopes ^{54}Fe , ^{56}Fe , ^{57}Fe , and ^{58}Fe . Various natural and biological processes are known to fractionate these, leading to significant variations in iron isotope ratios in different geological environments (e.g., Anbar et al. 2000; Craddock and Dauphas 2011; Dauphas and Rouxel 2006; Johnson and Beard 2006; Johnson et al. 2010). During high-temperature magmatic processes, Fe is only fractionated to a minor degree resulting in the narrow range in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios for igneous rocks of about 0.4‰ ($\delta^{56}\text{Fe}$ ‰ between ~−0.2 and +0.2, Beard and Johnson 2004 in their Fig. 1; Richter et al. 2009). This is not the case for low-temperature systems where significant abiotic fractionation occurs in aqueous environments (e.g., Anbar et al. 2000; Bullen et al. 2001) or as a result of bacteria that exploit Fe redox gradients to gain energy (e.g., Johnson and Beard 2006). Following fractionation, iron-bearing materials may make their way into geological sediments, which may subsequently be exposed on land and exploited by humans. Because iron is one of the most important transition elements in (bio)geochemical processes and cycles, geologists and geochemists are increasingly turning to Fe isotopes to gain information about a range of paleoceanographic processes (e.g., Beard et al. 2003).

Table 1 Minerals found in Nasca red and black pigments discussed in text, chemical formulas, and general color

Common name	Chemical formula	General color
Hematite	Fe_2O_3	Red-brown
Goethite	$\text{FeO} \cdot \text{OH}$	Yellow-brown
Magnetite	Fe_3O_4	Black-brown
Ilmenite	FeTiO_3	Black-grey
Magnesioferrite	$\text{Mg}(\text{Fe}^{3+})_2\text{O}_4$	Black-brown
Jacobsite	$(\text{Fe} \cdot \text{Mn})_2\text{O}_4$	Black-brown
Bixbyite	$(\text{Mn} \cdot \text{Fe})_2\text{O}_3$	Black
Ramsdellite	MnO_2	Black-grey
Geikielite	MgTiO_3	Black-red
Rutile	TiO_2	Red-clear
Barite	BaSO_4	White-clear
Quartz	SiO_2	White-clear

Geology of the Nasca region

Our focus is on the Nasca region, south coast of Peru (Fig. 1). Geologically, this area includes a southwest to northeast trending Cordillera de la Costa (Coastal Range), consisting of Mesozoic to Tertiary sedimentary layers with Paleozoic igneous rocks. The region also includes the Ica-Nazca depression, a broad desert basin comprised of Tertiary marine and Quaternary alluvial deposits, and the Andean Cordillera Occidental (Western Andean Range) that rises rapidly from the desert plain to an elevation of more than 4,000 m. The Andean Cordillera Occidental consists of Mesozoic and Tertiary formations with Cretaceous intrusions (Eitel and Machtle 2009; Stöllner 2009; Montoya et al. 1994). Most metal ore deposits in the Nasca region are found in Cretaceous rocks of the Coastal Batholith composed of granites, granodiorites, tonalites, and gabbro diorites, and the Cretaceous rocks of the Bella Unión Complex consisting mostly of andesites and occasionally with pockets of younger intrusive subvolcanic rocks (mostly dacites) (Montoya et al. 1994; Stöllner 2009: p. 401). Such varied regional geology has proven effective in archaeological studies attempting

to trace the provenance of various materials (Weigand et al. 1977; Wilson and Pollard 2001).

We have undertaken investigations in several valleys of the Nasca region. The Southern Nasca Region, comprising the valleys Aja, Tierras Blancas, Taruga, and Las Trancas, has the general characteristics of south coast geology described above. The Andean Cordillera Occidental rises from the modern town of Nasca at about 500 m elevation and is composed primarily of the Guanero Formation, a marine sedimentary stratum from the Cambrian, intersected by river valleys containing Quaternary alluvial and aeolian deposits. The Guanero Formation has several Lower and Upper Cretaceous plutonic intrusions (Portachuelo and Copara formations of the Coastal Batholith), consisting of granodiorites and tonalites, and subvolcanic intrusions of the Bella Unión Complex, that are mostly andesitic in composition. In the Central Nasca Region of Palpa and Ingenio, the Cambrian Formation Guanero is buried in Quaternary alluvium, and the Andean Cordillera Occidental consists of the same plutonic and subvolcanic intrusive rocks as the Southern Nasca Region.

Our previous investigations in southern Peru showed that the exploitation of iron oxide ore was more than casual. Mina

Fig. 1 Map of Nasca region and locations mentioned in the text

Primavera is a large hematite mine in an artificial cave in the Ingenio Valley of the south coast that is the locus of continuing excavations (see Vaughn et al. 2007, 2013; Fig. 1). The mine is located in the foothills of the Andes as they rise up from the flat desert plain comprising the Ica-Nazca Depression of the south coast. The mine falls within the Portachuelo Formation, composed of Cretaceous marine sedimentary deposits with intervals of intrusive volcanic pyroclastics. Inside, thousands of siltstone hammerstones and bifaces used to remove the dark red material were found. Food refuse, gourds, and pottery indicate that miners probably camped in the cave. Large mortars in the floor of the cave to powder materials and the remains of textile bags testify to the processing and transportation of ore from the cave. We estimate that 700 m³ of ore was removed from the cave over the course of at least 1,400 years. Radiocarbon dates from the mine suggest these activities commenced more than 2,000 years ago and continued to at least AD 1350 (Vaughn et al. 2007). More recent excavations in 2010 imply even earlier mining activity (i.e., by as early as 200BC), but confirm that the principal exploitation of the mine occurred between ca. AD 1 and 450 (Vaughn et al. 2010).

On a larger geographic scale, only a small number of ancient mines have been recorded and reported by archaeologists in the Andes (see Tripcevich and Vaughn 2013). These include an ancient hematite mine (Salazar et al. 2011), copper mines (Cantarutti 2013; Lechtman 1976; Salazar and Salinas 2008; Shimada 1994), cinnabar mines (Burger and Matos Mendieta 2002), turquoise mines (Salazar et al. 2010), and a series of silver and gold mines mentioned in the chronicles that were also exploited by the Spanish (see Berthelot 1986 and Schultze 2013 for a summary). Survey for, and excavation of, additional mines will certainly help us better understand ancient mining (Eerkens et al. 2009). Until then, analysis of the artifacts themselves, as we attempt here, can also provide indirect and complementary data on these activities.

Methods

Three archaeometric methods, X-ray diffraction (XRD), electron microprobe (EM), and iron isotope analysis (IIA), were used as part of this study to characterize the mineralogy and composition of naturally occurring iron oxide samples and archaeological pigments applied to ceramic vessels. XRD and EM were used to help determine mineralogy and structure of pigment, as a baseline for the IIA, and are reviewed briefly. The focus of this paper is on the IIA.

First, all samples except one natural iron-oxide were analyzed by XRD to determine mineralogy. Naturally occurring iron oxide samples were powdered and analyzed using a Rigaku Ultima IV X-ray diffractometer, producing Cu K α

radiation, with a graphite diffracted beam monochromator, and operated at 40 kV and 40 mA. Samples were scanned from 2 to 60° 2-theta at the rate of 2° 2-theta per minute, with a step size of 0.02°. By contrast, pigments applied to vessels were analyzed in situ (i.e., while still on the sherd surface) using an Inel XRD with a position-sensitive detector. The beam was set to focus on the outer surface of each sherd, limiting the depth of penetration to approximately 10 μ m. We were able to examine the pigments only where they were exposed on the sherd surface. Samples were scanned from 10 to 60° 2-theta at a rate of 2° 2-theta per minute. Output from XRD scans was compared to a standard library of minerals to match peak intensities at different angles. Diffractograms were analyzed using Jade software (Materials Data Incorporated, Livermore, CA) for mineral identification.

Second, polished thin section samples were prepared from all pot sherds, and analyzed using a Cameca SX-100 EM. Backscatter electron (BSE) images were collected for each sherd. As well, lower-resolution scans for a subset of particular elements, including Ca, Cu, Fe, Mg, Mn, Na P, and Si, were generated using wavelength dispersive spectrometers (WDS). The BSE and WDS images allowed us to evaluate the spatial distribution of different elements, revealing information about the structure of pigments and mineralogy.

Third, for the IIA, pigment samples were removed from the exterior surface of sherds using a Foredom drill with a silicon-carbide drill bit, being careful not to include material from the underlying pigments or ceramic paste. Powdered pigment was collected on wax paper and transferred to a small glass vial for subsequent processing via mass spectrometry. As a control, we also examined the Fe isotope composition of the underlying clay paste in three sherds. This was accomplished by removing and powdering material from the areas of the interior of the sherd where no pigment had been applied. The purpose was to examine possible contamination from the underlying paste during sampling and/or possible exchange of Fe between the pigment and clay during ancient firing. EM images did not suggest diffusion of any iron into underlying matrix, but do show the presence of small numbers of iron oxide clasts within the fabric of the clay paste. Instead, the majority of the clay paste is comprised of aluminosilicate clays mixed mainly with clasts of quartz, feldspar, and biotite, though small numbers of other minerals are also present. Because iron is otherwise uncommon in the clay paste, these clasts likely comprise the vast majority to the Fe isotope signature.

Approximately 500 μ g of material was weighed out for each pigment, clay paste, or ore sample. Samples were digested in closed Savillex® PFA containers in a mix of concentrated HF-HNO₃. Following dry-down, fluoride complexes were removed at high temperature. Fe separations were done by anion-exchange chromatography using Biorad AG® 1-X8. Elements such as Cr and Ni wash out,

while Fe(III) adheres to the anion exchange resin in strong normality HCl (e.g., Beard and Johnson 2003; Dauphas et al. 2004). We use 8 N HCl to remove “matrix” followed by elution of Fe with 0.5 N HCl, H₂O and 8 N HNO₃ to ensure full Fe recovery (Leshner et al. 2009). Procedural blanks were 1–5 ng of iron, which ranged between 0.0002 and 0.001 % of total Fe and therefore are negligible.

Samples were analyzed by Nu Plasma HR (Nu032) MC-ICP-MS at the UC-Davis Interdisciplinary Center for Plasma Mass Spectrometry in dry plasma mode (DSN-100). Measurements are done in high mass resolution mode ($m/\Delta m$ ranging from 8,000 to 10,000) to resolve mass interferences from isobaric argide and oxide species on Fe isotopes ($^{40}\text{Ar}^{14}\text{N}^+$ on $^{54}\text{Fe}^+$, $^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$, $^{40}\text{Ar}^{16}\text{OH}$ on ^{57}Fe , and $^{40}\text{Ar}^{18}\text{O}$ on ^{58}Fe). Furthermore, ^{53}Cr is measured to monitor the potential isobaric interferences of ^{54}Cr on ^{54}Fe . Sample measurement alternates with IRMM-014 Fe standard, which allows for delta values to be calculated using sample standard bracketing (e.g., Belshaw et al. 2000; Beard et al. 2003; Schoenberg and von Blanckenburg 2005; see Dauphas and Rouxel 2006 for a review). Care is taken to keep concentrations of sample and standards within 5 % of one another. Iron isotope composition is expressed using the standard “ δ ” notation as:

$$\delta^x\text{Fe} = \left[\left(\frac{{}^x\text{Fe}/{}^{54}\text{Fe}}{\text{sample}} \right) / \left(\frac{{}^x\text{Fe}/{}^{54}\text{Fe}}{\text{standard}} \right) - 1 \right] \times 1,000$$

where standard is IRMM-014 and X is Fe isotopes 56 and 57.

Each sample analysis includes four or more replicate measurements with reproducibility of delta values <0.10‰ (2 S.D.) for $^{56}\text{Fe}/^{54}\text{Fe}$ and <0.15‰ (2 S.D.) for $^{57}\text{Fe}/^{56}\text{Fe}$. BCR-2 yielded $\delta^{56}\text{Fe}=0.103\pm0.042\text{‰}$, which is in good agreement with published (e.g., Dauphas et al. 2009) and long-term in-house values (Leshner et al. 2009).

Sample selection

In addition to modern iron oxide samples from mines and a pigment sample from Cahuachi (discussed below), we selected seven polychrome sherds from the Nasca region for IIA. Figure 2 gives an example of an Early Intermediate Period sherd from the Nasca region, showing red and black (and white, unanalyzed) pigments on a buff slip. We focus here on seven red pigments and five black pigments from these sherds. The sherds represent a range of time periods between 2000 and 550 years ago (see Table 2 for local cultural chronology) and were selected because other complementary analyses had been conducted on the pigments, giving us greater control over the mineralogy of our Fe-isotope studies.

Five small (ca. 1–5 g) iron oxide ore samples from (or close to) four mines in the Nasca region were also analyzed

Fig. 2 Early Intermediate Period Nasca sherd, showing red and black pigments

for this study. These represent fortuitously collected samples from a spatially distributed range of locations, and are not an exhaustive or systematic representation of iron oxides from the region. We do not suggest that these samples characterize the full range of isotopic variation at a particular mine or within a valley. Instead, we analyzed these samples simply to provide some comparative reference for the archaeological pigments. In other words, we aim to determine whether archaeological samples are less or more variable than this arbitrary and distributed sample from the Nasca region.

Table 2 Chronology for the Southern Nasca Region (SNR)

Horizon/period	Local period	Culture	Approximate calendar years
Late Horizon	–Inca–	Inca	AD 1476–1532
Late Intermediate (LIP)	–Tiza–	Tiza	AD 1000–1476
Middle Horizon (MH)	–Loro–	Loro, Wari	AD 750–1000
Early Intermediate	–Nasca–	Late Nasca (LN)	AD 550–750
		Middle Nasca	AD 450–550
		Early Nasca (EN)	AD 1–450
Early Horizon	–Formative–	Proto Nasca	100 BC–AD 1
		Paracas	800–100 BC
Initial Period	–Initial–		1800–800 BC

Sample initials refer to an internal sampling system: *EN* Early Nasca, *LN* Late Nasca, *MH* Middle Horizon; *LIP* Late Intermediate Period

Two samples come from Mina Primavera (see Vaughn et al. 2007), described above, and one each from three other locations. The latter samples were collected by KJV and JWE during surveys of the Nasca region (see Eerkens et al. 2009; Vaughn and Neff 2004) at localities near or within modern or recently abandoned copper and gold mining operations. The majority of these iron oxide samples appear to represent gossans of copper or other ore deposits, which could have been exploited for pigments in prehispanic times. Due to the sensitivity of precious metal deposits today, additional information on the nature of these modern mines was not available to the authors.

In addition, we examined iron oxide powder recovered from the civic-ceremonial center Cahuachi (see Carmichael 1998; Silverman 1993). This material was excavated by Alfred Kroeber during the Captain Marshall Field Second Archaeological Expedition to Peru, 1926 and curated at the Field Museum in Chicago (Kroeber and Collier 1998). The sample (Catalog # 1694.171208) consisted of a single bag of what was described as “paint” (collected as a powder folded in tissue paper). Grave Aj-10 where the bag was found consists of an adult male skeleton buried with numerous polychrome ceramics including a double spout bottle, textiles (including plain, embroidered, and crocheted specimens), a wicker basket, bone spear throwers, dart shafts, feathers, shell

ornaments, and other artifacts including the powder itself (Kroeber and Collier 1998: p. 79). The ceramics from this grave are all either Nasca 2 or Nasca 3; thus, the grave clearly dates to the Early Nasca phases of the Early Intermediate Period (see Table 2).

Results

We briefly discuss the results of the XRD and EM analyses first as they set the stage for interpreting the IIA, which is discussed afterwards.

XRD and EM

The XRD and EM analyses allowed us to establish the mineralogy of each pigment sample, the physical structure, and the superposition of different pigments over one another. Most importantly, these analyses allowed us to identify iron-bearing minerals, their rough abundance, and their spatial distribution in each pigment sample.

For example, Fig. 3 shows a photo of the exterior and five WDS maps for a cross section through one sherd (PNT-5; see Table 3) with three superimposed pigments, a black on the outside (left), overlying a red, which again overlays a white

Fig. 3 Electron microprobe images for PNT-5, showing three chemically distinct superimposed pigments in cross section: black over red over white. The *top left pane* shows the sherd in plan view. Remaining

panels show the same cross section. Backscattered electrons (BSE) shown in *upper middle pane*, *upper right* is iron. *Bottom row, left to right*, magnesium, phosphorous, and manganese

Table 3 Sherds included in this study and associated pigment mineralogy established by XRD and EM

Sample	Period	Red	Red mineralogy from XRD and EM (main components)	Black	Black mineralogy from XRD and EM (main components)	Clay paste
PNT-3	EN	✓	Hematite	✓	Hematite, Magnesioferrite, Bixbyite	
PNT-5	EN	✓	Hematite, Geikielite	✓	Hematite, Magnetite	✓
PNT-12	LN	✓	Hematite, Magnesioferrite			
PNT-14	LN	✓	Hematite	✓	Hematite, Ilmenite	✓
PNT-16	MH	✓	Hematite, Ilmenite	✓	Hematite, Magnetite, Ilmenite	✓
PNT-20	LIP	✓	Hematite, Ilmenite	✓	Hematite, Rutile, Ramsdellite	
PNT-21	LIP	✓	Hematite			

Symbol “✓” marks what material on the sherd (red pigment, black pigment, or underlying clay paste matrix) was analyzed for Fe isotopes. Mineralogy determined by XRD and EM

Sample initials refer to an internal numbering system we used: *EN* Early Nasca; *LN* Late Nasca; *MH* Middle Horizon; *LIP* Late Intermediate Period (see Table 2)

slip. The white slip then overlays the sherd paste. A backscattered electron (BSE) map is shown in the upper middle panel of Fig. 3, iron concentrations in the upper right, magnesium in the lower left, phosphorous in the lower middle, and manganese in the lower right panel. The BSE image does not distinguish between the black and red pigments, which are equally bright due to the higher density of heavier elements (Fe and Mn in particular). The Mn map clearly shows a thin layer of black pigment with elevated levels of manganese on top of the red pigment. Manganese in the black pigment is concentrated in clasts that are rich in both Fe and Mn. This was confirmed by XRD analyses, which showed the presence of bixbyite, a manganese-iron oxide that can form from MnO_2 at temperatures above 450 °C but below 950 °C (when jacobsite forms; Schweizer and Rinuy 1982). The underlying red pigment is also elevated in Fe (upper right panel), but lacks significant amounts of Mn. Note also that the white pigment is lacking in measurable quantities of iron, while the sherd paste has minor amounts of iron, creating differences in contrast. Phosphorus is differentially concentrated in the paste of the white pigment, shown in lower middle panel. Finally, magnesium is especially concentrated in the sherd paste.

Relevant results from the XRD and EM analyses for both pigments and natural iron oxide samples are presented in Tables 3 and 4, respectively. Analyses reveal that the main Fe-bearing mineral in the pigments is hematite, present in high amounts in all red and black pigments included in this study. However, ilmenite was present in four pigments (two red, two black), magnesioferrite in two pigments (one red, one black), magnetite in two black pigments, and bixbyite in one black pigment.

Although Fe may exist in other components of a pigment (e.g., a binder) in trace amounts, Fe concentrations in the minerals listed in Tables 3 and 4 will be orders of magnitude higher. Indeed, XRD did not identify any other iron-bearing minerals. Thus, we argue that the vast majority of the Fe-

isotope signal in the pigments derives from the iron oxide component. By extension, mixing low-Fe binders should not appreciably shift the Fe-isotope ratios.

XRD analysis on five of the natural iron oxide samples establishes their mineralogy as well (Table 4). Results show that a limited range of minerals are present in these samples. As expected, hematite is the major mineral in all samples, but barite, quartz, and goethite were also noted in some. No other Fe-bearing minerals were detected. Note that goethite will form hematite when fired above 300 °C (Eastaugh et al. 2008: p. 207), and the firing temperature of prehispanic ceramics was certainly well above this figure. Thus, if iron oxide samples such as these were used to create pigments, the XRD results suggest that the Fe isotope signal in pigments will derive only from the hematite component.

Results also point out the similarity between the Mina Primavera and Cahuachi samples, showing all three have hematite and barite. The two remaining samples from the Middle Aja Valley and Quebrada Paccaya also have similar mineralogical signatures to one another, lacking barite, but containing hematite, quartz, and goethite. We believe the mineralogical similarity between Mina Primavera and Cahuachi is significant, particularly given isotopic similarities discussed below.

Table 4 Results of XRD analyses of five natural iron oxide samples

Sample	Major peaks
Mina Primavera 1	Hematite, barite
Mina Primavera 2	Hematite, barite
Middle Aja Valley	Hematite, quartz, goethite
Quebrada Paccaya	Hematite, quartz, goethite
Cahuachi	Hematite, quartz, barite

The Aja Valley and Cahuachi samples had two and one additional minor peaks, respectively, that were not identified

Table 5 Results of firing experiments

Experiment	Produced	Kiln	$\delta^{56}\text{Fe}$ (‰)		$\delta^{57}\text{Fe}$ (‰)	
	Pigment		Start	End	Start	End
1. Hematite only	Red	Oxidizing	0.65±0.06	0.71±0.18	0.94±0.14	1.05±0.29
2. Hematite on tile	Red	Oxidizing	0.65±0.06	0.62±0.05	0.94±0.14	0.90±0.05
3. Hematite on tile	Black	Reducing	0.65±0.06	0.61±0.05	0.94±0.14	0.90±0.11
Tile			0.50±0.06			

Errors reflect 2 S.D. based on four or more replicate analysis of samples (see “Methods” section)

Iron isotope analysis

Three complementary iron isotope analyses were undertaken and are discussed below. First, we fired pigment samples on a clay substrate with known Fe isotope composition in oxidizing and reducing atmospheres. These experiments allowed us to examine potential changes in Fe isotope composition of pigments under thermal and atmospheric conditions similar to those that Nasca area potters likely used in prehispanic times. Second, we analyzed red and black pigment samples from several archaeological sherds. Finally, we analyzed natural iron oxide samples from the region, including modern mines, a known ancient iron oxide mine (Mina Primavera), and an ancient red ochre sample from the civic-ceremonial center of Cahuachi. Each of these analyses is discussed in turn below.

Firing experiments

Experiments were designed to imitate the conditions during ancient firing in oxidizing and reducing atmosphere to produce red and black pigments, respectively. The goal was to examine the effects of firing on the Fe isotope ratios in the produced pigments. For all experiments, the starting material was the same powdered red ochre from Mina Primavera, which XRD analysis showed is mainly hematite mixed with some barite. This material was placed in a kiln and fired in oxidizing (experiments 1–2) and reducing (experiment 3) atmospheres (Table 5). Because Nasca ceramics lack glazes we set our maximum temperature at 900 °C, a rough estimate for prehispanic firing temperatures. For all three experiments, temperatures were ramped up 100 °C/h for the first 9 h, with the final temperature held for 4 h.

We did not expect to see any isotopic shift, as Fe does not form gases at these low temperatures; thus, the pigment represents a closed system for Fe. To examine possible clay–hematite interactions, the powdered hematite was fired separately (sample 1) as well as applied to a dried (previously unfired) clay tile characterized by lower $\delta^{56}\text{Fe}$ ~0.50±0.06 and FeO=0.70 wt% (experiments 2 and 3, Table 5).

As seen in Table 5, firing hematite to form red (oxidizing) and black (reducing) pigment had no detectable effect on the iron isotope ratios. Even the presence of a clay substrate did not change this result, suggesting little or no isotope diffusion between the pigment and underlying clay matrix. Unfortunately, we were unable to analyze the resulting pigments by XRD or EM. However, EM images of the archaeological sherds themselves corroborate this finding, showing there is no migration of Fe into the underlying clay substrate. This result parallels studies of other isotopes such as those of Pb suggesting that heating to high temperatures does not significantly alter isotope ratios (Cui and Wu 2011; Habicht-Mauche et al. 2000).

Pigments and pastes from sherds

Table 6 and Fig. 4 show Fe isotope compositions of the seven red and five black pigments from the Nasca region, as well

Table 6 Fe isotope analyses on ancient samples, including red and black pigments and underlying ceramic paste

Sherd	Period	Description	$\delta^{56}\text{Fe}$ (‰)	$\delta^{57}\text{Fe}$ (‰)
PNT-3	EN; N3	Red	0.21±0.09	0.29±0.17
PNT-3	EN; N3	Black	−0.10±0.07	−0.16±0.08
PNT-5	EN; N4	Red	0.38±0.06	0.51±0.10
PNT-5	EN; N4	Black	−0.08±0.14	−0.14±0.18
PNT-5	EN; N4	Ceramic paste	0.28±0.05	0.39±0.09
PNT-12	LN; N6	Red	0.19±0.05	0.27±0.04
PNT-14	LN; N6	Red	0.56±0.05	0.82±0.12
PNT-14	LN; N6	Black	−0.10±0.08	−0.17±0.06
PNT-14	LN; N6	Ceramic paste	0.20±0.11	0.31±0.10
PNT-16	MH	Red	0.23±0.12	0.36±0.11
PNT-16	MH	Black	−0.23±0.05	−0.33±0.12
PNT-16	MH	Ceramic paste	−0.01±0.14	0.00±0.16
PNT-20	LIP	Red	0.08±0.07	0.08±0.09
PNT-20	LIP	Black	0.36±0.07	0.54±0.15
PNT-21	LIP	Red	0.19±0.08	0.36±0.09

Errors represent 2 S.D. based on four or more replicate analysis of samples (see “Methods” section)

Fig. 4 Plot of $\delta^{56}\text{Fe}$ versus $\delta^{57}\text{Fe}$ for ancient pigments and iron oxide samples. Bars represent two standard deviations. Red pigments are in red, black pigments in black, ceramic paste depicted as open symbols, and hematite samples as stars. Symbols show archaeological periods given by diamonds for (early and late) Nasca period, squares for Middle Horizon, and triangles for Late Intermediate Period. Diagonal line shows linear regression through scatter of all points

from the underlying clay paste of three sherds. In Fig. 4, $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ for ore samples and pigments are marked by time period (symbol) and type (color). Note that the strong correlation between the two isotope ratios simply reflects the naturally occurring mass-dependent fractionation for ^{54}Fe , ^{56}Fe , and ^{57}Fe isotopes, which is illustrated by the $\delta^{57}\text{Fe} \approx 1.5 \delta^{56}\text{Fe}$ relationship and the near zero intercept (slope=0.67 and intercept of 0.004 in Fig. 4; $R^2=0.998$). The two most striking observations are the significant $\delta^{56}\text{Fe}$ variation for the pigments, well outside analytical precision, and the fact that red and black pigments fall in two distinct groups, whereas ore hematite samples vary significantly across both pigment groups.

Red pigments

Most red pigments (from the Nasca period, the MH, and one from the LIP period) as well as the LIP black pigment form a cluster (the “red cluster” in Fig. 4; identified visually) with $\delta^{56}\text{Fe}$ from 0.15 to 0.55‰. Two red pigments fall outside this cluster (LIP PNT-20 and LN PNT-14); the latter with the highest $\delta^{56}\text{Fe}$ observed for any pigment in this study (Fig. 4).

Black pigments

Three Nasca and one Middle Horizon black pigments are characterized by indistinguishable and slightly negative $\delta^{56}\text{Fe}$ ranging from ~ -0.3 to -0.05 ‰ (the “black cluster”

in Fig. 4), making them distinct from the red pigments discussed above. This is not surprising given the difference in mineralogy of the blacks, indicating hematite mixed with manganese-bearing minerals. Again, the exception is LIP PNT-20, which clusters with the red pigments. PNT-20 is also distinct by its unusual mineralogy, containing rutile and ramsdellite; minerals that no other pigment had in measurable amounts (Table 3). Rutile and ramsdellite have little or no Fe (some rutiles contain small amounts of Fe), and would not significantly alter the Fe-isotope ratios. However, the presence of these unusual minerals could indicate exploitation of a different source of iron oxides, for example, if these minerals were naturally present (i.e., co-occurring) in the ores that also contained hematite. If so, this alternative source of hematite for the LIP black may have had similar Fe-isotope ratios to the red pigments. Additional research is clearly needed to address this issue, but we suggest the unusual mineralogy combined with the unusual Fe-isotope signature of the PNT-20 black pigment, relative to other blacks, is not fortuitous.

Ceramic paste

The isotopic compositions of the underlying ceramic pastes of both Nasca sherds (PNT-5 and PNT-14) are similar and plot with the red pigment cluster (Table 6, Fig. 4). By contrast, the ceramic paste from the Middle Horizon sherd (PNT-16; open triangle in Fig. 4) is isotopically much lighter and unlike any Nasca sherds. The sample size is quite small

here, and it is unclear what is contributing to the variation in Fe isotopes in the underlying clay pastes.

Natural iron oxide samples

Six regional hematite samples from the Nasca Region have $\delta^{56}\text{Fe}$ between -0.2 and 1.3‰ (Table 7, Fig. 4). Samples from the four modern mines have uniquely different compositions, whereas the two samples collected inside the ancient mining site at Mina Primavera, as well as the hematite powder from an ancient grave in Cahuachi (see Fig. 1 and “Sample selection” section) have overlapping compositions ($\delta^{56}\text{Fe}$, $\sim 0.7\text{‰}$). Compared to the archaeological pigment samples ($\delta^{56}\text{Fe}$, -0.2 to 0.6‰), regional iron ores thus cover a larger isotopic range.

Again, we do not suggest that one or two samples are sufficient to characterize isotopic variation within a mine, nor that we can directly connect archaeological pigments to such a mine using Fe isotopes alone. We merely aim to establish such hypotheses, which can be tested in future analyses, and produce some comparative data for the archaeological samples.

Discussion

The most interesting result of this pilot study is that red and black pigments from the Nasca Region are characterized by different iron isotopic compositions (cf. red and black clusters in Fig. 4). A *T* test (two-tailed, unequal variance) shows that the mean $\delta^{56}\text{Fe}$ of red and black is not the same ($p=0.043$), suggesting they are drawn from different underlying populations.

We envision two end-member scenarios to explain the difference in iron isotopes for the red and black pigments. First, the difference could be due to mineralogical variation.

For example, two of the black pigments include magnetite, and it is possible that this mineral has much lower $\delta^{56}\text{Fe}$, which would bring down $\delta^{56}\text{Fe}$ in the pigment overall. Other black pigments could similarly contain minor amounts of magnetite, undetected by XRD, that could alter $\delta^{56}\text{Fe}$. Likewise, it is possible that the single black outlier (PNT-20) lacks this mineral altogether, causing it to cluster with red pigments. Unfortunately, we are unable to analyze separately iron oxide components within pigments (e.g., hematite, magnetite, ilmenite) to evaluate this possibility. We note, however, that the mixing proportions would have had to remain relatively unchanged for centuries in order to explain the clusters in Fig. 4.

Second, it is possible that hematite, the major mineral component of both colors, has different $\delta^{56}\text{Fe}$ in red vs. black. If so, the difference in $\delta^{56}\text{Fe}$ was likely in the original hematite because, as the firing experiments showed, Fe isotope ratios are not altered under oxidized or reduced conditions, and as the EM studies show, Fe does not migrate into the underlying clay paste. Of course, it is possible that potters used different firing conditions than our limited range of experiments. Furthermore, we were unable to analyze the mineralogy of the post-fired experimental pigments using XRD, and it is possible that some recrystallization took place during firing. We suspect, however, that careful selection for particular varieties or hues of hematite on the part of prehispanic potters accounts for the differences in $\delta^{56}\text{Fe}$ in the red vs. black pigments, leading to distinctive $\delta^{56}\text{Fe}$ in the two colors. Additional research is necessary to resolve this issue.

A second significant finding concerns variation in $\delta^{56}\text{Fe}$ within red and black pigments, relative to the unmodified ochre samples collected from the Nasca region at large. As shown in Table 7, the $\delta^{56}\text{Fe}$ in the unmodified samples ranges between -0.2 and 1.3‰ . By contrast, $\delta^{56}\text{Fe}$ in red pigments ranges between 0.1 and 0.6‰ , and black between -0.2 and 0.4‰ (including the one clear outlier, PNT-20, that groups with the red cluster). An *F* test of equality of variance comparing $\delta^{56}\text{Fe}$ in red pigments vs. unmodified ochre samples suggests variances are not the same ($p=0.006$), that is, that the range of isotopic variation in red pigments is significantly less than in unmodified iron oxide samples. An *F* test comparing black pigments and unmodified iron oxides is in the same direction, indicating less isotopic variation in the former, but is less significant ($p=0.089$). If we remove the one LIP black from the comparison, which is clearly anomalous, an *F* test is significant ($p=.004$). This result suggests that potters were selecting a more narrow range of iron oxides for both red and black, much narrower than exists in the environment overall.

High natural Fe isotopic variation, even over small geographic areas, has been documented in a small number of geological studies. For example, Makl et al. (2006) report Fe isotope compositions of iron ore minerals in the Schwartzwald region, SW Germany, to investigate the

Table 7 Iron isotope ratios of hematite samples from the Nasca Region

Sample location	Description	$\delta^{56}\text{Fe}$ (‰)	$\delta^{57}\text{Fe}$ (‰)
Mina Primavera 1	Modern sample from sediment	0.73 ± 0.08	1.08 ± 0.10
Mina Primavera 2	Modern sample from cave roof	0.65 ± 0.06	0.94 ± 0.14
Middle Aja Valley	Modern sample near mine	0.07 ± 0.06	0.10 ± 0.14
Quebrada Paccpaya	Modern sample near mine	1.31 ± 0.06	1.96 ± 0.19
Mina Vetilla	Modern sample near mine	-0.19 ± 0.06	-0.28 ± 0.10
Cahuachi	Ancient iron oxide sample	0.73 ± 0.09	1.11 ± 0.18

Errors represent 2 S.D. based on four or more replicate analysis of samples (see “Methods” section)

potential of Fe isotopes as an indicator of ore formation and alteration processes. They find iron isotopic compositions of primary minerals to be controlled by hydrothermal fluids mixing with meteoric fluids to form hematite ($\delta^{56}\text{Fe}$, -0.5 to $+0.5\text{‰}$) and by hydrothermal fluids mixing with CO_2 -rich fluids to form siderite with isotopically light iron ($\delta^{56}\text{Fe}$, -1.4 to -0.7‰). Post-depositional fractionation leading to precipitation of secondary minerals later occurred between the primary ore minerals and alteration fluids (e.g., transforming the siderite into secondary isotopically light hematite). The result is large isotopic variations on a centimeter scale for the ore hematite due to iron isotope fractionation during fluid processes and mass balance (that is, how much iron precipitated from the fluid). Likewise, Busigny and Dauphas (2007) observe a large, but negative, suite of $\delta^{56}\text{Fe}$ values, ranging from -1.35 to $\sim 0\text{‰}$ in hematite and goethite concretions in sandstones from the Navajo Formation, Utah. As well, Chan et al. (2006) show even greater variation between -2.0 and 0.9‰ in iron oxide concretions from the same formation, but also suggest some geographic patterning to that variation.

How potters came to select this more narrow suite of iron oxides in the Nasca region should be the subject of future research. If such large isotopic ranges on a small scale such as those reported by Makl et al. (2006) and Busigny and Dauphas (2007) exist for all iron ores, including those in the Nasca region of Peru, it suggests intentional selection of particular iron oxides *within sources* by Nasca inhabitants. That is, miners and/or potters may have been selecting particular mineral grains for pigments, perhaps by color or texture, and rejecting others. Alternatively, it is possible that Nasca ochre sources are unlike those in SW Germany or Utah, and display less isotopic variation. In this case, the differences between pigment colors could be due to different ochre sources. Our pilot study focused on sampling pigments rather than potential source materials. To answer this question, then, we will need more intensive sampling at iron oxide sources, such as Mina Primavera (Vaughn et al. 2007).

Finally, we consider the bag containing the red ochre excavated from a grave at the civic-ceremonial center Cahuachi. This material is the best candidate we have for a pre-fired pigment material used in the Nasca region (see [Natural iron oxide samples](#) section above for more details). Previously, one of us (KJV) has argued that the majority (approximately 80 %) of Early Nasca polychrome finewares, a pottery type found at residential sites in the southern Nasca region, were produced at Cahuachi (Vaughn et al. 2006; Vaughn and Van Gijseghem 2007). In particular, the clay pastes of these Nasca finewares are similar in chemical composition to a clay adobe collected near Cahuachi, but unlike clays collected elsewhere (Vaughn and Neff 2004). By extension, most fineware pots were presumably painted at Cahuachi as well. Thus, linking the ancient Cahuachi

hematite sample to a particular location or mine, and to pottery pigments themselves, would be of tremendous value in understanding the organization of pottery production in the region.

Figure 4 shows that the Cahuachi sample is indistinguishable from the Mina Primavera samples, and uniquely different from other naturally occurring iron oxide samples (Table 7). Furthermore, the XRD results showed that barite is an important secondary mineral in all three samples, but is not present in the other natural iron oxide samples, again suggesting a link. Mina Primavera is a large and extensive hematite mine in the Ingenio Valley that was exploited in ancient times, presumably for pigments (Vaughn et al. 2013). As we mentioned above, more regional sampling of iron oxides is needed to be confident in the assignment of the Cahuachi sample to this mine. But the fact that Mina Primavera was heavily exploited for hematite during the Early Nasca period makes the link between the sample from an Early Nasca grave at Cahuachi and Mina Primavera very plausible.

Compared to the Cahuachi sample and the two Mina Primavera samples we analyzed, red and, in particular, black pigments are characterized by significantly lighter $\delta^{56}\text{Fe}$ (Fig. 4). Only PNT-14, a Late Nasca period red is close to Cahuachi and Mina Primavera, but is still slightly isotopically lighter. The Mina Primavera and Cahuachi source materials we analyzed, thus, are very unlikely to result in the Fe isotope ratios observed for the red and, in particular, black pigments. Thus, given the data at hand, Mina Primavera is not a likely candidate for the red or black pigments we studied. On the other hand, the black pigments (except PNT-20) have $\delta^{56}\text{Fe}$ identical to an iron oxide sample from Mina Vetilla, but significantly lighter than other iron oxide samples analyzed in this study (Table 7). In contrast, none of the studied iron oxide samples have compositions that correspond to the “cluster” observed for the red pigments.

We have yet to fully characterize intra-ore variation within individual iron oxide deposits, though two samples from Mina Primavera collected approximately 20 m apart are isotopically indistinguishable. As discussed above, ore minerals may vary significantly on a centimeter scale, and in order to be more confident about linking the Cahuachi raw pigment and Mina Primavera, or linking pigments applied to pottery to particular iron oxide sources, additional survey and analyses of regional iron oxide samples will be necessary.

Conclusions

Several lines of evidence suggest that Fe-isotope analysis of archaeological pigments and modern iron oxide samples can

help address important issues in the prehistory of the Nasca region. Firstly, firing hematite-based ochres at 900 °C in oxidizing and reducing atmosphere preserved Fe isotope ratios in the produced pigments. Thus, iron isotope compositions of pigments applied to pre-Columbian pottery are unlikely to be explained by exchange between the clay paste and hematite during firing. Secondly, EM analyses of these pigments show iron to be either absent or present in very low amounts in non-oxide components; over 95 % of the Fe in the studied pigments is estimated to come from the ore component. This means that admixture of other minerals, for example as binders or to alter the color (e.g., adding kaolinite to hematite to create a lighter color of red), will have only a minor effect on iron isotope compositions of the pigments. These two findings strongly suggest that Fe isotopes in pigments from the Nasca region have remained largely unchanged from the ore material collected by ancient miners.

Independent of age, the iron oxides incorporated into red and black pigments in this study show restricted isotopic ranges that are distinctly different for the two colors ($\delta^{56}\text{Fe}$ from 0.08 to 0.56‰ and from −0.23 to −0.08‰, respectively, removing the one LIP black pigment outlier). That, relative to the red pigments, black pigments (with one exception) are isotopically lighter (enriched in ^{54}Fe) may indicate that the iron-based minerals incorporated into the two colors have different geological origins, either different in their geographic location, or as different generations of Fe-bearing minerals from the same geographic location. Alternatively, it may indicate the incorporation of isotopically enriched minor Fe-based minerals in the black pigments (e.g., magnetite, bixbyite) that pull the overall $\delta^{56}\text{Fe}$ signal down.

Compared to the pigments, the variation for our smaller population of naturally occurring iron oxides in the Nasca Region ($n=6$) varies to a much higher degree ($\delta^{56}\text{Fe}$ from −0.2 to 1.3‰) suggesting people selected a narrow range of the locally available hematite to incorporate into pigments. Perhaps only certain hematite hues, varieties, or sources were of suitable quality for producing pigments on pots, or had enough iron oxide material available to make mining worthwhile. No source material was identified in this study that matches iron isotopic compositions of the red pigments.

Together, our findings suggest iron isotopes may represent an exciting new tool that may assist archaeologists to better understand the organization of mining for pigment minerals and pottery production. With additional sampling of raw materials from the region, this approach may also assist in provenance analyses of iron oxide materials. The small sample size requirements for mass spectrometry analysis combined with the increasing availability of instrumentation will continue to make this path more attractive in archaeometry.

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References

- Anbar AD, Roe JE, Barling J, Nealson KH (2000) Nonbiological fractionation of iron isotopes. *Science* 288:126–128
- Beard BL, Johnson CM (2004) Fe isotope variations in the modern and ancient Earth and other planetary bodies. *Reviews in Mineralogy & Geochemistry* 55:319–357
- Beard BL, Johnson CM (2003) High and low temperature applications of Fe isotope geochemistry. *Geochemical News* 117:8–13
- Beard BL, Johnson CM, Skulan JL, Nealson KH, Cox L, Sun H (2003) Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chemical Geology* 195:87–117
- Belshaw NS, Zhu XK, Guo Y, O’Nions RK (2000) High precision measurement of iron isotopes by plasma source mass spectrometry. *International Journal of Mass Spectrometry* 197:191–195
- Berthelot J (1986) The extraction of precious metals at the time of the Inka. In: Murra J, Wachtel N, Revel J (eds) *Anthropological history of Andean politics*. Cambridge University Press, Cambridge, pp 69–88
- Bonavia D (1959) *Una pintura mural de Pañamarca, Valle de Nepeña. Arqueológicas* 5, Publicación del Instituto de Investigaciones Antropológicas, Museo Nacional de Antropología y Arqueología, Lima
- Bonavia D (1985) *Mural painting in ancient Peru*. University of Indiana Press, Bloomington
- Bullen TD, White AF, Childs CW, Vivit DV, Schulz MS (2001) Demonstration of significant abiotic iron isotope fractionation in nature. *Geology* 29:699–702
- Burger RL, Matos Mendieta R (2002) Atalla: a center on the periphery of the Chavín Horizon. *Latin American Antiquity* 13:153–177
- Busigny V, Dauphas N (2007) Tracing paleofluid circulations using iron isotopes: a study of hematite and goethite concretions from the Navajo Sandstone (Utah, USA). *Earth and Planetary Science Letters* 254:272–287
- Cantarutti GE (2013) Mining under Inca rule in north-central Chile: the Los Infieles mining complex. In: Tripcevich N, Vaughn KJ (eds) *Mining and quarrying in the ancient Andes: sociopolitical, economic and symbolic dimensions*. Springer, New York, pp 185–211
- Carmichael PH (1998) Nasca ceramics: production and social context. In *Andean ceramics: technology, organization, and approaches* (ed. I. Shimada), 213–231. University of Pennsylvania Museum of Archaeology and Anthropology
- Chan MA, Johnson CM, Beard BL, Bowman JR, Parry WT (2006) Iron isotopes constrain the pathways and formation mechanisms of terrestrial oxide concretions: a tool for tracing iron cycling on Mars? *Geosphere* 2:324–332
- Craddock PR, Dauphas N (2011) Iron isotopic compositions of geological reference materials and chondrites. *Geostandards and Geoanalytical Research* 35:101–123
- Cui J, Wu X (2011) An experimental investigation on lead isotopic fractionation during metallurgical processes. *Archaeometry* 53:205–214

- Dauphas N, Janney PE, Mendybaev RA, Wadhwa M, Richter FM, Davis AM, van Zuilen M, Hines R, Foley CN (2004) Chromatographic separation and multicollection-ICPMS analysis of iron. Investigating mass-dependent and independent isotope effects. *Analytical Chemistry* 76:5855–5863
- Dauphas N, Pourmand A, Teng FZ (2009) Routine isotopic analysis of iron by HR-MC-ICMS: how precise and how accurate? *Chemical Geology* 267:175–184
- Dauphas N, Rouxel O (2006) Mass spectrometry and natural variations of iron isotopes. *Mass Spectrometry Reviews* 25:515–550
- Degryse P, Schneider JC, Muchez P (2009) Combined Pb-Sr isotopic analysis in provenancing late Roman iron raw materials in the territory of Sagalassos (SW Turkey). *Archaeological and Anthropological Sciences* 1:155–159
- Eastaugh N, Walsh V, Chaplin T, Siddall R (2008) *Pigment compendium: a dictionary and optical microscopy of historic pigments*. Routledge, London
- Eerkens JW, Vaughn KJ, Linares Grados M (2009) Pre-Inca mining in the Southern Nasca Region. Peru, *Antiquity* 83:738–750
- Eitel B, Machtle B (2009) Man and environment in the eastern Atacama Desert (southern Peru): Holocene climate changes and their impact on pre-Columbian cultures. In: Reindel M, Wagner GA (eds) *New technologies for archaeology: multidisciplinary investigations in Palpa and Nasca, Peru*. Springer, Berlin, pp 17–37
- Erlanson JM, Robertson JD, Descantes C (1999) Geochemical analysis of eight red ochres from Western North America. *American Antiquity* 64:517–526
- Gale NH, Stos-Gale ZA (1982) Bronze Age copper sources in the Mediterranean: a new approach. *Science* 216:11–19
- Gale NH, Woodhead AP, Stos-Gale ZA, Walder A, Bowen I (1999) Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry. *International Journal of Mass Spectrometry* 184:1–9
- Gullapalli P (2009) Early metal in South India: copper and iron in megalithic contexts. *Journal of World Prehistory* 22:439–459
- Habicht-Mauche JA, Glenn ST, Milford H, Flegal AR (2000) Isotopic tracing of prehistoric Rio Grande glaze-paint production and trade. *Journal of Archaeological Science* 27:709–713
- Haustein M, Gillis C, Pernicka E (2010) Tin isotopy—a new method for solving old questions. *Archaeometry* 52:816–832
- Henshilwood CS, d'Errico F, van Niekerk KL, Coquinot Y, Jacobs Z, Lauritzen S, Menu M, García-Moreno R (2011) A 100,000-year-old ochre processing workshop at Blombos Cave, South Africa. *Science* 334:219–222
- Holl AFC (2009) Early West African metallurgies: new data and old orthodoxy. *Journal of World Prehistory* 22:415–438
- Johnson CM, Beard BL (2006) Fe isotopes: an emerging technique for understanding modern and ancient biogeochemical cycles. *GSA Today* 16:4–10
- Johnson CM, Bell K, Beard BL, Shultis AI (2010) Iron isotope compositions of carbonatites record melt generation, crystallization, and late-stage volatile-transport processes. *Mineralogy and Petrology* 98:91–110
- Kiehn AV, Brook GA, Glascock MD, Dake JZ, Robbins LH, Campbell AC, and Murphy ML (2007) Fingerprinting specular hematite from mines in Botswana, Southern Africa. In: M. D. Glascock, R. J. Speakman, and R. S. Popelka-Filcoff (eds) *Archaeological chemistry: analytical techniques and archaeological interpretation*, ACS Symposium Series No. 968, Oxford University Press, pp. 460–479
- Klein S, Brey GP, Durali-Müller S, Lahaye Y (2010) Characterisation of the raw metal sources used for the production of copper and copper based objects with copper isotopes. *Archaeological and Anthropological Sciences* 2:45–56
- Kroeber AL, Collier D (1998) *The archaeology and pottery of Nazca*. Altamira Press, Walnut Creek
- Lechtman HN (1976) A metallurgical site survey in the Peruvian Andes. *Journal of Field Archaeology* 3:1–42
- Leshner CE, Lundstrom C, Brown EL, Huang F, Glessner JJ, Barford GH, and Thy P (2009) Iron isotopes for the layered series of the Skaergaard intrusion, *EOS Transactions, American Geophysical Union*, 90(52), Fall Meeting Supplement, Abstracts, V21A-1953
- Llagostera A, Weisner R, Castillo G, Cervellino M, Costa MA (2000) El Complejo Huentelauquén bajo una perspectiva macroespacial y multidisciplinaria. *Contribución Arqueológica* 5:461–480
- Mackay A, Welz A (2008) Engraved ochre from a Middle Stone Age context at Klein Kliphuis in the Western Cape of South Africa. *Journal of Archaeological Science* 35:1521–1532
- Makl G, von Blanckenburg F, Wagner T (2006) Iron isotope fractionation during hydrothermal ore deposition and alteration. *Geochimica et Cosmochimica Acta* 70:3011–3030
- Marean CW, Bar-Matthews M, Bernatchez J, Fisher E, Goldberg P, Herries AIR, Jacobs Z, Jerardino A, Karkanas P, Minichillo T, Nilssen PJ, Thompson E, Watts I, Williams HM (2007) Early human use of marine resources and pigment in South Africa during the Middle Pleistocene. *Nature* 449:905–908
- Montoya M, García W, Caidas J (1994) *Geología de los Cuadrangulos de Lomitas, Palpa, Nasca y Puquio*. Instituto Geológico Minero y Metalúrgico, Lima
- Mooney SD, Geiss C, Smith MA (2003) The use of mineral magnetic parameters to characterize archaeological ochres. *Journal of Archaeological Science* 30:511–523
- Nielsen S, Andersen JH, Baker JA, Christensen C, Glastrup J, Grootes PM, Hüls M, Jouttijärvi A, Larsen EB, Madsen HB, Müller K, Nadeau M, Röhrs S, Stege H, Stos ZA, Waight TE (2005) The Gundestrup cauldron: new scientific and technical investigations. *Acta Archaeologica* 76:1–58
- Petersen G (2010) *Mining and metallurgy in ancient Perú*, translated by W. E. Brooks, Special Paper 467, The Geological Society of American, Boulder, CO
- Phipps EJS (1989) *Cahuachi textiles in the W. D. Strong collection: cultural transition in the Nasca Valley, Peru*, Unpublished Ph.D. dissertation, Department of Art History, Columbia University
- Popelka-Filcoff RS, Miksa EJ, Robertson JD, Glascock MD, Wallace H (2008) Elemental analysis and characterization of ochre sources from southern Arizona. *Journal of Archaeological Science* 35:752–762
- Popelka-Filcoff RS, Robertson JD, Glascock MD, Descantes C (2007) Trace element characterization of ochre from geological sources. *Journal of Radioanalytical and Nuclear Chemistry* 272:17–27
- Richter FM, Watson EB, Mendybaev RA, Dauphas N, Georg RB, Watkins J, Valley JW (2009) Isotopic fractionation of the major elements of molten basalt by chemical and thermal diffusion. *Geochimica et Cosmochimica Acta* 73:4250–4263
- Salazar D, Salinas H (2008) Tradición y transformaciones en la organización de los sistemas productivos mineros en el norte de Chile prehispánico: San José del Abra, Siglos I al XV d.C. In: Cruz P, Vacher JJ (eds) *Mina y Metalurgia en los Andes del Sur Desde la Epoca Prehispánica Hasta el Siglo XVII*. Instituto Francés de Estudios Andinos, Sucre, pp 163–200
- Salazar D, Salinas H, McRostie V, Labarca R, Vega G (2010) Cerro Turquesa: diez siglos de producción minera en el extremo norte de Chile. *Actas del XVII Congreso Nacional de Arqueología Chilena*, Valdivia 2:1085–1097
- Salazar D, Jackson D, Guendon JL, Salinas H, Morata D, Figueroa V, Manriquez G, Castro V (2011) Early evidence (ca. 12,000BP) for iron oxide mining on the Pacific coast of South America. *Current Anthropology* 52:463–475
- Salinas H, Salazar D (2008) Cadenas operativas y sistemas de explotación minera prehispánica. In: Jackson D, Salazar D, Troncoso A (eds) *Puentes Hacia el Pasado*. Departamento de Antropología, Universidad de Chile, Santiago, pp 73–92

- Schoenberg R, von Blanckenburg F (2005) An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high resolution multicollector ICP-MS. *International Journal of Mass Spectrometry* 242:257–272
- Schultze CA (2013) Silver mines of the northern Lake Titicaca basin. In: Tripcevich N, Vaughn KJ (eds) Mining and quarrying in the ancient Andes: sociopolitical, economic and symbolic dimensions. Springer, New York, pp 231–251
- Schweizer F, Rinuy A (1982) Manganese black as an Etruscan pigment. *Studies in Conservation* 27:118–123
- Scott DA, Doughty DA, Donnan CB (1998) Moche wall painting pigments from La Mina, Jequetepeque, Peru. *Studies in Conservation* 43:177–182
- Shimada I (1994) Pre-Hispanic metallurgy and mining in the Andes: recent advances and future tasks. In: A. Craig and R. West (eds) In quest of mineral wealth: aboriginal and colonial mining and metallurgy in Spanish America. Louisiana State University Series: Geoscience and Man, vol. 33, Geoscience Publications, Baton Rouge, pp. 37–73
- Silverman H (1993) Cahuachi in the ancient Nasca world. University of Iowa Press, Iowa City
- Smith MA, Pell S (1997) Oxygen-isotope ratios in quartz as indicators of the provenance of archaeological ochres. *Journal of Archaeological Science* 24:773–778
- Stöllner T (2009) Gold in southern Peru? Perspectives of research into mining archaeology. In: Reindel M, Wagner GA (eds) New technologies for archaeology: multidisciplinary investigations in Palpa and Nasca, Peru. Springer, Berlin, pp 393–407
- Stos-Gale ZA, Gale NH (2009) Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID). *Archaeological and Anthropological Sciences* 1:195–213
- Tripcevich N, Vaughn KJ (eds) (2013) Mining and quarrying in the ancient Andes: sociopolitical, economic and symbolic dimensions. Springer, New York
- Vaughn KJ, Conlee CA, Neff H, Schreiber K (2005) A compositional analysis of Nasca pigments: implications for craft production on the prehispanic South Coast of Peru. In: Speakman RJ, Neff H (eds) Laser ablation ICP-MS: a new frontier in archaeological characterization studies. University of New Mexico Press, Albuquerque, pp 138–154
- Vaughn KJ, Conlee CA, Neff H, Schreiber K (2006) Ceramic production in ancient Nasca: provenance analysis of pottery from the Early Nasca and Tiza cultures through INAA. *Journal of Archaeological Science* 33:681–689
- Vaughn KJ, Eerkens JW, Linares Grados M, Edwards MJ (2007) Hematite mining in the ancient Americas: Mina Primavera, a 2,000 year old Peruvian mine. *JOM* 59:21–25
- Vaughn KJ, Neff H (2004) Tracing the clay source of Nasca polychrome pottery: results from a preliminary raw material survey. *Journal of Archaeological Science* 31:1577–1586
- Vaughn KJ, Van Gijseghem H (2007) A compositional perspective on the origins of the Nasca cult. *Journal of Archaeological Science* 34:814–822
- Vaughn, K. J., Van Gijseghem, H., Eerkens, J. W., Linares Grados, M. (2010) Two millennia of prehispanic mining in Nasca, Peru. Paper presented at the Primera Reunión Internacional sobre Minería Prehispánica en América, Taltal-San Pedro de Atacama, Chile
- Vaughn KJ, Van Gijseghem H, Grados ML, Eerkens JW (2013) Minería de Hematita en la Costa Sur del Perú: Investigaciones Arqueológicas en la Mina Primavera. *Chungará, Revista de Antropología Chilena* 45:131–142
- Weigand PC, Harbottle G, Sayre EV (1977) Turquoise sources and source analysis: Mesoamerica and the southwestern USA. In: Earle TK, JE E (eds) Exchange systems in prehistory. Academic Press, New York, pp 15–34
- Weinstein-Evron M, Ilani S (1994) Provenance of ochre in the Natufian layers of el-Wad Cave Mount Carmel, Israel. *Journal of Archaeological Science* 21:461–467
- Wells PS (1990) Iron Age temperate Europe: some current research issues. *Journal of World Prehistory* 4:437–476
- Wilson L, Pollard AM (2001) The provenance hypothesis. In: Brothwell DR, Pollard AM (eds) Handbook of archaeological sciences. Wiley, Chichester, pp 507–517
- Yacovleff E, Muelle JC (1934) Notas al trabajo colorantes de Paracas. *Revista del Museo Nacional* 3:154–168