Chemical Mapping to Evaluate Post-Depositional Diagenesis among the Earliest Ceramics in the Teotihuacan Valley, Mexico

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Abstract: Chemical and mineral sourcing techniques are commonly employed in archaeology to reconstruct patterns of ceramic exchange and raw material procurement practices for the past, but the effects of post-depositional diagenesis are still often ignored despite a number of key studies warning that the composition of ceramics from archaeological deposits often diverges greatly from their original composition at the time of production. This current study on diagenesis derives from a large chemical and petrographic analysis of some of the earliest ceramics (1500–100 cal Before Common Era [BCE]) in the Basin of Mexico at a time when the development of ceramic trade networks helped to spread early stylistic canons across Mesoamerica. One important site, Altica, consistently presents ceramics that are high in barium. We use laser ablation-inductively coupled plazma—mass spectrometry (LA-ICP-MS) to map the cross-sections of several samples from this site with the idea that post-depositional intake of mobile cations would appear as enriched at the surfaces of the pottery and around pores. Conversely, cations that leach out of the fabric would exhibit depleted concentrations in those same areas. We find that barium and a suite of other elements (e.g., copper, zinc, lead, tin, arsenic, calcium, strontium, and vanadium) have been chemically altered due to nearly 3000 years of burial in the soil. We explore the implications of those revelations for properly sourcing archaeological ceramics found at the Altica site and provide additional guidance for archaeologists and geochemists who employ ceramic compositional sourcing elsewhere.

Keywords: archaeology; ceramics; sourcing; post-depositional diagenesis; Mesoamerica

1. Introduction

Compositional sourcing of archaeological ceramics has become a staple method to recover lost information about the social relations of production and exchange in the past. Bulk chemical characterization—where a fragment of the sample is homogenized into a powder or solution prior to analysis—has historically been the most common method applied to sourcing analysis, but the heterogeneity of ceramics and their often sponge-like properties that take up chemicals from the burial matrix introduce variability that can deter successful source identification. Bulk analyses cannot separate the intended object of study (natural and cultural variation) from the confounding factors of post-production use and post-depositional diagenesis. The detrimental effects of chemical weathering on archaeological ceramics for sourcing studies have been recognized for decades [1], but most composition studies today continue to uncritically apply bulk chemistry to reconstruct social and economic behaviors without considering post-depositional changes. In this study, we apply chemical mapping via laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to tease apart the “good” from the “bad” sources of variability in a sample of archaeological ceramics previously characterized through the bulk chemical technique of neutron activation analysis (NAA).

The data considered here derive from a large study of some of the earliest pottery produced in the Basin of Mexico. Stoner and Nichols [2] irradiated 1154 fragments of pottery
from Early Formative through Late Formative contexts (1500–100 cal BCE) (Figures 1 and 2). The site of Altica in the Teotihuacan Valley provided the single largest portion of the sample (n = 117) as it was the focus of recent excavations [3,4]. Based on NAA, the bulk chemical compositions of Altica ceramic sherds display a trimodal distribution. Complementary petrographic analysis revealed that one group was imported from a metamorphic region of Mesoamerica, likely southwest Puebla (Group A1 this study). The remaining two groups were produced within the Basin of Mexico using volcanic-derived materials, but they display widely divergent compositions. The larger of those two groups represents purely local production at Altica or its immediate surroundings (Group A2). The final group (Group A3) displays a composition in range with ceramics produced to the south at the larger Formative sites of Coapexco, Tlapacoya, or Colotzingo, except for the significantly higher concentrations of barium among the Altica ceramics. Previous research has shown barium to be particularly problematic for post-depositional diagenesis in pottery [5,6].

Figure 1. The Basin of Mexico geology and sites of pottery sampling.
Figure 2. Sample of ceramics in the larger compositional analysis sorted from oldest (top) to youngest (bottom). Scale bar = 1 cm.

We turn to LA-ICP-MS to map the distribution of various elements in the cross-sections ceramics from Altica, with control samples from Tlapacoya, to evaluate the first hypothesis that Altica sherds were elevated in barium due to their burial environment. Ceramic sherds that have experienced significant post-depositional contamination from, or leaching into, the surrounding soil matrix might show a differential enrichment or depletion of environmentally mobile elements at the surfaces or around pores in the fabric. Chemical mapping in a raster pattern stretching from the interior to exterior surface of each sherd shows that barium and several other elements are strongly concentrated at the surfaces of pottery from Altica, but the pattern is much weaker or absent in the two known imports in the sample. The data presented here support differential barium contamination from the soil matrix over the past 3000 years, but the relatively unaltered profiles of the imports leave some ambiguity that calls for additional testing. This result fails to disprove the second hypothesis that Group A3 pottery arrived at Altica through a trade relationship with the southeastern Basin of Mexico. More research on raw materials surrounding Altica will be necessary to fully eliminate the possibility that they were produced using local materials.
2. Compositional Approaches to Ceramic Production and Exchange in Archaeology

Archaeological ceramics, while composed entirely of natural materials, display compositions that derive from culturally situated decisions made by potters during the production sequence [7–9]. Within a day’s roundtrip walk of most settlements, the potter had a range of suitable materials available to make their craft. Through his ethnographic study of traditional potting technologies across the world, Arnold [10] demonstrates a dominant pattern of local material procurement for both clays and tempering materials. These bulky, low-value materials were typically not traded over long distances, and the logistical and social costs of procuring them dramatically increases with distance from the place of production. The result is that about one-third of traditional potters procure materials from within 1 km of their village, and very few go further than 7 km for clay or 9 km for temper [10]. Of course, this localized resource procurement pattern is strongest among pre-modern societies, especially those that lack efficient transportation networks. In ancient Mesoamerica, a region where all movement of goods was done on the backs of human porters, there is almost no evidence that potters traveled beyond their local environments to obtain bulky wet clays or aplastics to temper the paste. There is, however, substantial archaeological sourcing evidence that pottery, with value added through the production process, was traded both through regional markets and over long distances beginning around 1400 cal BCE [2,11,12].

The multitude of cultural and natural influences on ceramic compositional variability make it a difficult material to source using bulk composition alone. Pottery is the product of mixing water, clay, and aplastics that either occur naturally in the clays or that were added by the potter. That paste is then formed into a vessel or other object (such as a figurine), dried, and fired at temperatures ranging from 500 to 1200 °C. These three main constituents are the primary influences on a ceramic’s bulk chemistry. Surface treatments such as slips or glazes, as well as dirt from the burial environment, affect the bulk chemistry if not removed. Sourcing studies that focus on bulk paste composition typically remove surface adherents through burring or scraping prior to analysis [13]. As we demonstrate in this paper, however, surface burring might not be sufficient to remove the effects of chemical diagenesis that penetrate the ceramic body.

Because of the cultural inputs of ceramic composition, sourcing pottery in archaeology works differently than the geological sourcing rocks. The original source of the materials is a target of some archaeological sourcing techniques, but bulk chemical analyses typically seek to match the composition of unknowns to reference groups that represent sites of production on the landscape. Reference groups are clusters of chemical data points that display relatively less chemical variance within groups than between groups [14]. For regions of the world that lacked efficient transportation systems, sourcing specialists invoke the “criterion of abundance”, which assumes that the most common composition represented among pottery found at any site was the typical “recipe” produced by local potters: their fingerprint [13,15]. This, of course, does not rule out the possibility that more than one recipe was employed by local potters [2], so not all chemical divergences from the dominant paste composition identified at a site represent pottery imports.

The “source” represented by a reference group may differ in scale depending on the region. The Basin of Mexico is an interior-drainage basin where raw materials intermix near the lake at its center. “Source” there typically refers to broad subregions, or zones of production and distribution that span dozens of towns and villages [16–21]. The composition of materials and ceramics in this region, like many other regions around the world, forms a chemical gradient rather than discreet resource zones. Under these tenuous sourcing conditions, any confounding variables, such as post-depositional contamination, can derail provenance identification.

Bulk chemical analysis cannot differentiate among the cultural, natural, and post-production sources of ceramic composition. Because ceramics are cultural artifacts made from natural materials, bulk chemistry is an appropriate estimation of all the ingredients that form the producer’s “recipe”. In all cases, however, post-depositional chemical changes
potentially cause compositional divergences that can inhibit source assignment or lead to the identification of the wrong source. The only way to assess the potential impact of long-term burial is to break the bulk composition into its components for individual study [21].

Any chemical or mineral changes that occur after the potter finishes their product works contrary to the successful archaeological reconstructions of ceramic production and exchange. Such changes can derive from absorption of mobile elements from the burial matrix through the porous fabric that typifies most low-fired earthenwares [22]. Enrichment of those elements may occur through physical infiltration of mobile cations in solution or very small particles in suspension [23,24]. Chemical substitution can also occur in the molecular structure of the clays: strongly influenced by firing temperature; the original composition of clays; and the characteristics of the burial matrix (pH, oxidation/reduction state, relative levels of organic activity) [5,6,25–31]. Chemical substitution would produce an inverse pattern of chemical depletion for elements that are displaced and leached out of the ceramic into the burial matrix. Zeolites often develop in the glassy phases of high-fired ceramic fabrics [27,32,33]. Chemical changes due to use are potentially significant for reconstructing past behavior but will also confound sourcing efforts [34]. Sample preparation can cause enrichment of certain elements, particularly if steel components are used [35–37]. Other points of significance for interpreting bulk chemical data, but not related to weathering, are processes that produce spatially patterned variation withing the ceramic fabric. These processes include migration of soluble cations to the surfaces of the ceramic during drying and firing [31] or application of surface pigments or glazes that leach into the ceramic body [38].

The current study focuses on how potential post-depositional chemical changes are presented in the cross-sections of pottery sherds. The sample from the site of Altica in the Teotihuacan Valley was prepared for NAA at the University of Missouri Research Reactor following their standard protocols, which involves using a silicon carbide burr to abrade all surfaces for the removal of any superficial dirt or pigments [13]. Our concern in this case, and for sample preparation in all cases, is that removing the ceramic surfaces does not sufficiently remove all factors that cause the archaeological sherd to chemically diverge from its original composition. We propose chemical mapping of sherd cross-sections to understand what those changes are, which informs our interpretations of ancient trade networks based on bulk chemical analysis.

3. Materials and Methods

3.1. Archaeological Background

In 2014, Deborah Nichols and Wesley Stoner initiated a regional sourcing project coupled with excavations at the site of Altica in the Teotihuacan Valley in the northeastern corner of the Basin of Mexico. The project focused on the Formative periods, especially the Early (1400–1000 cal BCE) and Middle (1000–400 cal BCE) Formative. We wanted to understand how exchange relationships, focusing on the archaeologically visible materials of ceramics and obsidian, fostered the rise of increasingly complex societies [39]. During these times in Mesoamerica, most regions shared, to varied degrees of coherence, a stylistic canon expressed mostly on portable material culture. Archaeologists refer to this phenomenon as a style-horizon [40]. During the Early Formative, materials associated with the Olmec heartland in the southern Gulf lowlands of Veracruz were found in the states of Oaxaca, Chiapas, Mexico, Puebla, Guerrero, Morelos and to a lesser extent in other states and countries [41]. During the subsequent Middle Formative, the style horizon expanded to cover even more area and include more sites. The Olmec culture was still in focus, but shared ceramic styles shifted to a more generalized type of white-slipped dish with widely shared decorative motifs, like the double-line-break [42,43] (see Figure 2). By the Late Formative (400–100 cal BCE), regional style zones fragmented into distinctive cultural traditions that were more restricted over space.
3.2. Pre-Hispanic Pottery Production in the Basin of Mexico

The Basin of Mexico is an interior drainage basin in the central volcanic highlands of Mexico. Before the modern growth of Mexico City, a large lake occupied the center of the basin. The region is covered by Tertiary and Quaternary volcanic tephra that weathers into the clays used for pottery production [44]. Clays of the Toltolcingo and Noche Buena [45–47] formations, with the latter being the more accessible to pre-hispanic potters, comprise primarily smectite and illite minerals. Clays of this composition are not ideally suited for making fine paste ceramics due to their high water-absorption characteristics. Rapid expulsion of water during firing causes shrinking, which can result in breakage during firing. Prepared pastes with a proportionately high percentage of their volume taken up by aplastics (e.g., crushed rock, shell, volcanic ash) shrink less upon firing and those gains serve to halt the propagation of cracks that develop in the clay fraction during firing and use. For this reason, ancient potters often intentionally tempered poor-quality clays by adding aplastics. In the Basin of Mexico, the earliest ceramics, like those featured in this study, tended to be the coarsest among all pottery produced over the entire pre-Hispanic sequence [21].

The pottery in our sample appears to have been fired at relatively low temperatures, below 750 °C. We note that the preferable methods to assess firing temperatures among archaeological ceramics would rely on x-ray diffraction to identify mineral changes within the clays or scanning electron microscopy to observe the microstructure and degree of sintering in the fabric [48,49]. We can, however, make qualitative assessments based on macroscopic observations of firing cores and microscopic observations in thin section. In thin section, the clay fraction of most specimens in the sample is optically active with clay sheets aligned parallel with the vessel walls (Figure 3). This indicates that firing temperatures did not rise high enough to fully melt the crystalline structure of the clay sheets [50]. Most of the early pottery is generally dark colored, which indicates a reducing firing environment with temperatures too low to completely drive off all organics, or that they were intentionally smudged with an organic material (e.g., buried in ash after firing). Even sherds that display lighter colored red or brownish-red colors within 1 mm of the surfaces tend to possess dark cores (Figure 4). This occurs because the surfaces are generally exposed to more oxygen and higher temperatures than the cores of the vessel walls. Surface oxidation can be produced by rapid cooling in open air after firing. Organics generally begin oxidizing and migrate to the surfaces between 200–400 °C and are completely driven off between 750–850 °C [50–51]. Carbon combusts completely at the surface around 500 °C but higher temperatures or longer firing durations are required to progressively drive off organics in the core of the ceramics [51]. Oxidation at the surface but incomplete combustion/oxidation of organics in sherd cores may indicate that firing temperatures were somewhere between 550 and 700 °C, which is typical for open firings [51,52]. We caution that rate of temperature change and the duration of firing can also influence the color profile of ceramic cross-sections. A rapid temperature ramp but short overall firing duration in a kiln, for example, might also produce dark cores when firing organic rich clays. Kilns have not yet been discovered for the Formative period in the Basin of Mexico. Even in regions of Mesoamerica where kilns were in use, they were typically not used to fire ceramics at high temperatures [53].
Figure 3. Thin section of a typical Early to Middle Formative pottery fabric with an optically active ground mass (sample FTV502, polarizers crossed). Large minerals depicted include primarily clinopyroxene, orthopyroxene, plagioclase, and volcanic glass. This sample pertains to Group A3 in the current study. Scale bar is 500 μm.

Figure 4. Ceramic cross-section showing the dark core and oxidized surfaces that are typical of ceramics from the Basin of Mexico. Note the sharp margins between oxidized/reduced zones of the fabric. Also note the thin veneer of a darker reddish hue at the surfaces that made contact with soils for the past 3000 years. This dark hue correlates with chemical anomalies due to post-depositional diagenesis.
Linear cracks formed during firing for most of the ceramics in this sample, running parallel to the vessel walls and between the unsintered clay sheets. Low-temperature firing and a porous fabric are two characteristics of this early pottery that might foster post-depositional infiltration of contaminants from the soil or cation substitutions at the surfaces.

### 3.3. Previous NAA Characterization

The Basin of Mexico may be the best-sampled region in the world for compositional studies of ceramics, though it is also one of the most difficult regions to source materials. Ceramics produced in all parts of the Basin used similar clays and universally contained volcanic aplastics. There are chemical gradients, however, that make sourcing possible [20,21,54]. Some transition metal concentrations generally increase moving from the Teotihuacan Valley in the northeastern corner to the southeastern corner of the Basin. This pattern results from the increasingly mafic compositions of younger volcanic rocks moving from the rhyolite/dacite composition rocks in the Teotihuacan Valley to the basalts and andesitic basalts of the southeast Basin [44]. Similar patterns are observed moving north to south in the western half of the Basin as well. These patterns are neither smooth nor homogenous.

The Patlachique Range, where Altica is situated, is dominated by Pliocene and Miocene rhyolite and dacite formations [44,55], but the areas to the east of the site are overlain by Pleistocene and Holocene andesites with geographically restricted breccias of more basaltic composition about 5–10 km further east. The other end of the hypothesized trade relationship we evaluate here, the site of Tlapacoya, sits on an andesitic cone but the larger region is dominated by basalt and andesitic basalt of the Cerro el Pino that overshadows Cerro Tlapacoya to the north. The southern end of the Sierra Nevada that encloses the southeastern margin of the Basin is also composed of andesitic basalt. The sites of Coapexco and Colotzingo, situated higher in the flanks of the Sierra Nevada, were occupied around the same time as Altica [56]. These three sites were sampled in our larger study and present bulk compositions similar to the suspected imports (Group A3) recovered at Altica [2].

Slayton [47] and Hopkins [46] both characterized clays about 5 km north and northwest of Altica. While it is unlikely that Altica potters obtained materials from these precise locations, two important facts derive from those samples. First, the clays sampled nearest to Altica display barium concentrations in the range of 310–570 µg/g. Altica ceramics display average barium concentrations of about 1700 µg/g, excluding those definitively imported from outside the region. Second, the 5 clay samples collected by Hopkins [46] situated about 5 km north of Altica at Belem and San Miguel Xolco contained concentrations of chromium and other transition metals (Co, Fe, Ni, Sc) that are less than half the concentrations detected among Group A3 ceramics at Altica.

The current study is focused on intra-regional patterns of exchange, specifically from the perspective of the small village site of Altica in the Teotihuacan Valley. We were initially attracted to Altica because of the unusually high percentage of white-ware imports identified there [39,57]. A total of 68 (59% of the Altica sample) ceramics sampled from Altica were imported from a metamorphic region, likely southwestern Puebla [2]. For the purpose of the current study, we refer to these interregional imports as Group A1 (Figure 5; Table 1). We note, though, that our sampling strategy targeted suspected imports, over-inflating the apparent importance of ceramic imports at the site.
Figure 5. Altica chemical groups depicted on logged axes of chromium and calcium determined via bulk NAA data. The Tlapacoya reference group is depicted as a 90% confidence ellipse in the upper right corner of the plot.

Table 1. Barium statistics in Altica and Tlapacoya reference groups and the sample in this study.

| Group     | Barium Mean μg/g | Barium Range | Sample | Specimen IDs in Sample | Description                                                                 |
|-----------|------------------|--------------|--------|-------------------------|-----------------------------------------------------------------------------|
| A1        | 856.25           | 507–2511     | 2      | FTV039, FTV040          | Ceramic imports from a metamorphic region of Mexico, likely southwestern Puebla. |
| A2        | 1665.48          | 346–3275     | 6      | FTV043, FTV056, FTV482, FTV489, FTV491, FTV493 | Ceramics that fit the expectations of localized production using materials found in proximity to Altica. These contain relatively low concentrations of light transition metals that are typical for volcanic materials of a felsic composition, such as rhyolite or dacite. |
| A3        | 1780.5           | 633–2598     | 6      | FTV501, FTV502, FTV504, FTV505, FTV506, FTV507 | Ceramics that do not conform to known materials available within proximity to Altica. These ceramics contain higher concentrations of light transition metals, which is representative of more mafic volcanic rocks, such as basalts and andesitic basalts. |
| T1 (Tlapacoya Reference) | 696.15          | 380–1576     | 2      | PTO744, PTO784          | Ceramics from the site of Tlapacoya in the southeastern Basin of Mexico. This is one of the hypothesized sources for imports to Altica. |

Beside the imports mentioned above, the next largest ceramic chemical group (n = 34; 30% of Altica sample) at Altica generally resembles the composition of other ceramics sourced to the Teotihuacan Valley for other time periods, with some differences based on the practice of more heavily tempering early ceramics than those made during later time periods [21]. We refer to these locally produced ceramics as Group A2 (see Figure 5). They derive from relatively felsic composition materials, lower in most transition metals (Co, Cr, Fe, Sc, and Ti) but higher in some rare earth elements as well as Cs, Hf, Rb, Ta, and Th compared to ceramics produced in other subregions of the Basin of Mexico. Petrographic analysis confirms that these ceramics were tempered with crushed rock and volcanic ash with a composition that most resembles a devitrified dacite. Volcanic glass devitrifies rather
rapidly, on a geological time scale, and devitrification indicates that the materials derived from an older eruption, likely during the Miocene or Pliocene. The primary mineralogical distinctions between these ceramics and Group A3 discussed below are lower percentages or absence of pyroxene and olivine and higher percentages of quartz and K-feldspar.

The smaller, but not insignificant, Group A3 (n = 13; 11% of Altica sample) displays a more mafic composition, containing higher concentrations of the transition metals mentioned above. In thin section, these ceramics present higher proportions of amphibole, biotite, pyroxene and more rarely olivine than Group A2. The volcanic glass present within these sherds does not display the same degree of devitrification as Group A2, suggesting that the materials derive from Quaternary volcanic eruptions. We must not rule out at this stage that a more mafic source of clays or temper is situated to the east of Altica where breccias of an andesitic to basaltic composition are exposed. Based on chemical comparison to Altica’s contemporaries represented in the broader Basin of Mexico ceramic compositional database, Tlapacoya presents the closest match for Group A3, but any site in the southeastern Basin of Mexico could have produced ceramics of this composition using nearby materials. It is important to note that two of the sherds in this category were differentially fired white-rimmed black wares that date to the earliest part of Altica’s occupation (see Figure 2: “Valle Borde Negativo”). This ceramic type is very rare at Altica, but much more common among the larger sites in the southern Basin of Mexico, a fact that bolsters the argument that they may have been imported into Altica or brought to the site by its founders.

Barium is the only element among the Group A3 ceramics that strongly diverges from the composition of the southeast Basin reference groups, so evaluating post-depositional contamination of barium is of top importance to evaluate the potential for Group A3 to be interpreted as trade wares. Table 1 shows summary statistics for barium and our sampling strategy for each of these compositional groups. Figure 6 depicts the barium and strontium concentrations of the specimens from each group. The great spread among both Groups A2 and A3 on the barium axis itself is a potential indicator of differential post-depositional chemical alterations.

![Figure 6](image-url)

**Figure 6.** Altica chemical groups depicted on linear axes of barium and strontium determined via bulk NAA.
Alex and her colleagues [57] were the first to identify the high-barium levels in Altica ceramics. They proposed based on a relatively weak negative correlation that barium might have substituted for sodium in the ceramics buried at Altica, but they argue that the presence of some ceramics that were not high in barium makes diagenesis unlikely [57]. They refer to the presence of the imported Group A1 ceramics discussed above. The assumption that all ceramics at Altica should present similar concentrations of barium is tenuous for several reasons. First, we expanded sampling of metamorphic-tempered imports in our more recent study and show that there are some Group A1 ceramics that trend into the range of barium concentrations of Group A2 and A3 ceramics. Second, most of those imports possess a thick white slip that sealed the surfaces and might have resisted enrichment or leaching deeper into the ceramic fabric. Six of those Group A1 imports are not slipped and have a mean bulk barium concentration of 1396 µg/g, compared to 856 µg/g for A1 ceramics as a whole (see Table 1). Finally, the imported ceramics could be made from different clay or fired to different temperatures, which could influence the rate of uptake of leached soil contaminants.

Other ceramic samples from the Teotihuacan Valley have also produced high barium concentrations. Ceramics from Teotihuacan tempered with tepetate display bulk concentrations of barium in the range of Altica ceramics. Tepetate is a colloquial term used by the people of the region to refer to the bedrock that underlies agricultural soils. In this location, tepetate is a consolidated lahar composed principally of volcanic materials that underlies the quaternary soils of most of the region. Ceramics at Altica were not tempered with tepetate, but tepetate underlies the entire site with no more than 40–50 cm of overlying soil, deflated due to erosion, that constituted the burial matrix for the sherds in this study. All pit features at Altica were excavated into tepetate, and specimens from features display an average barium concentration that measures 230 µg/g higher than those samples recovered in the overlying soils (Stratum A or Stratum B). We recognize, however, that this is an oversimplification and does not consider minor differences in burial environment or the differences in the microstructure of the ceramic fabric due to variable firing temperatures. Buxeda [58], for example, demonstrates the role of crystalline microstructures, as induced by different firing temperatures, on the concentrations of several elements, including barium.

3.4. Chemical Mapping of Element Mobility in Archaeological Ceramics

We apply the principle that elements taken up into a ceramic fabric from the surrounding soil matrix may show higher concentrations of that element closer to the source of contamination: the surfaces of the sherd directly in contact with the burial matrix. Picon [6] and Golitko et al. [5] have demonstrated that ceramics are particularly susceptible to the uptake of barium from the burial matrix and have employed similar chemical mapping techniques to the current study. Baritic zeolites can also form through the devitrification of volcanic glass. As we noted above, many of the ceramics from Group A2 display significant devitrification, but Group A3, which displays similar barium concentrations, does not. Furthermore, if volcanic glass weathered into baritic zeolites within the matrix of the pottery, the pattern of barium enrichment observed in chemical mapping would be concentrated within or near volcanic grains rather than at the surfaces of the ceramics.

Barium is environmentally mobile in certain forms. Barium chloride, barium nitrate, and barium hydroxide are all water soluble. These minerals can occur in bedded volcanic deposits [59], such as the tepetate that underlies the site of Altica, and generally occur in trace amounts in all rocks and soils. \( \text{Ba}^{2+} \) substitutes for other divalent cations such as \( \text{Sr}^{2+} \) and \( \text{Ca}^{2+} \), and large monovalent cations such as \( \text{K}^{+} \), all of which are common components in most clays used to produce pottery as well as feldspars found in the dacitic and andesitic rocks in the Patlachique Range. Barium weathers out of rocks and sediment and is readily absorbed into clay minerals and oxides. Once in solution, barium bonds to sulfates and carbonates in soil and water to form environmentally stable minerals barite (barium sulfate) and witherite (barium carbonate) [59]. Once they are in these insoluble forms, they become
highly resistant to weathering, except under reducing or acidic environments. We have not tested the pH levels of soils around Altica. Thin section analysis of a sample of sherds from Altica, has not specifically identified either barite or witherite, though they could be present in very small grain sizes that evade detection. Our scanning of sherds using LA-ICP-MS shows few small intense spikes of Ba in some sherds that might represent silt-sized inclusions of barite or witherite minerals, or baritic zeolites, within the clay matrix, but the overwhelming majority of aplastics present very low concentrations of barium.

The double-edged sword of ceramic provenance studies is that any element present in the local burial environment that could be taken up by the pottery as contamination might also be present in the materials used to produce the pottery in the first place. In the case of post-depositional contamination, archaeologists would eliminate the altered elements, and possibly correct the concentrations of other elements to compensate for variable contamination across a sample [60]. However, if the element is present among the clays used to produce ceramics locally, it becomes part of the paste recipe employed by the potter and must not be removed during provenance investigations.

The main hypothesis to be tested is that the ceramics at Altica experienced significant post-depositional enrichment in barium. Support for this hypothesis might involve elevated barium concentrations at the surfaces of the ceramics with lower concentrations at the core. If barium were substituting for other cations in the structure of the ceramic, we should see depressed concentrations of elements with similar valence and ionic radii at the surfaces, namely calcium, potassium, or strontium. In the absence of chemical substitution, free Ba\(^{2+}\) cations suspended in ground water that filters through the cracks and pores of this low-fired, friable pottery could create similar chemical profiles. Contamination should also present similar high surface concentrations among the ceramic imports (Group A1), regardless of the difference in bulk concentrations that we already have demonstrated using NAA data. Data that may refute this hypothesis would be either barium concentrations evenly distributed among the clay fraction across the cross-section of the sherds, or numerous high-Ba mineral inclusions that appear in the scans in the absence of zonal patterning in the cross-section. Stoner [21] has already clearly demonstrated using LA-ICP-MS of the clay fraction compared to bulk chemistry measured through NAA that barium is more highly concentrated, and with higher standard deviations, in the clay fractions as opposed to the aplastics of Formative pottery in the region.

A confounding variable that cannot be controlled for in this study is the possibility that elements contained in abundance in the ceramic paste are driven towards the surfaces during the firing process [31]. If free cations, either in solution prior to drying or broken from their molecular bonds during firing, exceed the number of bonding locations in the clays they would have been carried toward the surfaces as water was rapidly driven from the fabric. Firing can therefore produce very strong superficial concentrations of mobile elements, like Na [31]. In a previous study, Stoner and colleagues [61] conducted experiments with Ohio Red clay doped with water of varying salinity. Two of those samples were scanned as part of this project. The first was mixed with water of 9% salinity. The purpose for our scanning this very high salinity sample, rather than one of a lower salinity, was to see the behavior of excess cations that could not find bonding locations in the ceramic fabric. Sodium is strongly concentrated at the surfaces by a factor of 5–6 times the concentrations at the core.

Would barium behave in similar ways if the original materials contain an abundance of Ba\(^{2+}\) cations that were not fixed into the molecular structure of clays? Schwedt and Mommsen [31] present a systematic firing experiment for 5 different clays and show that barium is homogeneous from the core to surface in all but one sample, Witt T, in which Ba concentrations were about 10% higher at the surface after firing to 800 °C. We note, however, that the unfired concentration of barium for that specimen was 373 µg/g, which is about 4.5 times lower than the average barium concentrations among Altica ceramics.

We caution that an absence of differential enrichment/depletion of certain elements at the surface compared to the core does not necessarily rule out post-depositional chemical
changes. Schwedt and colleagues [32], for example, show that analcime conversion in the glassy phase of relatively high-fired, calcium rich ceramics resulted in uniform sodium enrichment across the profile, but other elements, like calcium and cesium, were differentially depleted at the surfaces.

3.5. Sample and Methods for Scanning LA-ICP-MS

A raster pattern was ablated across the cross-section of 14 specimens from Altica (2 of Group A1, 6 of Group A2, and 6 of Group A3) (Table 1). Two sherds from Tlapacoya were scanned in the same manner, as ceramics from that site represent the closest chemical match for Group A3 in the NAA reference database.

A ESI NWR 193 nm Excimer Laser Ablation System (Elemental Scientific Lasers, LLC, Bozeman, MT, USA) coupled with a Thermo Scientific iCapQ Quadrupole Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was used to ablate a swath from surface to surface across a section of each sherd cut with a diamond blade on a lapidary saw. The raster pattern consisted of lines ablated from left to right in a block that measured 750 µm in height. Ablation began at the sherd edge and ended after the edge of the opposite surface. An earlier run used a zig-zag pattern of ablation, but it was determined that the small delay in the transport from ablation chamber to detector created a zipper like offset in the chemical data when interpolated.

LA-ICP-MS elemental maps were created using a series of 15 line scans across each pottery sherd. Prior to each line raster, a pre-ablation pass was used to clean the surface. The pre-ablation pass consisted of a 50 × 50 µm laser spot, a laser repetition rate of 20 Hz, and moved at 250 µm/s. Each line scan utilized a 50 × 50 µm square spot, with a laser repetition rate of 10 Hz, while moving across the sample at 70 µm/s. The center points for each line were separated by 50 µm on the y-axis. A total of 48 isotopes were analyzed (dwell time 10 ms each): 7Li, 23Na, 24Mg, 27Al, 28Si, 39K, 43Ca, 44Ca, 45Sc, 47Ti, 49Ti, 51V, 52Cr, 55Mn, 57Fe, 59Co, 60Ni, 63Cu, 66Zn, 75As, 85Rb, 88Sr, 89Y, 90Zr, 91Zr, 93Nb, 118Sn, 121Sb, 133Cs, 137Ba, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 169Er, 172Yb, 175Lu, 178Hf, 208Pb, 232Th, and 238U. During each analytical session 4 standard reference materials were analyzed. Two were matrix-matched standards: SRM679, and “New Ohio Red” (an in-house standard used for quality control at the University of Missouri Research Reactor (MURR). The line raster data was calibrated against SRM679 using 29Si (24 wt%). Glass standards NIST 612 and NIST610 [62] were used as a monitor for instrumental mass fractionation. All reported values are in µg/g [63,64]. The LA-ICP-MS data can be found in Table S1–S4 (Supplementary Materials).

3.6. Spatial Analysis Using GIS

Data were imported into ArcMap 10.7 using x, y coordinates in millimeters and superimposed over images for each sample. Input points were initially colorized according to their z values (concentrations of each element) to identify aberrant data points. Those that fell off the edge of the sherd, or where the ablation line crossed a void causing the signal to drop, were deleted prior to interpolation.

The input points were interpolated using a radial basis function with a spline-with-tension function. Radial basis function is an exact interpolation method, meaning that the resultant surface passes through each of the input points. The tension spline results in the lowest possible slope, which prevents the creation of artificially high peaks or low valleys between points. Since the surface we are interpolating features sharply defined edges (e.g., the edge between the clay fraction and mineral grains) we preserved that high contrast using a small search neighborhood of 100 µm with a minimum of 8 points (the nearest neighbors surrounding each point) and a maximum of 24 points (two nearest neighbors in every direction). This method most closely preserves the input values from the ICP-MS.

The ceramics in question are all very heavily tempered. Many specimens contain an aplastic fraction that takes up 50–65% of the volume of the pottery. In many situations, we would want to emphasize the chemistry of the aplastic fraction. In this case, though,
the chemical patterns of diagenesis we investigate should pattern mostly within the clay fraction or possibly as a corona around voids and mineral grains. To create a more targeted view of the clay fraction, and to create a dataset more amenable to multivariate statistics, we made an effort to remove the influence of large mineral grains from the data. Most large grains are clearly visible in the photographs of the sherds, but smaller grains are not. To aid in mineral grain detection, we ran Getis-Ord Gi* statistics in ArcMap to identify hot and cool spots for certain elements in each sample (e.g., Ba, Na, Ca, K, Fe). This method was extremely efficient at identifying mineral grains for deletion. Without this step, the zonal statistics across the sherd would reflect the random placement of minerals in the matrix, rather than the smoother trends from surface to core in the clay fraction. A final smoothing technique was employed through a low-pass filter using the median over a circular radius of 200 µm around each grid cell. The median eliminates high and low outliers that fall within the moving search neighborhood.

Once the trimmed and smoothed raster representation of the chemical data was created, we extracted data along a profile using the “stack profile tool” in ArcMap. This tool extracts data along a line drawn by the user, which permitted us to avoid some (not all) of the remaining mineral grains not removed by the trimming methods described above. The data for each profile line was exported to Excel where the graphic display was more easily manipulated.

Data were coded into 7 (or 9 for larger sherds) equally spaced zones, with “C” representing the core zone flanked by 3 zones on either side: L3, L2, L1, C, R1, R2, R3. These zones became the input groups for each sherd to calculate a canonical discriminant analysis (CDA) using Mahalanobis distances. This multivariate statistic seeks variables that explain the greatest amount of variance among predefined groups and creates new axes to maximize those differences. The elements that maximize the differences among zones appear as the greatest magnitude vectors. Plot symbols are coded by zone to create a visual impression of the relationship among variables and how they pattern in the cross-section of a sherd. Each point in the CDA scatterplots represents the original input data quantified by the mass spectrometer.

4. Results

We present the results according to ceramic group. An incredible amount of data was produced by this study, but we focus exclusively on elements that displayed strong zonal patterning across the samples. Getis-Ord Gi* hotspots are presented specifically for barium on the un-trimmed dataset to identify where the element is most concentrated for each sherd (e.g., sherd surfaces, aplastic grains, voids). Canonical discriminant analysis among the trimmed datasets highlights which elements are most strongly patterned and we use those results to select elements to depict in profile graphs. Each individual sherd presented different elements that formed strong zonal patterns, but there are some commonalities among all specimens from Altica.

4.1. Group A1

The two sherds in this group are both heavily tempered with a coarse-to-very-coarse metamorphic phillite [39]. Some fragments of trachitic andesite are also visible in thin section [39]. Unlike the other groups that we review below, the hot spots for barium are most concentrated in the aplastic grains, with the exception of a thin margin at the surfaces of FTV039 (Figure 7). The similarities in the chemical maps between FTV039 and FTV040 end there, so we will discuss each sample separately.
The elevated zone of barium at the surface of FTV039 only penetrates into the fabric about 300–400 µm, and the surfaces show barium levels up to 2.2 times greater than at the core (Figure 8). The surfaces are also higher in calcium and strontium, which may be due to the white slip that covers both surfaces. The laser ablated part of the white slip at the extreme right surface, and it is elevated in calcium, strontium, and barium. This pattern is therefore not likely contamination from the ground soil. Vanadium presents an inverse correlation with the other elements mentioned above as its concentrations dip slightly at the surface. The white slip, which is at least 200 µm thick, likely helped shield the core of this piece from absorbing contaminating elements from the soil.

Sample FTV040 does not show elevated concentrations of any of the same elements as FTV039. In fact, barium and potassium are depleted relative to the core on the right surface, where nickel is elevated (see Figure 8). Copper, manganese, and arsenic concentrations are also highly elevated at the surfaces. Elevated copper and arsenic values do not penetrate far into the ceramic fabric, a pattern seen in many of the other sherds in the Altica sample that likely represents post-depositional alterations. The divergences mentioned here might be due to the slipping materials as opposed to diagenesis, however a similar pattern presents itself for other ceramics from the site that are not slipped or painted.

4.2. Group A2

All of the ceramics from Group A2 share similar spatial patterns of chemical enrichment or depletion in the cross-section. Most mineral grains in these sherds are cool spots for barium, with few exceptions (Figure 9). The hot spots conform to the clay fraction and specifically are found at the surfaces of the sherds. We also see an association of high-barium hot spots with some of the larger voids, which indicates filtration of barium in solution through the porous fabric of the sherds. Hot spots associated with voids appear on their inside surfaces or in the clay fraction surrounding them.
Figure 8. Group A1 and T1 ceramics. (Left) Canonical discriminant analysis of trimmed data points coded by zone (zones that do not diverge from the core not shown). (Right) Profiles of trimmed and smoothed data for elements that show significant zonal patterning. The x-axis is the position in the cross-section of the sherd in mm; the y-axis is the concentration of elements (in $\mu g/g$) expressed as a ratio to the average core concentration for the same element.
The surface concentrations of barium in Group A2 range from about 45 to 100% higher than the average core concentrations (Figures 10 and 11). In all samples, the barium profile forms a shallow parabolic shape, demonstrating a gradient of increasing barium concentrations from core to surface. Sample FTV056 also shows this pattern, but with
concentrations sharply spiking upward within 300–500 µm of each surface. This sample is not slipped, but it is highly polished, which is another technique ancient potters used to seal the surfaces of serving wares. Polishing might have helped to keep the digenesis relatively close to the surface. In the cut section, one can see a thin veneer where the hue of the surface color is darkened. This veneer, which occurs in many of the specimens, corresponds to the area of barium enrichment (see Figure 4). We believe this to be clear evidence of post-depositional changes.

Figure 10. Samples FTV043, FTV056, and FTV482. (Left) Canonical discriminant analysis of trimmed data points coded by zone (zones that do not diverge from the core not shown). (Right) Profiles of trimmed and smoothed data for elements that show significant zonal patterning. The x-axis is the position in the cross-section of the sherd in millimeters; the y-axis is the concentration of elements (in µg/g) expressed as a ratio to the average core concentration for the same element.
Figure 11. Samples FTV489, FTV491, and FTV493. (Left) Canonical discriminant analysis of trimmed data points coded by zone (zones that do not diverge from the core not shown). (Right) Profiles of trimmed and smoothed data for elements that show significant zonal patterning. The x-axis is the position in the cross-section of the sherd in millimeters; the y-axis is the concentration of elements (in \( \mu g/g \)) expressed as a ratio to the average core concentration for the same element.
Other elements that show enrichment at the surfaces include those that tend to covary in nature, including the elemental pairs of copper and zinc, lead and tin, and arsenic and antimony (see Figures 9 and 10). Other surface-enriched elements include lithium, lanthanum (and some other rare earth elements), and sometimes calcium and strontium. In FTV056 and FTV493, calcium and strontium are inversely correlated with barium and the other enriched elements mentioned above, which suggests cation replacement in the post-depositional environment. The positive correlation between barium and lanthanum appears most strongly in FTV482, FTV491, and FTV493 and indicates that the two elements might substitute for each other at bonding sites within the clay. Vanadium is nearly universally depleted at the surfaces and likely was leaching out of the ceramics into the surrounding soils. Vanadium covaries with other light transition metals (Co, Cr, Fe, Mn, Ni) in nature, but in this case the pattern seen with vanadium is strongest.

4.3. Group A3

Group A3 ceramics display more mafic compositions, reflected through high concentrations of light transition metals, higher proportions of pyroxene and olivine, and lower percentages of quartz, K-feldspar, biotite, and amphibole among the aplastic fraction. Barium hot and cool spots among these specimens are similarly distributed as the Group A2 ceramics in that mineral grains are most commonly cool spots with some exceptions. Hot spots are more concentrated in the clay fraction, as Stoner [21] identified previously. FTV505 is a notable exception where several of the largest hot spots possess a white mineral grain at their center. We note that this sample does not show elevation of barium at the surfaces. The margins surrounding voids are also barium hot spots in this group (Figure 12).

Figure 12. Results of Getis Ord Gi* for Group A3 showing hot and cool spots across the samples. “V” marks macroscopically visible voids.
Barium occurs at levels up to two times the concentrations of the cores in at least one surface of the specimens FTV501, FTV502, FTV504, and FTV506 (Figures 13 and 14). A similar trend of surface elevation occurs in the other two specimens within this group, but the pattern is not as strong.

**Figure 13.** (Left) Canonical discriminant analysis of trimmed data points coded by zone (zones that do not diverge from the core not shown). (Right) Profiles of trimmed and smoothed data for elements that show significant zonal patterning. The x-axis is the position in the cross-section of the sherd in millimeters; the y-axis is the concentration of elements (in µg/g) expressed as a ratio to the average core concentration for the same element.
Figure 14. (Left) Canonical discriminant analysis of trimmed data points coded by zone (zones that do not diverge from the core not shown). (Right) Profiles of trimmed and smoothed data for elements that show significant zonal patterning. The x-axis is the position in the cross-section of the sherd in millimeters; the y-axis is the concentration of elements (in μg/g) expressed as a ratio to the average core concentration for the same element.

Other elements that are concentrated at the surfaces of ceramics of Group A3 are the same that were mentioned for Group A2, namely copper, zinc, tin, lead, and lanthanum (see...
Figures 13 and 14). In specimen FTV506, lithium and calcium show an inverse correlation with barium and the other surface-elevated elements listed above. In specimen FTV507, the left surface shows a sharp drop in calcium and strontium that contrasts the rise of barium and copper in the same zone. In most of the specimens of this group, vanadium concentrations noticeably decrease at the surfaces, similar to the pattern observed among the Group A2 specimens.

4.4. Group T1

Group T1 consists of two specimens from the Tlapacoya reference group. These sherds were never interred in the soils at Altica and thus were analyzed as a control. The data for PTO784 show a large signal drop in the zones R1 and R2 and anomalous concentrations in zone R3, so it was dropped from further analysis. PTO744 shows slight elevation of barium at the surfaces (see Figure 8). This is important to demonstrate that barium infiltrates ceramic surfaces at other sites in the Basin of Mexico as well, even though the bulk concentration in this sample is less than half the average for Altica sherds. This specimen is also elevated at the surfaces in calcium, zinc, copper, and arsenic. Like groups A2 and A3, most mineral grains are cool spots for barium concentrations, with a few exceptions (see Figure 7).

5. Discussion

The main element of interest to evaluate hypotheses is barium because it is the only element in the bulk compositional database that prevents secure assignment of Group A3 to a provenance in the southeastern Basin of Mexico. If the elevated levels of barium resulted entirely from post-depositional diagenesis taken up from the soils of Altica, the potential for a ceramics trade relationship between the southeastern Basin of Mexico and Altica in the Teotihuacan Valley would not be disproven. However, if no post-depositional barium enrichment is detected, the materials used to produce ceramics at Altica naturally possessed high barium content and trade from the southeastern Basin of Mexico would be disproven.

The results of chemical mapping show irrefutable signs of post-depositional diagenesis in all the group A2, A3, and T1 sherds. This evidence presents as elevated concentrations at the surfaces and/or associated with voids deeper in the fabric (Table 2). The primary elements implicated in this contamination include barium, lanthanum, copper, zinc, arsenic, lead, and tin. Secondary elements that show surface enrichment (and sometimes depletion) in some samples include calcium, strontium, lithium, and potassium. The only element that consistently shows the inverse pattern, chemical depletion at the surfaces, is vanadium. The patterns of enrichment or depletion across the sherds ranges from a smooth parabolic transition from core to surface to a relatively flat profile across the core that transitions sharply to enrichment at the surface. Elements behave differently in profile. Barium, lanthanum, and vanadium present a compositional gradient from core to surface, while copper and zinc tend to be more sharply elevated within 500 μm of the surface. Association of barium enriched margins surrounding some larger voids shows the path through which barium infiltrated the body of the ceramic, and provides some of the clearest data of post-depositional contamination.
Table 2. Summary of the mean levels of barium. Red colors represent higher barium concentrations, blue colors represent lower concentrations.

| ANID  | Group | L4  | L3  | L2  | L1  | C   | R1  | R2  | R3  | R4  |
|-------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| FTV039| A1    | 854.2 | 616.5 | 610.8 | 598.1 | 591.4 | 592.4 | 654.7 |
| FTV040| A1    | 806.5 | 800.9 | 897.9 | 763.8 | 756.9 | 771.8 | 689.8 |
| FTV043| A2    | 5549.1 | 4799.8 | 4059.5 | 3740.8 | 3740.8 | 3740.8 | 3740.8 |
| FTV040| A1    | 3168.8 | 2946.1 | 2792.3 | 2784.9 | 2571.6 | 2675.2 | 2865.1 | 3545.0 |
| FTV482| A2    | 3284.7 | 2713.5 | 2698.2 | 2801.3 | 2590.3 | 2893.8 | 3068.3 | 3181.0 |
| FTV489| A2    | 4450.1 | 3684.9 | 3485.4 | 3411.0 | 3653.3 | 3437.4 | 4787.0 |
| FTV491| A2    | 4208.1 | 3912.1 | 3451.8 | 3253.1 | 3222.9 | 3404.2 |
| FTV501| A3    | 3512.3 | 2544.0 | 2422.3 | 2384.6 | 2146.6 | 2466.0 | 3427.7 |
| FTV502| A3    | 4434.3 | 3445.6 | 3166.4 | 2908.1 | 3033.3 | 3168.6 | 4327.3 |
| FTV504| A3    | 3941.6 | 2957.1 | 2695.6 | 2838.9 | 2944.3 | 2890.9 | 3245.0 |
| FTV505| A3    | 3609.5 | 3269.4 | 3395.1 | 3245.0 | 3255.3 | 3648.3 | 4066.7 |
| FTV506| A3    | 3755.1 | 2965.4 | 2675.9 | 2649.4 | 2316.4 | 2222.8 | 2444.7 |
| FTV507| A3    | 4165.0 | 3581.9 | 3796.2 | 3557.3 | 3628.6 | 3745.2 | 3332.5 |
| PTO744| T1    | 1302.0 | 420.3 | 326.6 | 313.8 | 322.1 | 350.0 | 470.8 |
| PTO784| T1    | 261.2 | 297.0 | 357.3 | 288.0 | 239.7 | 215.7 | 227.4 |

Supporting the conclusion of post-depositional contamination is the surface elevation of barium in the imported sample FTV039. The extent of enrichment is not as pronounced as specimens in groups A2 and A3, and we attribute that to the slip that sealed the surface. Another possibility for this specimen, however, is that barium is found in higher concentrations in the slip and those cations migrated into the ceramic body, along with calcium and strontium. If this is the case, post-depositional chemical alteration would not be the cause of the barium enrichment in FTV039. We find it troubling that the other import of Group A1 does not show an equivalent pattern of barium enrichment at the surface. We must mention that both of these samples were collected on the surface of the field by the original survey team in the 1960s. We also are unsure what clay minerals comprise these samples, how they differ from the mostly smectite-illite clays of the Basin of Mexico, and how the slips that seal the surfaces of these specimens affected uptake of contaminants from the soil. We suggest that this last item, how sealing the surface either through slipping or polishing affected patterns of chemical diagenesis, should be evaluated with controlled experiments.

While we believe we have clearly demonstrated post-depositional chemical diagenesis among the sherds recovered from Altica, we are still uncertain about a number of potentially confounding variables. First, Altica ceramics could have been both produced with barium rich materials and subjected to post-depositional chemical changes. The cores of Altica ceramics also display very high barium concentrations: about ten times the barium concentrations of the clay fraction cores from Tlapacoya that we analyzed here. Even if part of the bulk barium enrichment comes from the soil matrix they were buried in, the magnitude of difference is so large that we require additional lines of evidence before ruling out local production at Altica using barium-rich materials. There are other sites to the south of the Teotihuacan Valley that present barium levels closer to those at Altica, including Molino de Flores, Coapexco, and Colotzingo, the latter two are also close chemical matches for Group A3.

6. Conclusions

We present a method in this paper that builds on previous work to model chemical profiles for ceramics in order to understand patterned mobility of certain elements in the fabric during drying, firing, and post-depositional contamination. Our method involves scanning a swath across a cut sherd section, stretching from interior to exterior surfaces. This technique generates a tremendous amount of continuous data, which presents some advantages and disadvantages over sampling a grid of spots across a sample. The elements
of interest, those that were patterned differently from core to surface, were concentrated in the clay fraction. To isolate the component of interest, we needed to trim the aplastics from the final data set using hot-spot analysis in ArcMap, cross-checked against the photograph of the analyzed sections. The data were then smoothed using a median low-pass filter. While this type of analysis was made difficult because the sherds were so heavily tempered, the thorough data sampling through laser scans with a tight spacing of 50 µm provided the flexibility of analysis in a GIS environment that enabled us to isolate different components of the fabric. Furthermore, the continuous data enabled a finer assessment of patterns of elemental enrichment/depletion in ceramic profiles, how sharply they are elevated or depressed across space, and compositional differences associated with voids.

We conclude that the strong patterns of elevated barium at the sherd surfaces and around some voids affirm the hypothesis that the soil matrix enriched Altica sherds with barium. While Covid-19 currently prevents us from obtaining soil samples from Altica, we note that analysis of tepetate tempered ceramics at Teotihuacan are also very high in barium. Tepetate, a consolidated volcanic lahar, underlies the entire site and has likely leached barium and other elements into the shallow, deflated soils at the site. We also note pervasive patterns of surface enrichment in the elements copper, zinc, lead, tin, arsenic in most of the specimens analyzed, as well as a persistent inverse trend of vanadium depletion at the surfaces.

With regard to the second hypothesis, that Group A3 ceramics were traded into Altica from the southeastern Basin of Mexico, the current data do not disprove this trade relationship. There are two additional variables that need to be evaluated prior to resolving the trade hypothesis. First, we need to rule out the possibility that barium is elevated at the surfaces due to a process of driving off free cations in solution towards the surface during the drying and firing processes. Schwedt and Moomsen [31] show that barium tends to be fixed in the clay, but one of their samples does show a similar surface enrichment pattern to the barium profiles we present here. This variable would best be evaluated in an experimental environment where we obtain smectite-illite clays that naturally contain about 2500–3000 µg/g barium and then fire them to different temperatures. The second variable that needs to be resolved is a thorough resource survey about 5–10 km to the east of Altica where more mafic materials have been identified by geological.

Finally, the clearest conclusion we make from our study is that blind comparison of bulk chemical compositions to reference groups is not alone sufficient to securely source archaeological pottery. The surface burring protocols designed to remove surface contaminants or pigments prior to grinding or dissolution will not completely eliminate troublesome elements as they penetrate too far into the ceramic fabric. Burring may eliminate contamination by some elements that are strongly concentrated at the surface, but many elements showed a gradient of elevated concentrations from core to surface that burring would not eliminate. Rather than change the protocol of removing surface contaminants, which we think is absolutely necessary, we advocate profiling a small sample of all chemical groups in each study to identify troublesome elements that might be affected by post-depositional diagenesis.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11040384/s1, Table S1: Raw LA-ICP-MS data for Slide 1a (FTV039, FTV040, FTV043, FTV504), Table S2: Raw LA-ICP-MS data for Slide 1b (FTV501, FTV502, FTV505, FTV506, FTV507), Table S3: Raw LA-ICP-MS data for Slide 2 (FTV506, FTV482, FTV489, FTV491, FTV493), Table S4: Raw LA-ICP-MS data for Slide 3 (NM04, NM08, PTO744, PTO784).

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