

**IDENTIFICATION OF POST-DEPOSITIONAL CHEMICAL ALTERATION OF CERAMICS FROM THE NORTH COAST OF PAPUA NEW GUINEA (SANDUAN PROVINCE) BY TIME-OF-FLIGHT-LASER ABLATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (TOF-LA-ICP-MS)\***

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*The measured chemical composition of archaeological ceramics can result from a variety of geological, cultural and taphonomic factors. In the present study, we evaluate the likelihood that elevated barium concentrations in ceramics from the archaeological site of Wom/Aiser, located on the northern coast of Papua New Guinea, result from post-depositional enrichment. Using time-of-flight-laser ablation-inductively coupled plasma-mass spectrometry, we mapped chemical compositional profiles across cut sections of ceramic sherds from four archaeological sites, all previously chemically characterized. We identify the formation of pronounced concentration gradients in samples from Wom/Aiser relative to sherds with low barium concentrations, consistent with post-burial uptake.*

**KEYWORDS:** POST-BURIAL CHEMICAL ALTERATION, POTTERY, PAPUA NEW GUINEA, TOF-LA-ICP-MS, BARIUM

## INTRODUCTION

The measurement of elemental composition of archaeological artefacts as a means of determining their place of production is a long-established archaeological method, that ultimately rests upon the so-called ‘provenance postulate’—namely, that archaeological artefacts can be securely linked to sources of raw material if the chemical variability between geographically discrete raw material sources is greater than variability within these sources (Weigand *et al.* 1977, 24). For some materials, such as obsidian, chemical variability overwhelmingly results from a single

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cause—the chemistry of the original source outcropping—and assignment of archaeological artefacts to geographical sources is therefore relatively straightforward.

The final measured chemical composition of archaeological pottery, in contrast, can reflect a complex combination of geological, cultural and taphonomic factors. In general, at least five hypotheses need to be considered as possible explanations for the measured elemental chemistry of archaeological ceramic objects—that the measured composition: (1) reflects the composition of original source clays and is controlled by local geology; (2) results from paste preparation techniques that have modified the original raw material composition of a sherd by addition of plastic or aplastic materials differing chemically from the primary utilized clay; (3) has been modified by use of the ceramic, for instance by leaching of organic substances into vessel walls; (4) has been altered as a result of the burial environment it was deposited in; or (5) reflects a combination of some or all of these five factors (Neff *et al.* 2003, 202). Chemical variability associated with production choices can carry valuable information both in the form of clay and intentionally or unintentionally added temper, all of which can prove valuable in assigning production location or inferring transport prehistorically. However, the effect of post-burial chemical alteration must be ruled out as a valid explanation for observed chemical patterning before arriving at anthropologically and archaeologically meaningful conclusions.

We report here on the identification of the post-depositional chemical alteration of ceramic sherds recovered at the archaeological site of Wom/Aiser (*c.* AD 1000–1500) in Sanduan province, Papua New Guinea (PNG). These sherds were analysed as part of a larger chemical study of pottery from the Sepik coast region of northern PNG, carried out by laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) (Golitzko, in press). Our suspicion of post-depositional alteration was raised by elevated barium concentrations measured in the Wom/Aiser sherds relative to other ceramics known to have been produced in regions of similar geology, as well as to local clays used by modern potters. Consequently, we chemically mapped six ceramic sherds in cross-section—three with high-barium concentrations from Wom/Aiser, and three with low-barium concentrations from other regional sites—using time-of-flight–laser ablation–inductively coupled plasma–mass spectrometry (TOF–LA–ICP–MS). In the three low-barium sherds, we failed to identify significant patterned differences in barium concentrations. These sherds also match the chemistry of local clays utilized by modern potters, and appear to largely reflect original pre-burial chemistry. In contrast, we identified distinct gradients of barium concentration in the analysed sherds from Wom/Aiser—either smooth gradients from inner to outer surface, or else a distinct build-up of barium along vessel walls—consistent with post-burial uptake.

#### BACKGROUND TO THE STUDY

The research presented here is part of a broader study of ceramics and clays from the Sepik coast (Fig. 1) of northwestern Papua New Guinea (Sanduan Province), targeted at reconstructing prehistoric patterns of interaction and exchange as they relate to the development and maintenance of high levels of linguistic and cultural diversity that characterize the coast today (Golitzko *et al.* 2010; Golitzko, in press). Methodologically, we were primarily interested in determining whether elemental chemistry could provide a more refined understanding of ceramic production provenance on the coast than that provided by mineralogy, and the geographical scale at which distinct production locales could be chemically distinguished from one another. Anthropologically, we were interested in addressing two primary issues regarding the nature of human social and economic life on the coast in prehistory: (1) the degree to which communities on the coast

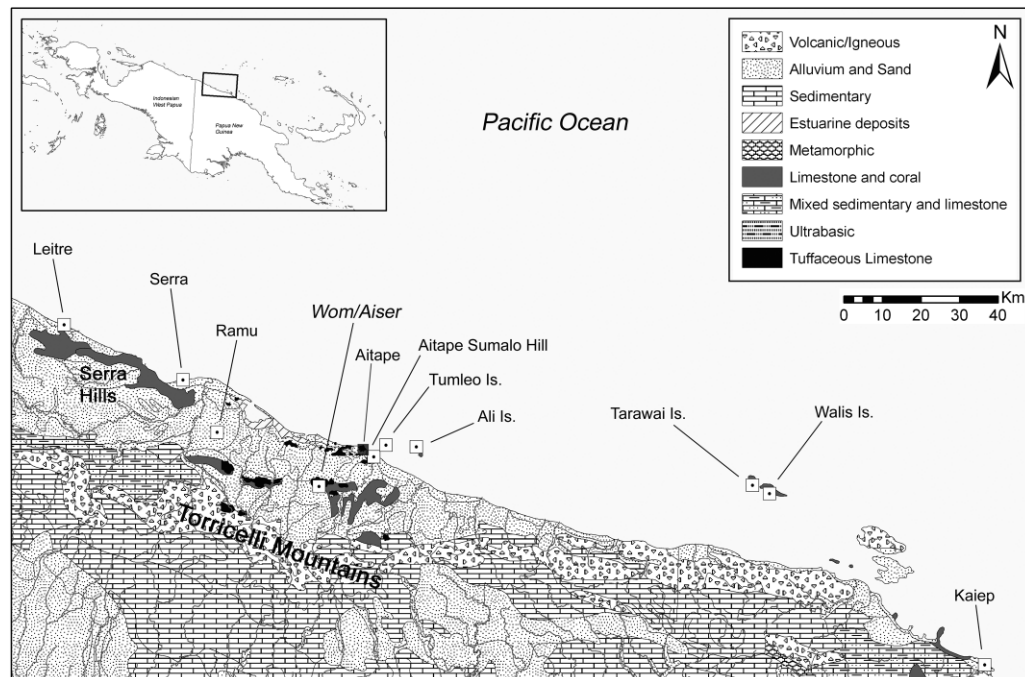


Figure 1 A map of the study area, with sites mentioned in the text and principal geological units indicated.

were interconnected prior to colonial pacification; and (2) the degree to which ceramic production, now largely focused at production centres on Tumleo Island and further east at Kaiep, was also restricted to particular communities in the past (e.g., Irwin 1978; Allen 1984).

A total of 306 ceramic and clay samples from archaeological sites near Leitre, Serra, Ramu Village, Wom, Aitape and Kaiep Village on the New Guinea mainland, and on Tumleo, Ali, Tarawai and Walis Islands (Fig. 1) were analysed by laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS), using a Varian quadrupole ICP–MS housed at the Field Museum of Natural History Elemental Analysis Facility (EAF). Fifty of these sherds had previously been petrographically analysed in thin section by William Dickinson (Dickinson and Shutler 2000, 240; Dickinson 2006, 88; Dickinson, in press).

Four distinct chemical profiles were identified among ceramics from the western end of the study area. The first of these, termed the Serra Hills chemical group, primarily includes ceramics recovered near Leitre and Serra, and chemically consistent with clays utilized by modern-day potters working at both villages. Serra Hills sherds can be chemically distinguished from sherds recovered at archaeological sites in the area around modern day Aitape—this is unsurprising given the geological differences between the two sections of the coast. The Sepik coast comprises the foothills and floodplains to the north of the Torricelli range, composed of Neogene sediments overlain by Quaternary detritus from the mountains. These floodplains have steadily prograded northwards since the early Holocene, in the Aitape area incorporating deposits of tuffaceous limestone associated with the pre-mid-Miocene Bliri volcanics (Norvick and Hutchinson 1980, 7, 33; Pigram and Davies 1987, 209). In contrast, the Serra Hills are composed primarily of late Pliocene silt, mudstone and limestone (Marchant 1969, 15; Norvick and Hutchinson 1980).

Sherds recovered at archaeological sites near Aitape and on adjacent Tumleo Island group into three distinct chemical compositional profiles, termed the Aitape-Barida 1, 2 and 3 chemical groups after the land systems monikers (Haantjens 1972) for geomorphological units present along the central Sepik coast. The majority of prehistoric ceramics collected on Tumleo Island fall into the Aitape-Barida 1 and 2 chemical groups, while the Aitape-Barida 3 group primarily includes pottery from mainland archaeological sites in the immediate vicinity of modern-day Aitape.

The site of Wom/Aiser is located some 14 km inland from Aitape (Fig. 1). Surface collections there produced a series of distinctive decorated sherds of a ware type now called Aiser. During excavations at the site of NGRP 46 on Tumleo Island, similar sherds were uncovered in archaeological units dated to *c.* AD 1000–1500 (Terrell and Schechter 2007, 65–6; Terrell and Schechter, *in press*). It is likely that both assemblages are roughly contemporaneous. The Wom Aiser style sherds display subtle stylistic divergence from Aiser sherds recovered on Tumeo, however, suggesting that they are the products of two distinct traditions, implying multiple production centres for Aiser ware prehistorically. The existence of two distinct production locations for Aiser ware seemed to be supported by initial statistical analysis of the data set (for detailed description of the statistical approach utilized, see Bishop and Neff 1989; Glascock *et al.* 2004), which indicated that Wom Aiser style sherds and Tumleo Aiser style sherds were statistically and chemically distinct from one another. Tumleo Aiser and Wom Aiser style sherds, however, are chemically distinguished only by differences in barium concentrations (Fig. 2), and therefore we questioned whether the observed chemical differences between the Tumleo and Wom ceramics might be better explained by post-burial uptake of barium in the Wom/Aiser sherds.

There are both chemical and mineralogical reasons for suspecting that most of the Wom/Aiser sherds were produced from the same basic raw materials as those on Tumleo Island, and that the elevated barium concentrations present in the Wom sherds result from post-burial uptake rather than a distinctive and identifiable chemical signature associated with production at Wom. Today, Tumleo potters—the principal producers on the coast—utilize clays weathered from local tuffaceous limestone deposits. When observed by the ethnographer Parkinson prior to the First World War, Tumleo potters exclusively obtained their clays from an outcrop on Tumleo Island locally referred to as the ‘Little Mountain’ (Parkinson 1900). After the disruptions caused by Japanese occupation during the Second World War, some Tumleo potters settled on the adjacent mainland near Aitape; however, they continued to use clays weathered from similar deposits (May and Tuckson 1982, 310), which weather out of a series of low hills both directly inland from Aitape and further south in the vicinity of Wom (Norvick and Hutchinson 1980, 1) (see Fig. 1). Clays used by Tumleo potters collected by Terrell and Robert Welsch during their fieldwork in the 1990s (Terrell and Welsch 1990, 1997) were obtained from both the ‘Little Mountain’ source on Tumleo and geologically similar mainland sources.

Chemical analysis of these clays suggests that all three chemical groups associated with Aitape-area ceramics (Aitape-Barida 1–3) can be generated using different types of clays weathered from these local tuffaceous limestones. Modern Tumleo potters distinguish at least three kinds of locally obtainable raw materials for potting, including clays of varying colour and working quality and decomposed limestone added as temper in varying quantities—the Sepik coast is the only location in all of Papua New Guinea where complex paste recipes comprised of several different plastic constituents have been observed in use by local potters (Tuckson 1977, 76–7; May and Tuckson 1982, 308–14). The sample of ceramics analysed from the Aitape area spans the last 2000 years of prehistory, and our chemical results indicate that raw materials obtained from local tuffaceous limestone deposits were the source of potting clay utilized by

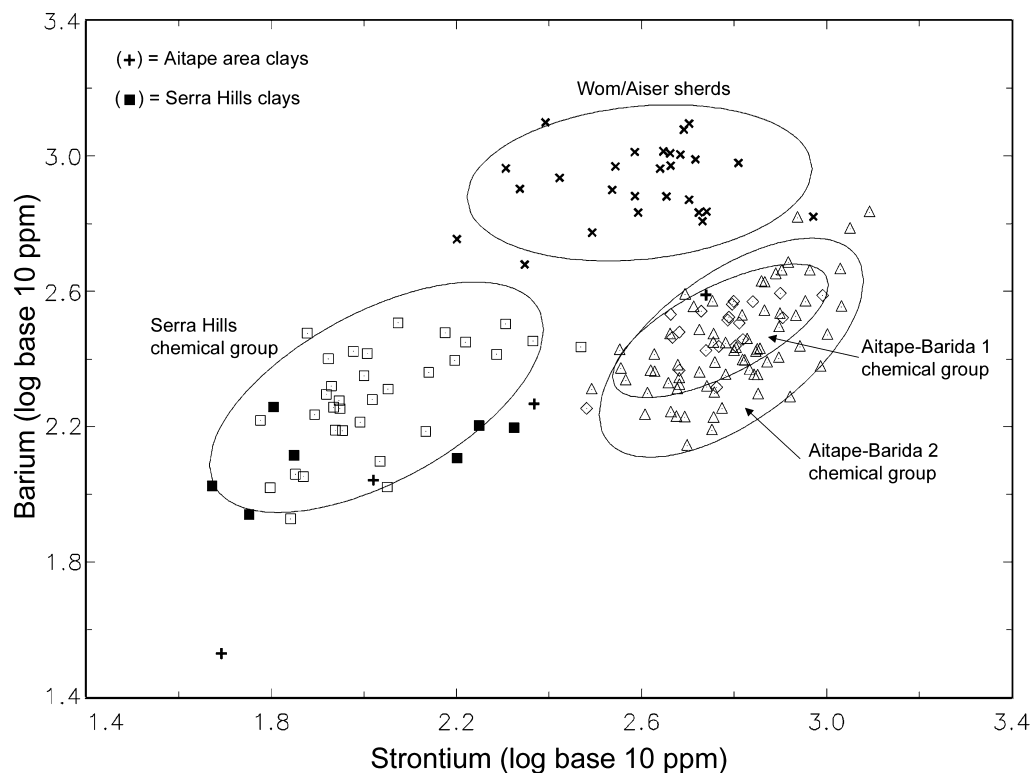


Figure 2 A bivariate plot of the logged (base 10) strontium and barium concentrations, showing the elevated concentrations of barium present in sherds from Wom/Aiser as compared to ceramics included in the Serra Hills and Aitape-Barida 1 and 2 chemical groups. Ellipses represent 90% confidence limits for group membership.

Aitape area potters from the very beginning of potting, around 2000 BP (Golitko, in press). In particular, the Aitape-Barida 1 and 2 chemical groups are best explained as the result of using relatively unmodified local clays.

Aitape-Barida 1 group ceramics also exhibit a distinctive mineralogical profile. In his petrographic study of Sepik coast sands and ceramic sherds, Dickinson identified seven distinct temper types (labelled groups A–G) representing various types of beach and fluvial sands weathered from the local geology. He considers the majority of these to have been manually added to clays, with the exception of temper group E, which he interprets as representing naturally occurring grains (Dickinson, in press). Notably, all sherds from Tumleo Island included in the Aitape-Barida 1 chemical group analysed petrographically by Dickinson have group E mineralogy.

With the exception of barium concentration, the majority of the 27 sherds analysed from Wom/Aiser, including all that are unequivocally identifiable as Aiser ware stylistically, are otherwise comparable chemically to ceramics recovered on Tumleo that are included in the Aitape-Barida 1 chemical group (Fig. 3). These include two of the four sherds from Wom/Aiser analysed in thin section by Dickinson, both of which were assigned to temper group E. Both chemistry and mineralogy, therefore, point towards the majority of the Wom/Aiser sherds having been produced from the clays associated with the same tuffaceous limestone deposits as Tumleo

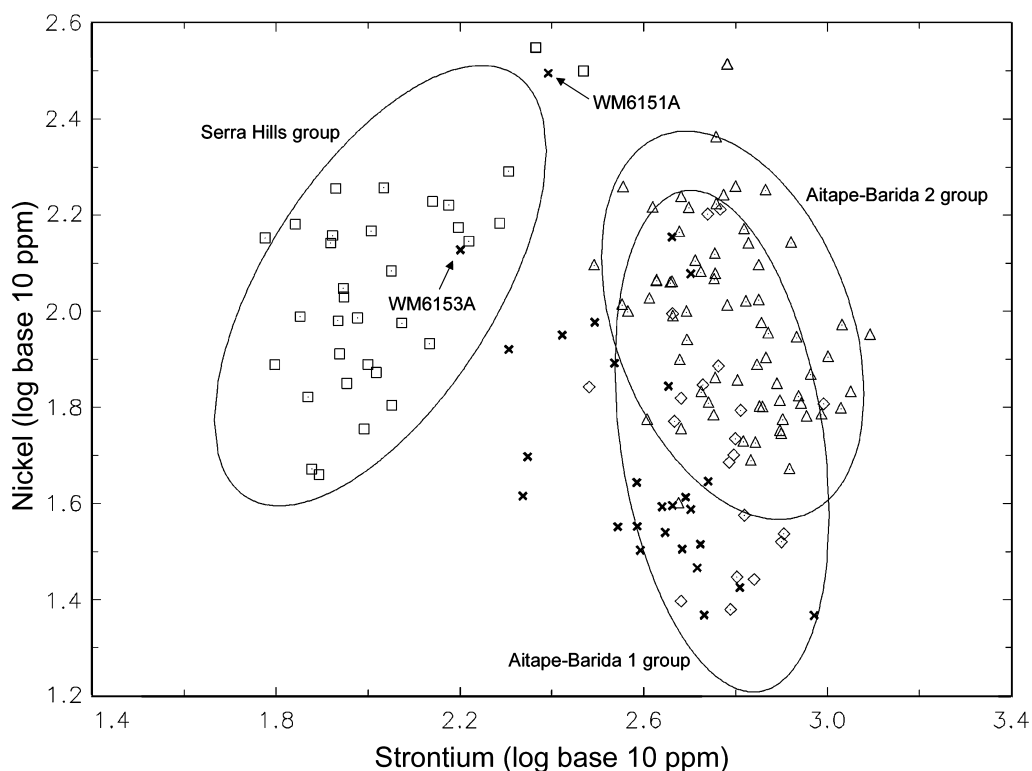


Figure 3 A bivariate plot of the logged (base 10) strontium and nickel concentrations, showing the similarity between the majority of the sherds analysed from Wom/Aiser with the Aitape Barida 1 and 2 chemical groups. Note that sherds WM6151A and WM6153A overlap chemically with sherds included in the Serra Hills chemical group. Ellipses represent 90% confidence limits for group membership.

Island sherds. These clays—for which a maximal barium concentration of 387 ppm was measured—cannot account for the elevated barium concentrations measured in the Wom/Aiser sherds.

Furthermore, elevated barium concentrations are present even in the few Wom sherds with chemical and mineralogical profiles consistent with production in the Serra Hills. Two of these, WM6151A and WM6153A, were analysed in thin section by Dickinson, and assigned to temper groups D and C, respectively—these temper groups are most common among sherds included in the Serra Hills chemical group, and with the exception of barium concentrations, WM6151A and WM6153A are similar to Serra Hills sherds (Fig. 3). Barium concentrations in analysed Serra Hills clays collected in the hills behind modern-day Serra and Lietre (Fig. 2) are particularly low, ranging between 87 and 181 ppm.

#### POST-DEPOSITIONAL CHEMICAL ALTERATION OF ARCHAEOLOGICAL CERAMICS

The possibility of chemical alteration of archaeological ceramics after deposition was first pointed out by Sayre, Dodson and Burr Thompson (1957, 40). In the ensuing years, considerable work has been done on the problem of post-burial alteration, and understanding has progressed

considerably as to the major types of alteration that may occur, and what factors promote or inhibit post-burial chemical changes. For instance, burial environment can play a significant role—soil development, pH, redox conditions and the level of organic activity in the burial context can all have a significant role in potential alteration in samples in terrestrial burial environments (Rottländer 1981, 1982); for instance, the fixing of manganese under reducing soil conditions (Picon 1985, 27). Organic activity creates a build-up of phosphates in the soil, and the leaching of these into archaeological ceramics has been documented, although sometimes interpreted as use-related (Duma 1972; Franklin and Vitali 1985; Freestone *et al.* 1985; Dunnell and Hunt 1990).

Initial composition and technological choices also play a role in determining both how susceptible to post-burial alteration a particular ceramic object is, and the nature of the alteration it is susceptible to. High- or over-fired ceramics are prone to particular kinds of post-depositional alteration, for instance. Although firing itself has been repeatedly shown to not significantly alter the abundances of elements typically measured in provenience studies (Rottländer 1981, 210; Kilikoglou *et al.* 1988, 39; Cogswell *et al.* 1996; Schwedt 2004, ch. 5; Schwedt and Mommsen 2007), mineral alterations associated with high-temperature firing—including the formation of metastable minerals such as gehlenite and vitreous silica-rich phases—play an important role in post-burial alteration. These vitreous phases are prone to breakdown and leaching (Heinmann 1982, 164–5; Maggetti 1982, 128; Rice 1987, 93–8, 419), and are also associated with the formation of zeolites such as analcime, which can result in significant uptake of some alkaline elements, and removal of others (Lemoine *et al.* 1981, 352; Picon 1991, 117–18; Buxeda i Garrigós *et al.* 2001, 364; Buxeda i Garrigós *et al.* 2002; Schwedt 2004; Schwedt *et al.* 2004, 2006; Iñáñez *et al.* 2007, 2009).

In ceramics produced from calcareous clays (CaO > ~5% of total composition), these effects can be compounded—calcium containing minerals act as flux, producing a more rapid and thorough formation of vitreous glassy phases at lower temperatures (Tite and Maniatis 1975, 123; Kornilov 2005, 392). Additionally, calcite may be transformed to metastable phases or redeposited as secondary calcite (Olin *et al.* 1978, 220–3; Maggetti 1982, 129; Picon 1987, 27; Cau Ontiveros *et al.* 2002), and can also play an important role in fixing other alkaline elements (Picon 1985, 1987, 1991).

Because most clays retain a significant cation exchange capacity until fired to fairly high temperatures (~1000°C), mobile elements may either be leached out or absorbed by the clay phase of ceramic fired at lower temperatures (Hedges and McLellan 1976, 206–7). Being the most reactive with water, the alkali and alkali-earth metals are typically the most mobile—fixation of cesium has been noted as a problem in low-fired ceramics, for instance (Buxeda i Garrigós *et al.* 2001, 360–2), as has leaching of strontium and other alkali elements (Picon 1985, 28; Picon 1987, 44). Barium has been noted as particularly susceptible to uptake from the burial environment, but increased concentration of barium can also occur as a result of the formation of baritic zeolites such as harmotome, barytic heulandite or brewsterite, related to the breakdown of either vitreous phases of high-fired ceramics, or else other glassy phases such as volcanic ash grains (Picon 1985, 1987, 1991; Kosakowsky *et al.* 1999, 384–5; Neff *et al.* 2003, 212–18; Alex 2009, 8).

Several methods have been used to examine potential post-depositional effects in ceramics in prior studies (Schwedt *et al.* 2004, 13), including soaking samples in solutions of simulated element load and pH to examine the expected degree of elemental mobility in a particular set of ceramics (Franklin and Hancock 1980, 118; Segebade and Lutz 1980; Tubb *et al.* 1980, 161–2; Heinmann and Maggetti 1981; Franklin and Vitali 1985), comparison of

concentration distributions within a data set assumed to be chemically homogeneous and therefore expected to exhibit normally distributed trace element concentrations (Rottländer 1981; Schwedt 2004; Schwedt *et al.* 2004; Adan-Bayewitz *et al.* 2006), and XRD, SEM-EDS or petrographic identification of diagenetic mineral phases (Freestone *et al.* 1985; Buxeda i Garrigós *et al.* 2002; Cau Ontiveros *et al.* 2002; Neff *et al.* 2003; Schwedt *et al.* 2006; Iñáñez *et al.* 2007, 2009).

In the present study, we utilize chemical mapping of cut sherd cross-sections using time-of-flight-inductively coupled plasma-mass spectrometry with laser ablation sample introduction (TOF-LA-ICP-MS) to detect gradients in chemical concentration indicative of elemental leaching from the burial environment. While it has been noted in some cases that analcime formation in high-fired calcareous ceramics can profoundly alter chemical concentrations without resulting in detectable concentration gradients across sherd cross-sections (Schwedt *et al.* 2006, 249), the analysed samples appear to have been produced from relatively non-calcareous clays. Even ceramics from Tumleo Island, characterized in part by higher calcium concentrations than those recovered elsewhere on the coast, average only 2.6% CaO, while analysed Wom/Aiser ceramics average 2.3% CaO. Equivalent firing temperatures are unknown, but traditional industries in the area rely on open firing and short soaking times, so it is assumed that temperatures rarely exceeded ~850°C (Rye 1976, 112–13; Rice 1987, 156–7). As such, it is unlikely that high-temperature meta-stable or vitreous mineral phases are common in the fabric of the analysed ceramics. Previous studies of mobile element leaching into low-fired sherds indicate that post-depositional processes result in pronounced formation of chemical gradients or build-up along vessel walls (Freestone *et al.* 1985, 164–5; Picon 1985, 28; Picon 1987, 41; Schwedt *et al.* 2004, 13; Duwe and Neff 2007, 407).

#### SAMPLE AND METHOD

##### *Sample*

Six samples were selected for elemental concentration mapping—in each case, specimens were selected that had been analysed in petrographic thin section. Three sherds exhibiting relatively low barium concentrations—one from Aitape, one from Leitre and one from Tumleo Island—were selected for analysis. Three sherds were selected from Wom/Aiser, one of which is assigned to temper group E, and with the exception of its barium concentration, it is chemically similar to Aitape area pottery. The other two are of different temper classes associated primarily with ceramics recovered from Serra and Leitre, and with the exception of barium concentrations, chemically consistent with production in the Serra Hills.

*AT649B1A*: This specimen was collected at a locality near Aitape, locally called Sumalo Hill, and is of a style called Sumalo ware, dating to between 1200–1400 BP. A concentration of 383 ppm of barium was measured at the EAF. Dickinson places this sherd into temper group G, which is broadly distributed across chemical groups included in the study. Sherd AT649B1A was assigned to the Serra Hills chemical group, and probably represents a vessel exchanged during prehistory.

*LT6032A*: This specimen was collected at Leitre Nowage Village, and probably dates to the relatively recent past. LT6032A was assigned to the Serra Hills chemical group, and there is no reason to suspect non-local production. A barium concentration of 261 ppm was measured at the EAF. Dickinson places it in temper group A, which is predominately, though not exclusively, associated with sherds included in the Serra Hills chemical group.



*TM178*: This specimen was collected at the Tumleo Wain locality, and is of Wain style, dating to some time within the past 500 years. The measured barium content is 334 ppm. Chemically, this sample falls into the Aitape-Barida 1 reference group, and is probably of local Tumleo Island production. Dickinson places this sample into temper group E.

*WM6151A*: This undecorated specimen was collected at Wom/Aiser, and has a measured barium concentration of 1255 ppm. Dickinson places this sherd into temper group D. With the exception of barium concentrations, this sherd is chemically indistinguishable from ceramics included in the Serra Hills chemical group.

*WM6153A*: Another undecorated Wom/Aiser sherd, with a measured barium content of 567 ppm. Dickinson places WM6153A into temper group C. With the exception of barium concentrations, WM6153A is chemically indistinguishable from ceramics included in the Serra Hills chemical group.

*WM616*: This sherd is of the characteristic Aiser stylistic variant found at Wom/Aiser. A barium content of 661 ppm was measured at the EAF. Dickinson places this sherd into temper group E, and with the exception of barium content, WM616 is chemically indistinguishable from sherds included in the Aitape-Barida 1 chemical group.

#### *Time of flight–laser ablation–inductively coupled plasma–mass spectrometry*

Concentration mapping was achieved by sampling a raster of points across flat sherd cross-sections. This is essentially the same method employed in prior LA–ICP–MS studies that have mapped elemental concentrations in paints or glazes across vessel surfaces (Speakman and Neff 2002; Speakman 2005), but instead of painted surfaces, ablation was performed on flat cross-sections cut for petrographic analysis. All analysis was performed on the GBC Optimass Time of Flight Mass Spectrometer housed at the Institute for Integrative Research in Materials, Environments, and Societies (IIRMES) at California State University Long Beach. Sample introduction was via a New Wave UP213 Laser Ablation system, using a helium/argon carrier gas (for more on the instrumentation at IIRMES, see Beck and Neff 2007; Duwe and Neff 2007).

Raster lines of 15–16 ablation spots, 55 µm in diameter and spaced at 0.4 mm intervals, were measured across each sherd cross-sectional surface—between nine and 14 lines of raster points were ablated depending on sherd thickness (Fig. 4). No attempt was made to avoid pore spaces or inclusions. Batches of three samples required approximately 8 h of run time—however, the mass spectrometer was set to automatically initiate a reading each time the laser began a new ablation, and the system was left to run overnight. Consequently, the actual operator time required for each run was only about 1 h, during which the ablation sequence was programmed into the laser and mass spectrometer control programs.

After every set of two raster lines (30–32 ablation spots), a blank was measured, as were a set of six standards—NIST standard glasses 610, 612 and 614 (Pearce *et al.* 1997), New Ohio Red clay (Glascocock 1992), a well-measured piece of obsidian from the Glass Buttes source in Oregon (Glascocock 1999) and Brill D standard glass (Brill 1999). The last two standards were included because of their relatively high barium concentrations (1188 and 4569 ppm, respectively), in order to ensure that values measured in the ceramic sample could be bracketed by higher concentration values in standards. Isotopes of 46 major, minor and trace elements were measured—Li, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th and U.

The resulting data were processed by first subtracting blank values from raw signal counts, after which the resulting blank subtracted signals were normalized to the simultaneously mea-

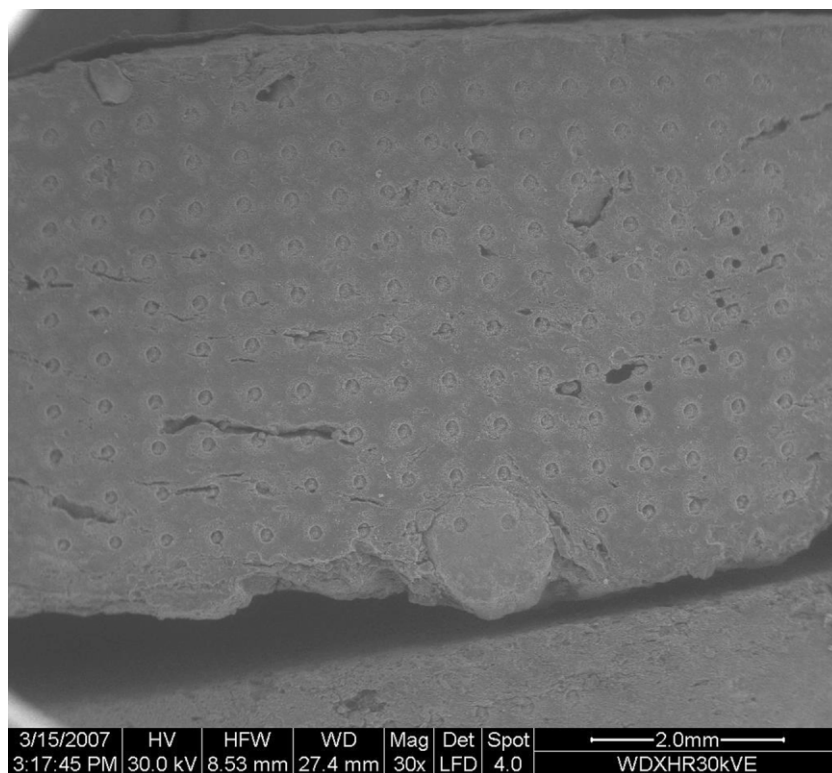


Figure 4 A SEM image of a cross-section of sherd WM6153A, showing a raster of ablation craters. Ablation craters from the initial LA-ICP-MS analysis at the EAF can be seen towards the far right-hand side.

sured signal count for  $^{29}\text{Si}$  to control for time variation in ablation intensity. Time-normalized signal strengths were then converted to normalized relative contribution by weight using oxide multipliers for assumed most abundant oxide species—the same procedure was applied to the measured standards, and a linear calibration line calculated for these. The oxide multiplied time-normalized signals were then summed to 100% for the samples to calculate the contribution of silica, and parts per million concentrations calculated from the standards—this method is presented in detail by Speakman and Neff (2005) and Gratuze *et al.* (2001).

## RESULTS

Identifying post-depositional enrichment or depletion is complicated by the so-called ‘constant sum problem’. Because concentrations within any specimen are measured as a proportion of the total composition (parts per million or weight percentages), the enrichment or dilution of one element will necessarily result in a corresponding dilution or enrichment of all other measured elements. Additionally, inherent chemical heterogeneity within each specimen and analytical error can both produce the impression of relative compositional differences that are not associated with post-burial alteration. To correct for the constant sum problem, we first applied a best relative fit (BRF) correction (Harbottle 1976, 48; Beier and Mommsen 1994; Schwedt *et al.* 2004, 94; Mommsen 2007) to the values measured in each sherd (e.g., Schwedt *et al.* 2004, 88–9; Schwedt *et al.* 2006, 241).

RQ-mode factor analysis (Neff 1994) was next performed on the variance–covariance matrix of BRF-corrected concentration measurements for each analysed sherd. This technique is particularly useful as it allowed us to simultaneously examine correlations between all measured elements and compositional patterning between individual ablation spots. The resulting biplots are shown in Figures 5–7. In each case, the first two factors extracted from the RQ-mode analysis are displayed, with ablation points coded by cross-sectional position—the inner and outer most rows of ablation points are coded separately, while all inner rows are coded with the same symbol. In most cases, the first two factors account for ~50% of the total data variance (AT649B1A, 41%/14%; LT6032A, 36%/16%; TM178, 33%/20%; WM6151A, 28%/16%; WM6153A, 31%/17%; WM616, 34%/19%).

Several trends are apparent in the six specimens—in all six, barium concentrations are positively correlated with potassium, rubidium and cesium concentrations. As these three elements are almost invariably contained in the same mineral phases (Schwedt *et al.* 2006, 248), this correlation is unsurprising. In the three low-barium specimens, barium concentrations are variably correlated with remaining alkali elements—in AT649B1A, for instance, barium is negatively correlated with calcium and magnesium concentrations, and only weakly correlated with strontium and sodium. LT6032A displays similar correlations, although sodium is more strongly correlated with barium than in AT649B1A. Even after best relative fit correction, there are a number of data points measured on LT6032A that form a diffuse ‘cloud’ with low factor 1 scores, and contrast with a tight cluster of points with higher factor 1 scores. LT6032A contains a particularly dense distribution of larger mineral grains, many of which were ablated during analysis. We interpret data points scoring low on factor 1 as representing these mineral grains. Elementally, they are characterized by relatively low rare earth concentrations, and are comparatively enriched in a series of elements including aluminium, silica, sodium, iron, calcium, manganese and magnesium. Conversely, the tightly clustered points scoring high on factor 1 and enriched in REEs and several other elements probably represent more clay-rich ablation spots.

In TM178, barium is positively correlated with strontium concentrations, weakly with sodium and calcium concentrations, and negatively correlated with magnesium. Additionally, two distinct clusters of points (Fig. 6) with high transition metal concentrations are apparent—one particularly enriched in iron, nickel, vanadium, arsenic and antimony, and the other enriched in manganese, cobalt, chromium, scandium and zinc, as well as magnesium. These points appear related to larger mineral grains, and may represent ferromagnesian grains noted in thin section by Dickinson (in press). In both AT649B1A and TM178, there is little apparent chemical difference between inner and outer measurement rows and core measurements evident on the RQ-mode biplots, suggesting that barium content is not strongly patterned across the measured sherd surfaces. Barium content may be somewhat enriched in innermost versus outermost ablation rows measured on LT6032A, suggesting some profile formation for barium concentration.

In the three high-barium Wom/Aiser ceramics, concentrations of all alkali elements are strongly positively correlated with one another on factor 1, and are generally negatively correlated with rare earth concentrations. With the exception of a few isolated ablation points with anomalous factor 2 scores, ablation spots on all three Wom/Aiser sherds form relatively tight clusters chemically. The loading of alkali elements on to factor 1 in the case of the Wom/Aiser sherds indicates that differences in alkali concentrations represent the most significant compositional trend in the three Wom/Aiser sherds. Additionally, factor 1 serves to separate the innermost and outermost rows in all three, indicating that alkali concentrations are significantly

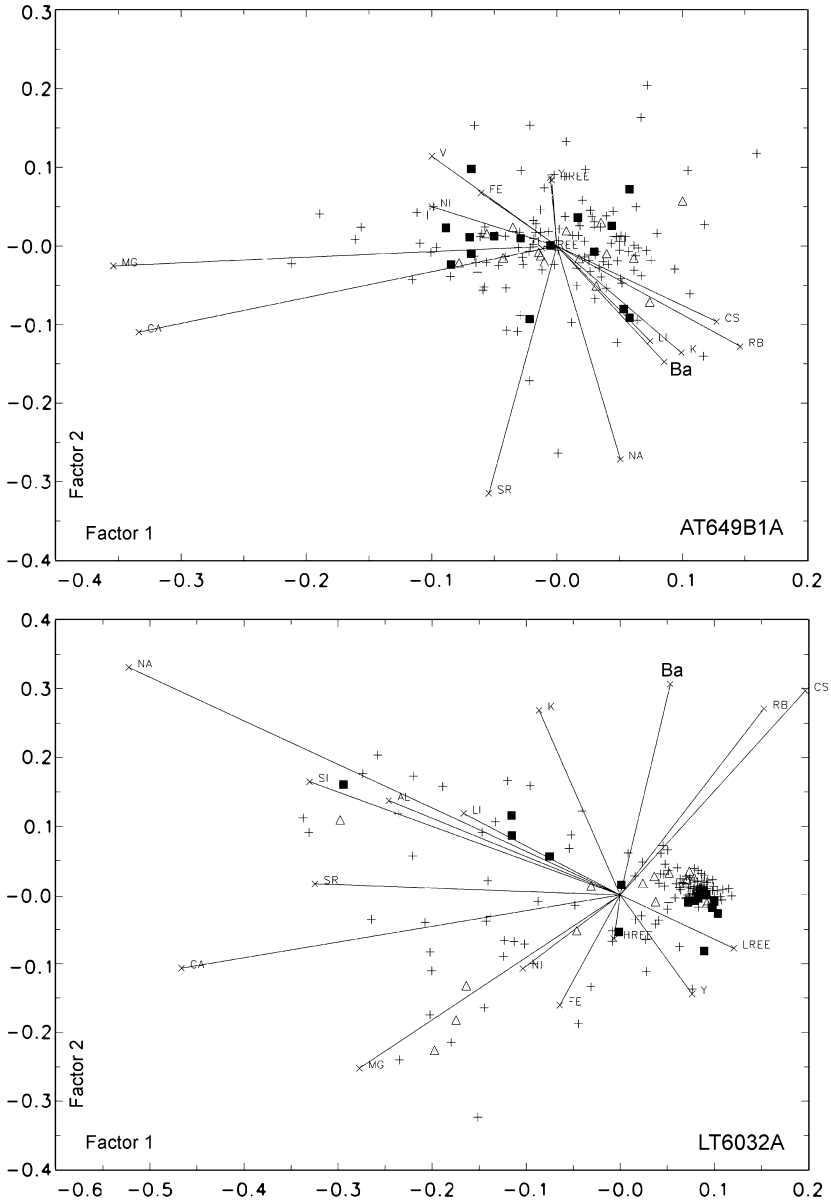


Figure 5 RQ-mode biplots of the first two factors calculated from the best relative fit corrected variance–covariance matrix of sherds AT649B1A and LT6032A, mapped by LA–TOF–ICP–MS. Only the principal vectors are shown for visual clarity, with light (LREE) and heavy rare elements (HREE) averaged into single vectors. Δ, innermost ablation row; ■, outermost ablation row; +, core ablation rows.

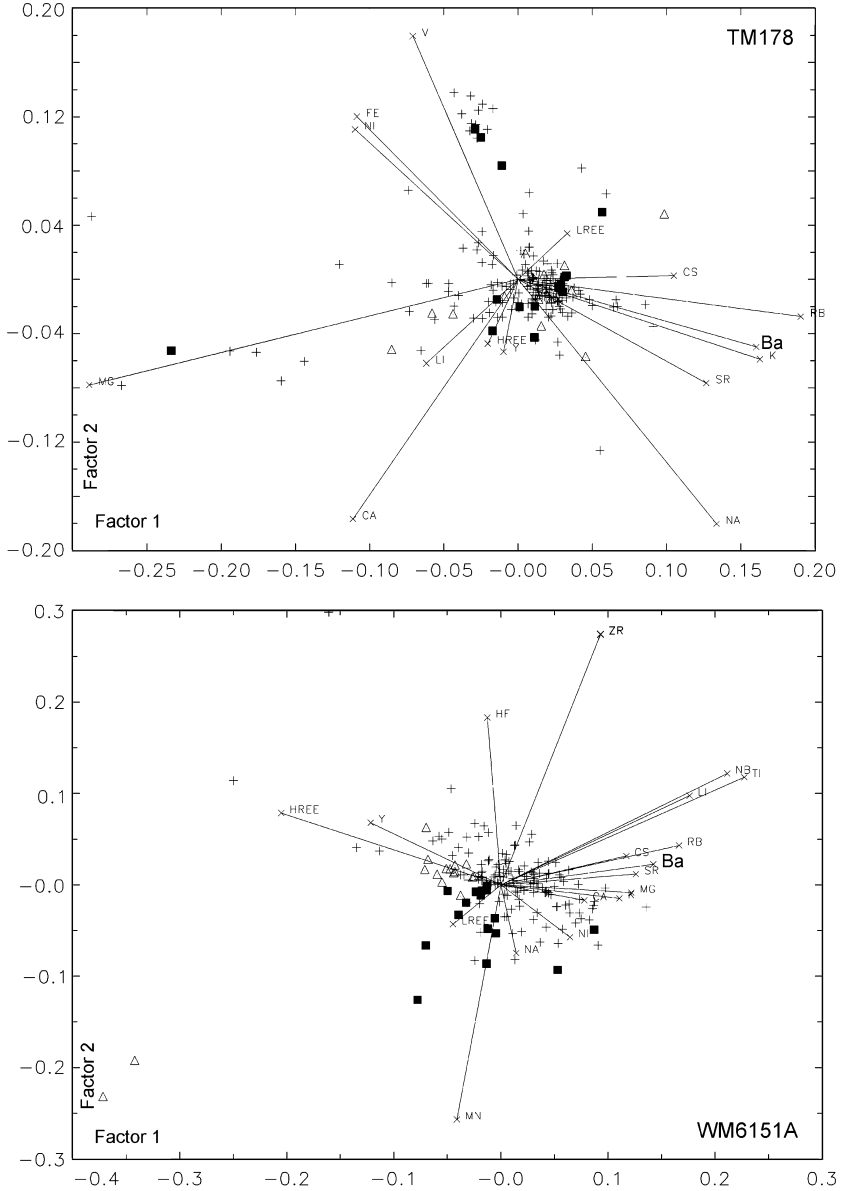


Figure 6 RQ-mode biplots of the first two factors calculated from the best relative fit corrected variance–covariance matrix of sherds TM178 and WM6151A, mapped by LA–TOF–ICP–MS. Only the principal vectors are shown for visual clarity, with light (LREE) and heavy rare elements (HREE) averaged into single vectors.  $\Delta$ , innermost ablation row;  $\blacksquare$ , outermost ablation row;  $+$ , core ablation rows.

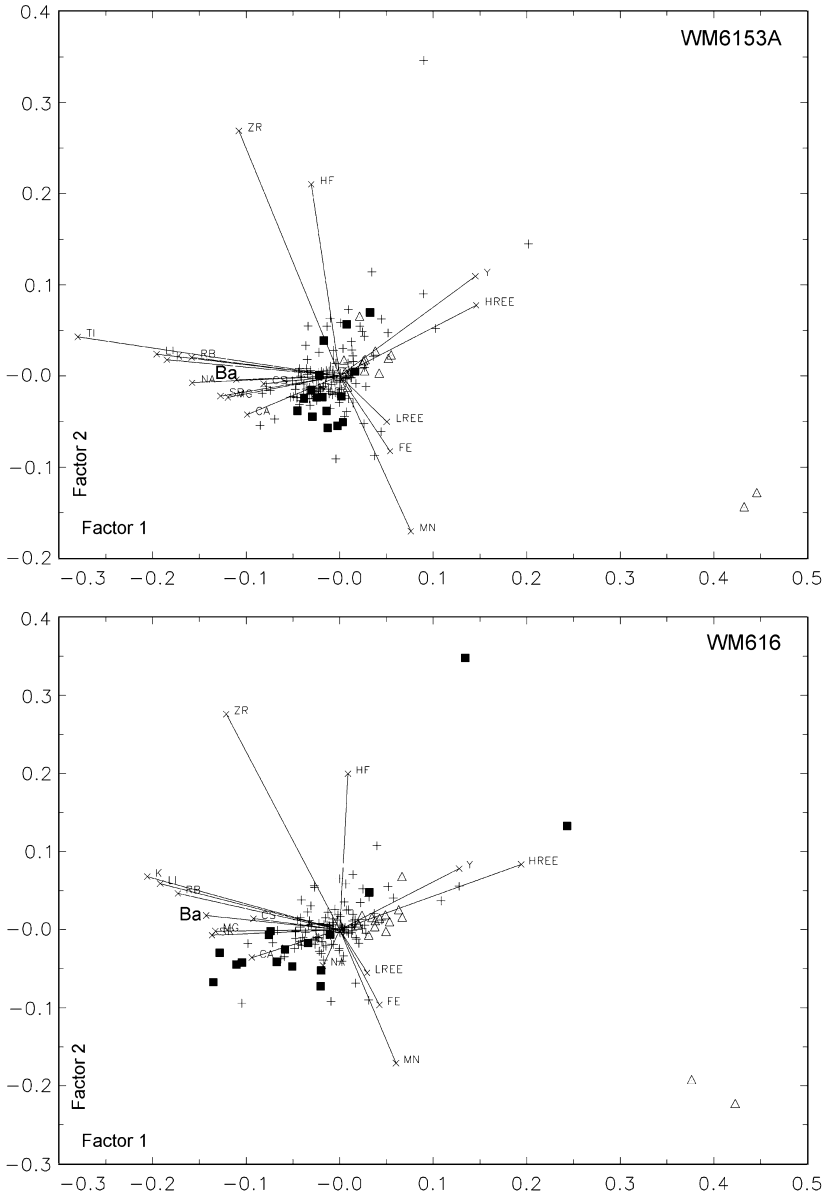


Figure 7 RQ-mode biplots of the first two factors calculated from the best relative fit corrected variance–covariance matrix of sherds WM6153A and WM616, mapped by LA–TOF–ICP–MS. Only the principal vectors are shown for visual clarity, with light (LREE) and heavy rare elements (HREE) averaged into single vectors.  $\Delta$ , innermost ablation row;  $\blacksquare$ , outermost ablation row;  $+$ , core ablation rows.

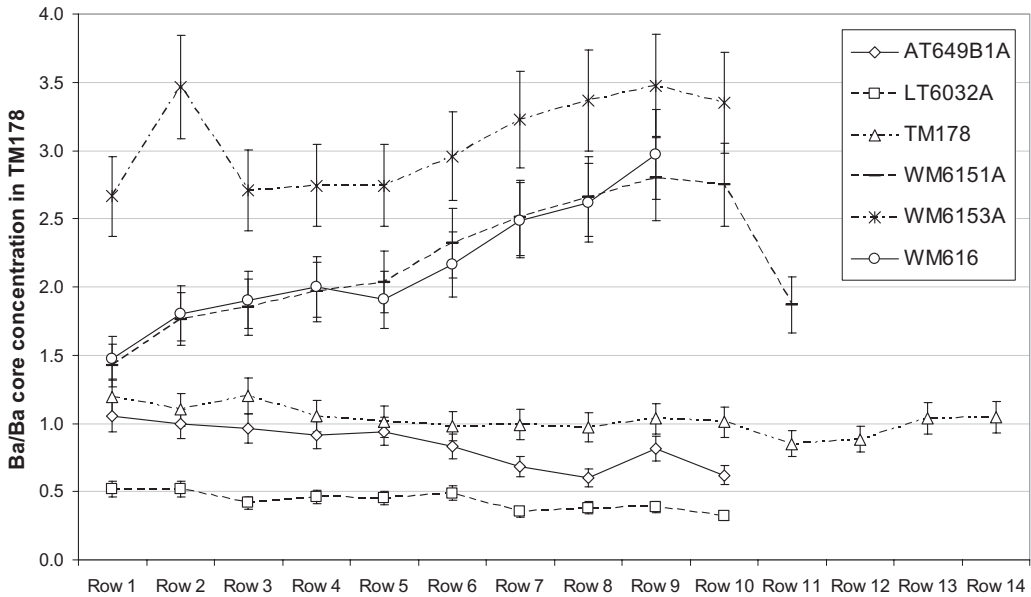


Figure 8 Row-averaged barium concentrations in each of the six sherds, corrected to the average core concentration in sherd TM178. The error bars express one-sigma estimates of analytical error derived from repeated measurements of New Ohio Red standard clay.

patterned across the cut surfaces of each sherd. This is particularly the case for sherd WM616, for which there is no overlap at all between the innermost and outermost ablation rows on the first two factors.

To more directly examine the relative distribution of barium across sherd surfaces, values were averaged by ablation row and plotted as compositional profiles from innermost to outermost ablation row. Data points identified in the RQ-mode biplots as reflecting the composition of larger mineral grains were identified and omitted from the average to reflect the composition of the finer fraction of each respective paste to the extent possible, as this is assumed to be the principal location of any post-burial leaching. To scale the sherds relative to one another and permit comparison on a single plot, each value was normalized to the core concentration—the inner six ablation rows in this case—of barium present in sherd TM178. TM178 was chosen because row-averaged barium measurements displayed the lowest variance of any of the analysed specimens.

On the resulting plot of relative concentrations (Fig. 8), it is evident not only that the Wom/Aiser sherds display considerably elevated concentrations of barium relative to the three low-barium sherds, but also that the absolute magnitudes of compositional gradients in the Wom/Aiser sherds—as suggested by the RQ-mode biplots—are substantially greater than those found in the low-barium sherds from Aitape, Leitre and Tumleo, ranging between 100% and 150% difference between high and low concentrations. Curiously, the actual shape of the profiles present in the Wom/Aiser sherds differs somewhat from that observed in prior studies of profile formation (e.g., Schwedt *et al.* 2006, 244–6)—rather than displaying relatively even enrichment or dilution close to both vessel walls, the Wom sherds display considerably greater enrichment along one side than the other, with only moderately lower concentrations towards the middle point of each sherd. WM6151A in particular displays obvious enrichment along only one vessel wall. This suggests

that the rate at which barium has entered these sherds has not proceeded evenly relative to the inner and outer surfaces. Two explanations for this observed pattern come to mind—possibly, the orientation of the sherds during burial has impacted the rate at which groundwater has interacted with the two sides of each sherd, resulting in one side absorbing barium and other mobile elements more rapidly from the burial environment. Alternatively, differential surface treatment of the inner and outer vessel surfaces during production may have resulted in differential porosity; for instance, if the outer surfaces were burnished, or one of the surfaces coated with sealant of some kind during production. Some Melanesian potters are noted as rubbing certain leaves on the surface of water vessels immediately after firing to prevent leakage, for instance (Rye 1976, 119). In the case of Aiser ware pottery, a red slip was probably applied (Terrell and Schechter, in press), which may have partially sealed pore spaces and voids through which groundwater might enter.

Gradients are much weaker in the low-barium sherds. In TM178, there is almost no evidence of significant differences in barium concentration at all—if analytical error is considered, none of the measured row averages exceeds one standard deviation from the core values in the sherd. Given the close match compositionally between this sherd—and others included in the Aitape-Barida 1 chemical group—and locally available clays, it appears that the measured composition of TM178 has been unaltered by burial, and is reflective of original choices made during production by potters on Tumleo Island. LT6032A and AT649B1A both display minor but significant differences in barium concentrations in some ablation rows, particularly in ablation rows six to ten. In comparison to the sherds from Wom/Aiser, however, profiles in the Leitre and Aitape sherds are relatively unpronounced—barium concentrations along either edge of LT6032A differ by at most 15% relative to core values. AT649B1A may demonstrate a higher degree of barium mobility, as there is about a 30% difference between maximal and minimal row average concentrations. Again, however, the ability to link these sherds to locally available raw materials suggests that alteration has been insufficient to obscure their basic compositional profile.

Given the observed compositional similarities between Wom/Aiser sherds and locally available raw materials—clays collected from the tuffaceous limestone that characterizes the Aitape area—both mineralogically and chemically with the exception barium content, it is likely that the overall effect of post-burial alteration has otherwise been relatively minor. Nonetheless, the results of the present analysis suggest that the concentrations of the majority—if not all—of the alkali elements may have been impacted in the Wom/Aiser sherds by post-burial conditions. However, alteration of alkali concentrations does not obscure the chemical similarities between Wom/Aiser ceramics and Aitape area clays once appropriate data transformations (Harbottle 1976, 48; Beier and Mommsen 1994; Buxeda i Garrigós 1999, 298; Schwedt *et al.* 2004, 94; Mommsen 2007) are applied. Table 1 displays Mahalanobis distance based probabilities of group membership (Glascock *et al.* 2004) for the 27 Wom/Aiser sherds analysed during the original Field Museum study, with barium concentrations omitted from the calculation and a best relative fit correction applied to the Wom sherds to address alteration of other alkali elements. Despite post-burial chemical alteration, the Wom/Aiser sherds can still be robustly linked to other western Sepik coast chemical groups—the majority of Wom sherds project confidently into the Aitape-Barida 1 chemical group, with Mahalanobis distance based group membership probabilities of between 5% and 99%. As their mineralogical composition suggests, sherds WM6151A and 6153A both have significant probabilities of inclusion in the Serra Hills chemical group, and negligible probabilities of inclusion in any of the three Aitape-Barida chemical groups, and probably represent ceramics transported to Wom/Aiser from production locales further to the west in the Serra Hills.



Table 1 Mahalanobis distance based probabilities of group membership in the four western Sepik coast chemical groups for the 27 sherds from Wom/Aiser chemically analysed

Specimen	Assignment	Group membership probability			
		Serra Hills	Aitape-Barida 1	Aitape-Barida 2	Aitape-Barida 3
WM6151A	Serra Hills	5.865	0.000	0.000	0.003
WM6151B	Aitape-Barida 1	0.000	33.360	0.000	0.001
WM6152A	Aitape-Barida 1	0.000	8.788	0.000	0.166
WM6152B	Aitape-Barida 1	0.000	72.400	0.000	0.006
WM6153A	Serra Hills	41.007	0.007	0.046	0.184
WM6153B	Aitape-Barida 1	0.467	21.092	0.044	6.233
WM6154	Aitape-Barida 1	0.000	65.000	0.015	0.006
WM6155	Unassigned	0.000	0.033	0.024	0.523
WM6156	Aitape-Barida 1	10.389	34.857	0.206	2.044
WM6157	Aitape-Barida 1	1.528	9.207	0.000	0.395
WM6158	Aitape-Barida 1	1.932	5.469	0.181	3.048
WM6159	Aitape-Barida 1	0.000	86.549	0.023	0.952
WM61510	Aitape-Barida 1	0.091	54.097	0.099	16.953
WM61511	Aitape-Barida 1	0.000	95.423	0.000	0.001
WM61512	Aitape-Barida 1	0.000	26.200	0.000	0.005
WM61513	Aitape-Barida 1	0.000	12.278	0.005	0.019
WM61514	Aitape-Barida 1	0.000	87.874	0.000	0.006
WM61515	Aitape-Barida 1	0.000	85.464	0.000	0.019
WM61516	Aitape-Barida 1	0.000	46.039	0.000	0.057
WM61517	Unassigned	0.000	0.519	0.000	0.000
WM61518	Aitape-Barida 1	0.000	32.727	0.001	0.026
WM61519	Aitape-Barida 1	0.000	99.863	0.352	2.040
WM61520	Aitape-Barida 1	0.000	29.055	0.000	0.031
WM61521	Aitape-Barida 1	0.000	89.557	0.007	0.005
WM61522	Aitape-Barida 1	0.000	98.316	0.233	0.170
WM61523	Aitape-Barida 1	0.000	98.648	0.000	0.115
WM616	Aitape-Barida 1	0.000	10.083	0.000	0.008

## CONCLUSION

As has been demonstrated in previous studies, post-depositional chemical alteration must be considered as a source of chemical variation in provenance studies of ceramics. In extreme cases of either elemental depletion or enrichment, post-depositional effects can significantly impact the ability to properly assign samples to chemical compositional groupings (Schwedt *et al.* 2004, 94–5). In the case presented here, initial suspicions of post-burial barium enrichment in sherds recovered at Wom/Aiser appear justified—in comparison to sherds from other sites similarly analysed, the Wom/Aiser sherds display either strong gradients of barium concentration from inner to outer surface, or else sharply elevated concentrations along vessel walls. While other alkali elements appear impacted as well, these are generally consistent with ceramics from other regional archaeological sites, as well as locally available raw materials, suggesting that post-burial alteration has not significantly obscured valuable provenience information.

The present study also points the way towards the utility of ICP–MS with laser-ablation sampling for micro-spot analysis of archaeological samples. In contrast to methods such as

electron microprobe or SEM–EDS/WDS previously utilized to micro-sample archaeological ceramics (Neff *et al.* 2003, 212–14), LA–ICP–MS has the ability to simultaneously measure far larger numbers of elements to much lower concentrations, and thus represents a powerful new tool for interpreting the results of ceramic compositional analysis.

While the analysis reported on here could, in principle, have been carried out using a conventional quadrupole ICP–MS, there are additional advantages to the use of time-of-flight ICP–MS in the study of post-burial uptake of elements. In particular, the rapid signal integration and simultaneous measurement of all elements enabled by TOF–ICP–MS allows for the analysis of very small volumes of material (Leach and Heiftje 2000; Frasier-Shapiro and Gilstrap 2007)—future studies could utilize this capability to analyse pore boundaries and the edges of inclusions in greater detail, as has been done in the study of diagenesis in tooth enamel (e.g., Cucina *et al.* 2007, 1885; Dudgeon and Commendador-Dudgeon 2007).

Our results indicate that our current data set cannot provide a robust demonstration of multiple production loci for ceramics in the broader area around Aitape using elemental chemistry alone, as the chemistry of sherds from sites on Tumleo and those from Wom/Aiser is identical once post-depositional chemical alteration is identified and accounted for. However, the existence of definable sub-styles of Aiser ware ceramics on Tumleo and at Wom/Aiser suggests two divergent traditions of production, that while technologically similar to one another, are characterized by differences in decorative motifs. It is interesting to note that Aiser ware style sherds found outside of the Aitape area—for instance, on Tarawai Island—are more similar to decorative styles associated with Tumleo Island, suggesting that despite the likely existence of two production loci for Aiser ware ceramics—one on Tumleo and the other possibly at Wom/Aiser—only those produced on Tumleo appear to have been widely transported prehistorically.

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