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Elemental fingerprinting of Kenya Rift Valley ochre deposits for provenance studies of rock art and archaeological pigments

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A B S T R A C T

The Kenya Rift Valley contains many ochre sources that are currently used by indigenous peoples for adornment, rituals, and art. Ochre pigments occur in rock art and archaeological sites spanning over 250,000 years. Chemical analysis for provenience of geological sources is the first step in the process of reconstructing provenance of archaeological artifacts for cultural heritage, archaeological, and paleoanthropological research. Development of an ochre source chemical composition database can facilitate reconstruction of social interaction networks and cultural heritage conservation efforts in this region. Techniques such as Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) and Instrumental Neutron Activation Analysis (INAA) are often used for compositional analysis and sourcing of ferruginous mineral pigments. Sourcing has proven challenging due to the diverse range of rocks and minerals that are classified as red and yellow ochres, and the diverse processes that induce variation in composition, including modes of formation, sedimentary transport of parent materials, and diagenesis. Attribution of samples to specific sources is possible only when variation within sources is less than differences between sources (the Provenience Postulate). Here we present the results of a study using LA-ICPMS to determine inter- and intra-source geochemical variations for ten ochre sources associated with three large volcanic centers in the central Rift Valley of Kenya. Our results show that differences in chemical composition among sources are greater than variation within sources, both at the scale of large volcanic centers and of individual ochre outcrops within these centers. Clear differentiation of source chemical fingerprints at local and regional scales satisfies the Provenience Postulate, and suggests that provenance studies of ochre artifacts, residues, and rock art in Kenya will be feasible.

1. Introduction

1.1. Overview of the study

Ochre is a term that encompasses a wide range of iron oxide minerals and iron oxide-rich rocks, clays, and soils that produce a colored streak. The use of red and yellow ochre pigments for symbolic purposes is a widespread and persistent human behavior (Wreschner et al., 1980). The creation of visual art and imagery to communicate information such as identities, symbols, signs, concepts, events, rituals, environmental features, and narratives is also an essential and enduring human attribute (Conkey et al., 1997; Nowell, 2006; Ross and Davidson, 2006; Ouzman, 2010; Fiore, 2014). While much of the human behavioral repertoire imbued with meaning is ephemeral (e.g. spoken language, dance), material symbols produced with mineral pigments are archaeologically persistent. The evidence for ochre use, symbolic and otherwise, extends back in time to greater than 250,000 years (Watts, 1999, 2009, 2014; McBrearty and Brooks, 2000; Barham, 2002; Deino and McBrearty, 2002; Hovers et al., 2003; Marean et al., 2007; Henshilwood et al., 2011; Burdukiewicz, 2014; Brooks et al., 2016).

In this study we test whether it is possible to distinguish among geologic deposits of ochre in the central and southern Kenya Rift

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Valley (KRV) of East Africa using Laser Ablation – Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). We undertook this pilot study in part because the diversity of geological contexts and formation processes represented in this region seemed likely to yield chemically distinctive ochres suitable for upholding the Provenience Postulate (Weigand et al., 1977) by elemental characterization, thus providing a basis for future sourcing studies of prehistoric and historic ochre artifacts and rock art pigments. The second rationale for this study is that the use of ochre in Kenya extends back in time to the Middle Stone Age (MSA) and continues to the present among Maasai and Samburu pastoralists, as well as other East African peoples (Section 2.2). This provides an opportunity for the ethnographic study of modern ochre source exploitation practices that are anthropologically significant in their own right, and may provide insight into prehistoric source selection criteria. In this pilot study we demonstrate that the Provenience Postulate (PP), which states that variation in composition within sources is less than differences among sources (Weigand et al., 1977), can be upheld for the ochre sources that we have analyzed in the Kenya Rift Valley. These results indicate the feasibility of additional ochre source survey and characterization in order to construct a more comprehensive database of source elemental "fingerprints" for provenience of archaeological ochre pigments and rock art in Kenya.

1.2. Provenience versus provenance: conceptual distinctions

Weigand et al. (1977) use the term provenience in their original definition of the Provenience Postulate, which only applied to chemical composition. Use of the term provenance is increasing, and is widely considered synonymous with provenience (Hirst, 2006). However, Joyce (2012, 2013) has thoroughly explicated important conceptual differences of these terms, as we will discuss below. Neff (2000) updated the PP to apply its principals to mineralogical composition and even qualitative characteristics, but substituted provenance for provenience because of the latter term's nearly universal use by archaeologists to refer to the location of discovery for an artifact (its archaeological context). Wilson and Pollard (2001) listed six assumptions and conditions that must be met as prerequisites for a geological/geochemical sourcing study, including Weigand et al.'s (1977) basic premise. The general theme of these definitions is an emphasis on the geographic location of a geologic material before it enters the archaeological record. This is analogous to the use of the term provenience by archaeologists to refer to the location of an artifact or feature within an archaeological site or on the landscape; both uses of provenience are limited to spatial considerations.

Pollard et al. (2014) reiterate the six conditions for satisfying the PP. They also expanded the scope of the versions of the PP described above, which they refer to as Traditional Provenance (but should be termed provenience as originally defined by Weigand et al., 1977), by considering the chronological dimension. Time is an important component of the anthropologically interesting dimension of artifact materiality inherent in the concept of object biography proposed by Gosden and Marshall (1999). This expanded definition aligns the concept of provenance more closely with its usage in art history and allied disciplines. It has been claimed that traditional provenance studies in archaeology treat transport as an instantaneous phenomenon without sufficient consideration of what happens between the place of raw material formation and the place of discovery of an object made from that material (Joyce, 2012, 2013; Pollard et al., 2014). This is not entirely accurate as even some early studies, such as Renfrew et al. (1966) on the prehistoric obsidian trade in the Near East, devoted considerable thought to modes of trade and transport. Joyce (2012, 2013) thoroughly discusses the conceptual distinction of provenience as geological location versus provenance as object biography, following conventional usage in the field of art history. Joyce's concept of provenance encompasses all aspects of the history of human interaction with an object including raw material acquisition, transport, modification, transfer of ownership (chain of custody), functions, and symbolic meanings.

Our survey of the geological literature shows that the term provenience is rarely used, and provenance is used mainly in sedimentary geology, where it refers to the origin *and* transport history of sedimentary particles from bedrock source to sedimentary deposition site (Haughton et al., 1991; Weltje and von Eynatten, 2004). Geologists' use of provenance is thus conceptually allied with that of art historians and archaeologists investigating object and place biographies. A summary of the results of a poll on usage of these terms in archaeology (Hirst, 2006) concludes with this apt analogy: "Provenience is an artifact's birthplace, while Provenance is an artifact's resume". However, as previously noted, archaeologists also use the term provenience for the spatial location of an object within an archaeological site (its deathplace).

Throughout this paper we will use provenience in this spatial sense to refer to both the location of geological sources of ochre, and the location of ochre pigments in archaeological and rock art sites (archaeological provenience). In contrast, our use of provenance includes all processes that a characterized material is subjected to by humans during its life history, beginning with its geological provenience and ending with its archaeological provenience. We also propose adding post-depositional processes (taphonomy, chemical diagenesis) to the life history concept of provenance. In the case of rock art, provenience analysis of pigments can be an important component of reconstructing place biographies: sites that have developed histories of use through the application of pigments from different sources over time. Fulfilling the requirements of the PP by discriminating among geologic sources is the essential first step in the anthropological archaeological investigation of provenance of objects, places, and people.

1.3. Ochre composition analysis

The single greatest analytical challenge for ochre provenience and provenance studies is that ochre is not a single type of rock or mineral (Popelka-Filcoff et al., 2008). Although other naturally occurring red streaking pigments are well known to archaeologists, for example, cinnabar (HgS), they are considered distinct from ochre because they are not colored by iron minerals (e.g., Mioč et al., 2004). Ochreous rocks, clays, and soils may derive their color from chromophore minerals such as hematite (α-Fe_2O_3), goethite (α-FeOOH), ferrihydrite ($Fe_5O_8H \cdot H_2O$), lepidocrocite (γ-FeOOH) (Cornell and Schwertmann, 2003), and jarosite ($KFe_3[SO_4]_2(OH)_6$) (Jercher et al., 1998), to name a few well-known examples. No more than 1–1.5% iron is required to color a lateritic soil red or orange (Cornell and Schwertmann, 2003) and render it suitable for use as a pigment. These chromophore minerals may also be considered ochre in their own right when they occur independently or as the primary constituent of a rock, such as hydrothermal vein hematite or an iron oxide-rich gossan formed by the surface weathering of an Fe-rich ore body exposure. Due to the diversity of materials involved there is no single best approach to a provenience study of ochre. Rather, the choice of analytical method needs to be tailored to the variables that are most likely to uphold the PP while simultaneously minimizing damage to the cultural materials of interest. Thus, the optimal method for a given study is whichever technique facilitates the measurement of variables that exhibit high intra-source homogeneity and high inter-source heterogeneity.

Geochemical characterization and sourcing studies of ochre have used techniques such as LA-ICPMS (Green and Watling, 2007; Eerkens et al., 2012; Bu et al., 2013; Zipkin et al., 2015), solution