Reading Moabite Pigments with Laser Ablation ICP-MS: A New Archaeometric Technique for Near Eastern Archaeology

Color was everywhere in the ancient Near East and, as historians of art have argued, an essential part of the visual aesthetic landscape. Whether employed in statuary, wall paintings, garments, or everyday objects, color affected viewers' experiences and communicated implicit messages of power, divinity, and piety. When investigating color, archaeologists typically have relied on low-level visual recording instruments such as Munsell color charts to compare color across artifact assemblages. Archaeologists oftentimes were left wondering what ingredients were needed to create pigment recipes and to what extent these recipes were shared across craft-production centers. Until recently, scholars lacked an affordable high-resolution and minimally destructive approach with which to identify pigment recipes and measure the distribution of recipes among assemblages.

A new archaeometric application has emerged—laser-ablated–inductively-coupled plasma–mass spectrometry (LA-ICP-MS)—that brings an innovative approach to the investigation of ancient pigments and promises a new frontier in material culture studies (Speakman et al. 2007; Speakman and Neff 2005). LA-ICP-MS provides a means to determine the chemical composition of an object with high precision using a mass spectrometer and a laser. For analyses, a small sample is placed inside a chamber where a laser burns away, or "ablates," a tiny portion of the desired sample. Using an argon carrier gas (or helium or a mixture of both argon and helium), the ablated material is delivered to the ICP-MS where it is ionized using an argon gas plasma. The resulting ions are then introduced into the mass spectrometer where they pass through a series of focusing lenses, an electrostatic analyzer, and a magnet field that separates the ions according to their mass/charge ratio. Finally, the ions pass through a very small opening in the detector where their atomic mass ranges are measured and subsequently logged in an on-board computer.

At its current stage in development, LA-ICP-MS presents many advantages that make it an ideal application in archaeological research and has proven useful in characterizing the provenance of ceramics, paints, glazes, obsidian, and glass. Due to its high-precision, relative accessibility, and affordability, ICP-MS's popularity is growing so quickly that many scholars predict the application may eventually replace neutron activation analysis as one of the preferred choices for chemical characterization studies of archaeological materials. LA-ICP-MS is particularly well suited to the investigation of pigments such that objects can be analyzed with almost unnoticeable damage. Missouri's University Research Reactor (MURR) and, more recently, the Smithsonian's Museum Conservation Institute and California State University-Long Beach's archaeometry laboratory, have led the way in the investigation of pigments on New World ceramics. In the Middle East, the analysis of pigments with LA-ICP-MS is relatively new and only a handful of studies have been undertaken so far (e.g., Diebold et al. in Speakman and Neff 2005).

Although the application is growing in popularity, some cautionary caveats are still necessary when using LA-ICP-MS in pigment research. Standardization of data remains the most challenging aspect, given the lack of well-characterized matrix matched standards. Instruments can also drift between periods of recalibration, skewing the results of a bulk

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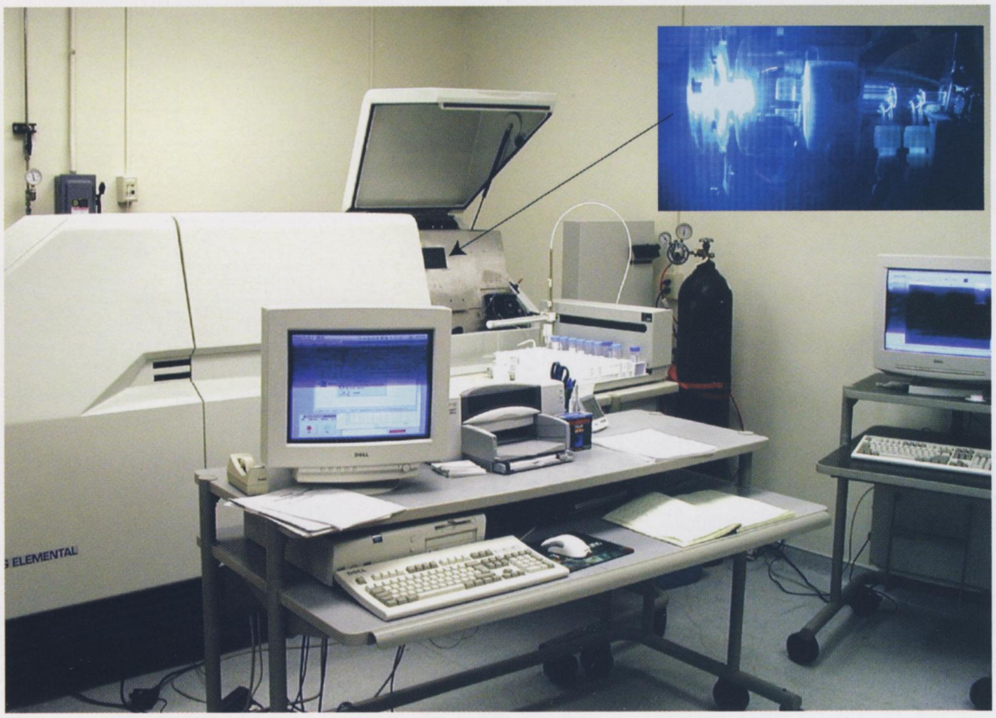
sample set processed over a lengthy period of time. Additionally, when the microprobe's laser interacts with the object, the sample amount that is removed and delivered to the ICP-MS is difficult to control due to the thickness of pigment and the object's levelness in the ablation chamber; differing amounts of sample can affect signal intensity output. Finally, the microprobe can penetrate through the pigment into the paste material, contaminating the sample that is subsequently analyzed. This can be corrected by reducing the time that the laser interacts with the sample. Overall, the use of laser ablation in conjunction with ICP-MS is much more desirable than its alternative, solution-based ICP-MS, which is both time consuming and requires the use of hazardous acids.

We recently conducted a pilot project to investigate ceramic vessel pigments from Moab, an Iron Age kingdom located in modern south-central Jordan. Moab's decorated ceramic-vessel industry began in the latter half of the Iron Age I period (1200–1000 BCE), during a period of relatively low regional political and economic integration (Porter 2007). Vessels were decorated with vertical red bands on the rim with descending vertical wavy lines, usually painted on a white slip (Porter 2007: fig. 5.4.1, nos. 1, 4, 14, 16, 19, 20). In the later Iron Age II period (1000–500 BCE), an era of greater political complexity under the Moabite kingdom (Routledge 2004), vessel decorations were more elaborate, characterized by red, white, and black bands painted above red or white slips. Despite Nelson Glueck's early identification of this latter vessel type and its association with Moab (1940:179–80), next to no attempts to systematically study this vessel style have occurred.

With this in mind, we selected thirty-one Iron Age pigments from Dhiban, one of Moab's most important administrative centers. These vessels were sampled from a well-stratified and well-recorded section of Dhiban's Field L monumental building (Routledge 2004: 161–73). The building's ninth-century construction is possibly associated with an early Moabite king, Mesha, whose consolidation of the region under his rule is documented in a thirty-four-line inscription found at Dhiban in 1868 (Dearman 1989). We hypothesized that given the complex political and economic organization of the Moabite kingdom, decorated vessels—possibly markers of elite identities—would have been produced under specialized conditions. We analyzed these pigment samples from Dhiban, as well as twelve more from other Moabite settlements, using LA-ICP-MS at MURR in 2004. The laser traced a delimited area using a two hundred-micron spot size, with 60 percent



VG Axiom high-resolution magnetic-sector ICP-MS. Inset: enlarged view of the argon plasma and injector torch assembly.

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power, and a repetition rate of twenty shots per second. Samples were analyzed for a suite of twenty-nine elements. Elemental concentration data were assembled into a single tabulation. The entire dataset underwent log transformation and was subjected to standard pattern recognition approaches, such as the inspection of bivariate plots.

Although the sample size was limited, our study concluded that it is possible to identify distinct pigment recipes using LA-ICP-MS. When red pigment samples' elemental concentrations of iron and magnesium oxides were compared, five chemical groups were distinguished (Groups 1–5). Likewise, when black pigment samples' elemental concentrations of manganese (Mn_2O_3) and lead oxides (PbO) were compared, three chemical groups were distinguished, Groups 6–8. An additional eight samples went unclassified; these unclassified samples suggest the presence of additional chemical groups that an increase in sample size would identify.

Several observations of these data reveal surprising

Red Pigments	No	Site	Form	Century	Slip/Paint
Group 1	282	Dhiban	Bowl	early 8th	slip
	305	Dhiban	Bowl	late 8th/early7th	slip
	329	Thamayil	Body sherd	late 7th/early 6th	paint
	331	Thamayil	Body sherd	late 7th/early 6th	paint
Group 2	204	Dhiban	Body sherd	9th	paint
	325	Dhiban	Body sherd	late 8th/early7th	paint
	343	Dhiban	Bowl	late 7th	slip
Group 3	328	Thamayil	Body sherd	late 7th/early 6th	paint
	336	Dhiban	Body sherd	late 8th/early7th	slip
	342	Dhiban	Decantur	late 7th	slip
	345	Dhiban	Bowl	late 7th	paint
	347	Dhiban	Body sherd	late 7th	paint
	365	Dhiban	Body sherd	early 8th	paint
	366	Dhiban	Bowl	late 8th/early7th	paint
	366-2	Dhiban	Bowl	late 8th/early7th	paint
Group 4	202	Dhiban	Bowl	9th	slip
	303	Dhiban	Bowl	late 8th/early7th	slip
	307	Dhiban	Bowl	late 8th/early7th	slip
	344	Dhiban	Bowl	late 7th	slip
Group 5	237	KMA	Bowl	11th /early 10th	paint
	240	KMA	Bowl	11th /early 10th	paint
	248	KMA	Bowl	11th /early 10th	paint
Unclassified	287	Dhiban	Base	early 8th	slip
	309	Dhiban	Krater	late 8th/early7th	paint or slip?
	320	Dhiban	Bowl	late 8th/early7th	paint
	321	Dhiban	Bowl	late 8th/early7th	paint or slip?
	330	Thamayil	Body sherd	late 7th/early 6th	paint
	341	Dhiban	Bowl	late 7th	slip
	348	Dhiban	Body sherd	late 7th	slip

Black Pigments	No	Site	Form	Century	Slip/Paint
Group 6	294	Dhiban	Body	early 8th	slip
	320	Dhiban	Bowl	late 8th/early7th	slip
	331	Thamayil	Body	late 7th/early 6th	slip
	336	Dhiban	Body	late 8th/early7th	slip
	345	Dhiban	Bowl	late 7th	slip
	347	Dhiban	Body	late 7th	slip
	348	Dhiban	Body	late 7th	slip
Group 7	325	Dhiban	Body	late 8th/early7th	slip
	329	Thamayil	Body	late 7th/early 6th	slip
	332	Thamayil	Body	late 7th/early 6th	slip
Group 8	328	Thamayil	Body	late 7th/early 6th	slip
	330	Thamayil	Body	late 7th/early 6th	slip
	365	Dhiban	Body	early 8th	slip
Unclassified	343	Dhiban	Bowl	late 7th	slip

List of samples (n=43) sorted by compositional group.

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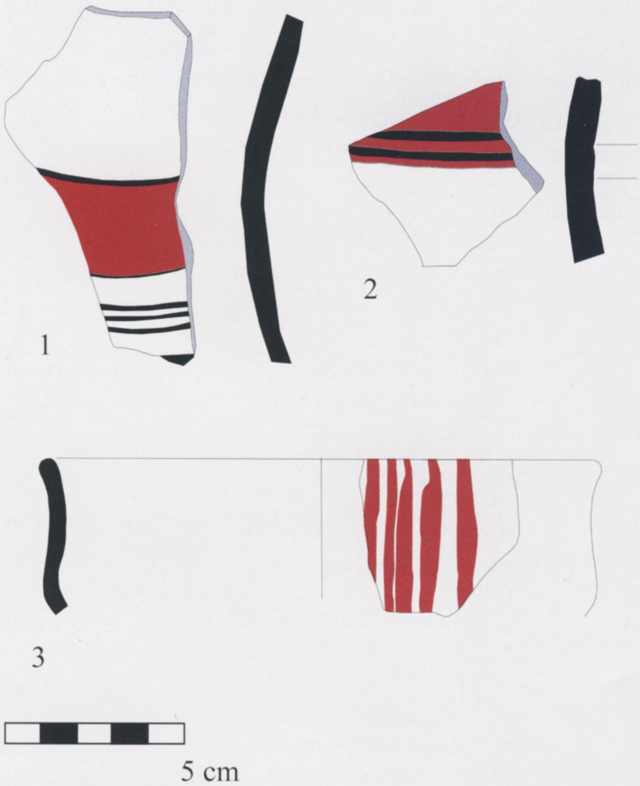
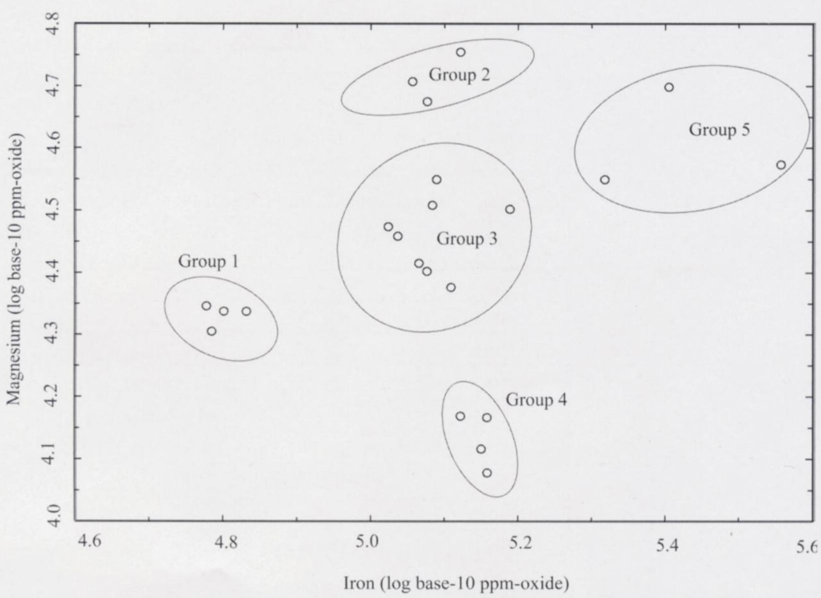


Examples of sampled ceramic vessels from 1) Thamayil, 2) Dhiban, and 3) Khirbat al-Mudayna al-'Aliya.



Bivariate plot of red pigments (n=29) comparing iron and magnesium oxide levels. Elemental concentrations are log base-10 ppm-oxide. Unassigned samples (n=7) not shown.

aspects regarding pigment use in Moabite vessel production. Both slips and paints appear in the same compositional groups, strongly suggesting that craftspersons rarely differentiated recipes for the two decorations. The lone exception is Group 4, a collection of slips characterized by lower magnesium levels. Another observation is that each chemical group contains samples from different centuries, strongly suggesting that pigment recipes remained stable over time. Our investigation did reveal several distinctions, however, between Dhiban's Iron II pigments and earlier Iron I pigments (Group 5). Three red samples selected from Khirbat al-Mudayna al-'Aliya (KMA) (n=3), an Iron I agro-pastoral village perched on the edge of the Wadi Mujib (Routledge and Porter 2007), were significantly higher in iron and magnesium oxides compared to the Iron II samples.

We hypothesized that given the extra effort required of producers to manufacture painted vessels, these objects would have been reserved for elite consumption. We also hypothesized that painted vessels found in non-elite contexts would bear a different pigment recipe from those found in elite contexts. Such differences, we assumed, would reflect attempts to imitate restricted vessels. To test this question, we sampled nine additional pigments from Thamayil (n=9) (Routledge 1995), a late-seventh or early-sixth-century rural agricultural farmstead located on the eastern edge of the Karak Plateau. Surprisingly, samples from Thamayil appeared in five out of eight groups with only one sample unassigned to a group. These results suggest that vessel pigments from both elite and non-elite contexts were manufactured under similar production conditions, and were consumed across the Moabite social hierarchy.

Altogether, these data reveal how complex Moab's ceramic vessel industry was during the Iron Age. The use of slips and paints in themselves suggests

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the industry was relatively specialized in the Iron II period, but these pigment data reveal additional clues to vessel production. These results suggest two interpretive scenarios: pigment materials and recipes were broadly shared across Moab's vessel production workshops, or vessels were produced at a yet-to-be-determined location and then distributed throughout the region. It is tempting to suggest that vessel production took place in Dhiban's vicinity, given its administrative importance during the early Iron II period. Yet, additional sampling from other Moabite settlements as well as petrographic and neutron activation analysis of the vessel themselves could help us distinguish between the two. Currently, we are expanding our dataset with additional Iron Age pigments from Porter's field project at Dhiban in Central Jordan (Porter et al. 2005). Increasing the sample size as well as collecting samples of naturally available resources near Dhiban will help to reverse engineer pigments to discover original recipes. This ongoing research will no doubt further our understanding of Moab's enigmatic ceramic vessel industries.

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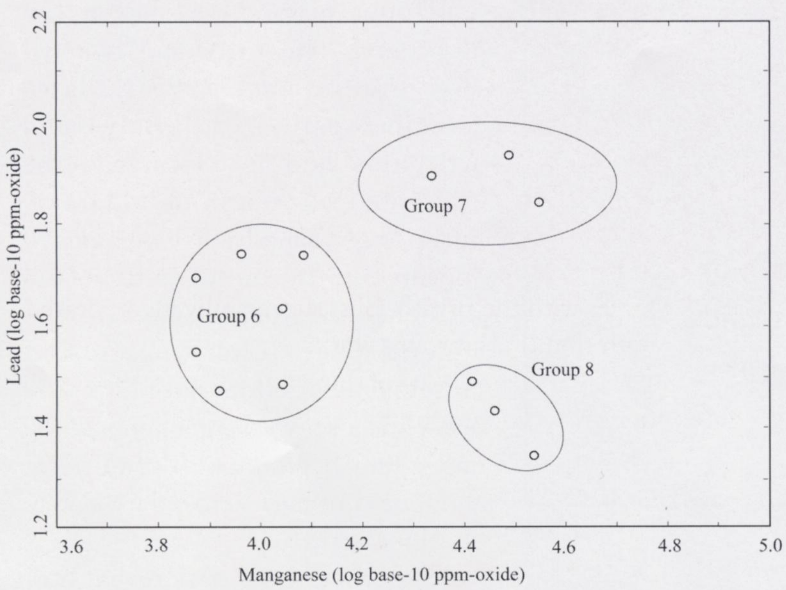

Bivariate plot of black pigments (n=14) comparing iron and magnesium oxide levels. Elemental concentrations are log-base 10 ppm. Unassigned samples (n=1) not shown.

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