Directly dated starch residues document early formative maize (*Zea mays* L.) in tropical Ecuador

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The study of maize (*Zea mays* L.) domestication has advanced from questions of its origins to the study—and debate—of its dietary role and the timing of its dispersal from Mexico. Because the investigation of maize's spread is hampered by poor preservation of macrobotanical remains in the Neotropics, research has focused on microbotanical remains whose contexts are often dated by association, leading some to question the dates assigned. Furthermore, some scholars have argued that maize was not introduced to southwestern Ecuador until ≈4150–3850 calendar years before the present (cal B.P.), that it was used first and foremost as a fermented beverage in ceremonial contexts, and that it was not important in everyday subsistence, challenging previous studies based on maize starch and phytoliths. To further investigate these questions, we analyzed every-day cooking vessels, food-processing implements, and sediments for starch and phytoliths from an archaeological site in southwestern Ecuador constituting a small Early Formative village. Employing a new technique to recover starch granules from charred cooking-pot residues we show that maize was present, cultivated, and consumed here in domestic contexts by at least 5300–4950 cal B.P. Directly dating the residues by accelerator mass spectrometry (AMS) radiocarbon measurement, our results represent the earliest direct dates for maize in Early Formative Ecuadorian sites and provide further support that, once domesticated ≈9000 calendar years ago, maize spread rapidly from southwestern Mexico to northwestern South America.

ceramic residues | microfossil analysis | AMS radiocarbon measurement | crop dispersals | agricultural origins

In the 1950s village sites were discovered in southwestern Ecuador that predated by at least 1000 years the first sedentary villages in Mexico and Peru, the heartlands of later civilizations. Much debate has centered on the subsistence base of the Early Formative cultures of coastal Ecuador and whether maize was grown and consumed as a food item. Tracing maize's diffusion from Mexico, the accepted origin of its domestication (1–3), is important to the understanding of its domestication and dispersal and to shedding light on the transition of mobile hunter-gatherer peoples to sedentary farmers.

Before the development of microbotanical techniques the poor preservation of macrobotanical remains hindered documentation of the introduction of maize into South America, as in other regions of the tropical Americas. As a result, archaeobotanical research in Ecuador has centered on microbotanical remains whose contexts are usually dated by association, with the notable exception of the direct dating of phytolith assemblages (4–6). Zevallos and colleagues were the first to suggest that maize was part of the agricultural base of Early Formative sites in southwestern Ecuador (7, 8). Their discovery of a carbonized maize kernel embedded in a ceramic sherd, modeled adornos of possible maize cobs decorating Early Formative ceramic vessels, and apparent punctate impressions of maize kernels on the same pottery convinced many scholars that maize was a staple food of the Valdivia culture of Ecuador. Others, however, doubted the evidence and argued that the earliest certain evidence of maize in Ecuador dated to the Middle Formative—no earlier than ≈3700 cal B.P.‖ (9). Later work by Pearsall at Real Alto (OGCH-12) (Fig. 1), an Early Formative village site in southwestern Ecuador, resulted in the recovery of maize phytoliths from the Early Formative component and dated by associated charcoal to 4740–4300 cal B.P. (10). Further phytolith work at the preceramic Las Vegas site (OGSE-80), including determining radiocarbon ages on phytolith assemblages that incorporated maize leaf phytoliths identified by Piperno, indicates that maize was being cultivated in Ecuador during the Archaic by ≈7500 cal B.P. (4, 6). Despite this, others have concluded from their research that maize was not introduced into coastal Ecuador until ≈4150–3850 cal B.P., was used first and foremost in ceremonial contexts as a fermented beverage, and was not important in everyday subsistence (11, 12). Further, some question the dependability of associated dates for documenting the presence of maize and the timing of its dispersal from Mexico (13); thus, our results are pertinent to this debate as well.

Our research focused on the analysis of every-day cooking vessels and grinding stones for starch granules (Fig. 2) and phytoliths to assess whether maize was present in domestic contexts and to reaffirm that maize was a dietary component in the Early Formative. In particular, new recovery methods have resulted in the isolation of starch granules from charred residues adhering to the interior surfaces of ceramic cooking-pot sherds, which have allowed us to directly date the context from which the maize starch was recovered and to confirm the presence of maize in the earliest ceramic context from Ecuador. The cooking pots and grinding stones are from the beginning of the Early Formative Valdivia culture and were recovered during excavations by Raymond at the site of Loma Alta (OGSEMa-182), situated in the Valdivia Valley of southwestern Ecuador.

Loma Alta

Possibly occupied as early as ≈6450 cal B.P. (14), by using the two-sigma range of the oldest charcoal radiocarbon dates, Loma Alta is one of the earliest village sites recorded in Ecuador. The principal occupation occurred during the first two phases of the eight-phase Valdivia ceramic sequence. The size, permanence, deep midden deposits (>1.5 m), and location of the village adjacent to prime agricultural land 12 km inland from the sea suggest an agriculturally based economy (15). Grinding stones and abundant ceramics related with the early occupations are

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‖All dates given as calendar years (cal B.P.) before present.

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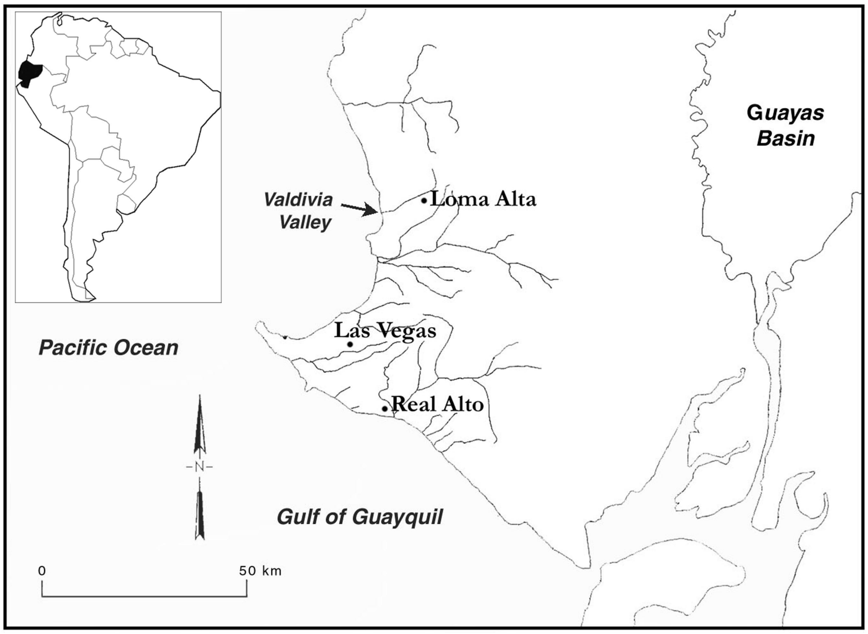

Fig. 1. Map of southwestern coastal Ecuador showing the location of sites mentioned in the text. Loma Alta and Real Alto are ceramic-bearing Formative Period Valdivia sites, whereas the Las Vegas site is preceramic.

indicative of the processing, detoxifying, cooking/fermentation, and serving of plant foods. Like most sites in the tropical Americas, however, the preservation of macrobotanical remains was poor and was limited to a few charred bits (16). In the Early Valdivia occupation there was almost no evidence for intrusion of ceramics from the later occupation. An accelerator mass spectrometry (AMS) date on rare carbonized maize kernels from the lower levels, though, was far too young (2730–2350 cal B.P. at two-sigmas; Beta-103315**) to be associated with the early occupation and demonstrated that there was some mixture of small remains between the occupation layers of the site. Thus, analysis of datable residues from ceramic vessels and residues from large grinding stones, unlikely to move about in sediments, from the earliest levels offered the best opportunity for chronologically accurate results.

Eight sherds of ceramic cooking vessels, eight grinding stones, and seven sediment samples, associated with the ceramic sherds, were selected for analysis. The sherds were correlated with the initial occupation at Loma Alta and were recovered from sediments overlying an Early Valdivia living floor. Because the sherds derive from the bases of their respective vessels, they lack diagnostic decoration [see supporting information (SI) *Materials and Methods* and Fig. S1*A*]. However, in their thickness and fabric they are consistent with Early Validivia cooking vessels, and all stylistically diagnostic sherds from the same contexts were Early Valdivia in style. Five grinding stones (FS 153, 380, 1056, 1051, and 1064), including three from which maize starch was recovered, are also associated with Early Valdivia ceramics. Another grinding stone that produced maize residues (FS 689) is probably Early Valdivia. The remaining two grinding stones (FS 705 and 799) are affiliated with the later site occupation.

Starch Analysis

For almost 150 years it has been recognized that starch granules of different botanical sources can be identified by microscopic examination of their morphological characteristics (18–20). Starch residues, extracted from stone tools and in soils and sediments, have been used to identify and provide evidence for the presence, use, and processing of plant foods in the past (see ref. 21 for a recent review). Limited research, however, has been conducted to recover and identify starch from charred food residues on ceramic vessels (22–25) because of the tendency for starch to gelatinize and paste, whereby the molecular structure within the granule is disrupted and ultimately destroyed when exposed to heating in excess water (26). Our results demonstrate that identifiable starch granules can be extracted from charred cooking residues by employing a new technique that gently oxidizes the charred matrix and isolates starch granules by heavy-density liquid separation.

The interior charred residues (see *SI Materials and Methods* and Fig. S1*B*) from eight cooking-pot sherds were processed for starch recovery (see *SI Materials and Methods* and Table S1). All contained starch granules (Table 1) that were well preserved (Fig. 2 *A* and *B*) allowing taxonomic identification. Of the 116 starch granules recovered, the majority were identified as maize (n = 73), with 85% of those being hard endosperm maize, such as flint or pop, and 15% soft endosperm (flour) maize. Some of the ceramic residue maize starches showed damage consistent with milling, as characterized by replicate studies (27–29). Importantly present as well were almost fully gelatinized starches exhibiting swelling and partial loss of birefringence, and numerous starch aggregates (Table 1, Fig. 2*C*), all of which indicate that starch was extensively heated in water (20, 30) as in the cooking of a soup or stew. Sediment samples from the matrix of seven of the eight pottery samples were also processed for starch recovery; four resulted in the recovery of maize starch (Table 1, Fig. 2*D*). Although some maize starch granules recovered from the sediment samples had milling damage, no partially gelatinized starches or starch aggregates were observed. These findings support the argument that the maize starches recovered from the directly sampled charred sherd residues are indeed from the cooking residues and not from sediment transference.

Eight grinding stones were processed for starch residue recovery, four of which were productive for maize starch (Table 1, Fig. 2*E*). The assemblage of 30 maize granules recovered allowed for a high degree of certainty in species identification

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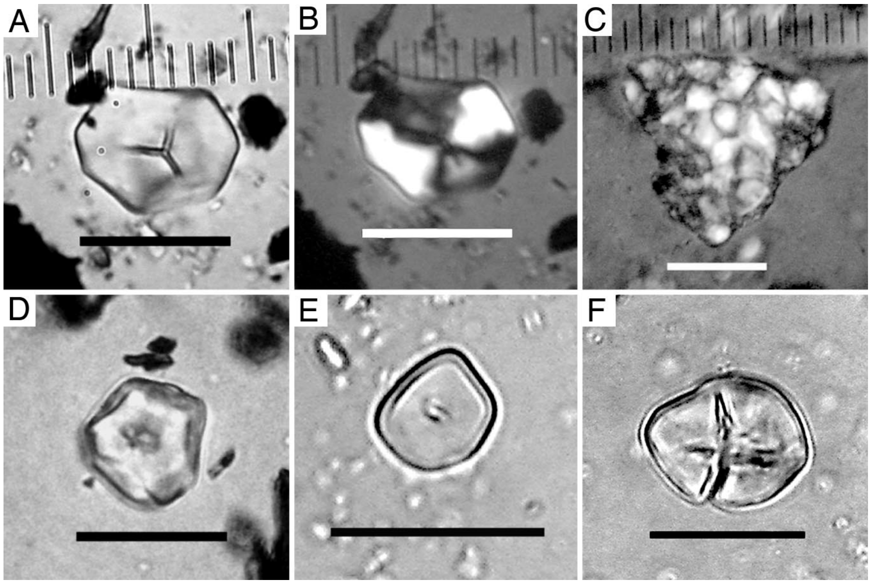

Fig. 2. Selected starch granules recovered from Loma Alta. (*A* and *B*) Maize starch granule recovered from charred interior residues of pottery (FS1016, sample 13) under polarized A and cross-polarized B light showing strong birefringence and excellent preservation. (*C*) Starch aggregate from FS1063, sample 10, of many starch granules fused together by cooked, gelatinized starch. (*D*) Maize starch granules from the sediment sample FS1063, sample 156, with damage to the hilum area from milling. (*E*) Example of undamaged maize starch granule from grinding stone tool residues. Approximately 50% of the maize starch granules from the grinding stone tool residues did not exhibit milling damage, allowing for secure identification. (*F*) Grinding stone tool residue SS-292 with enlarged fissures radiating from the hilum, indicating that maize was processed by milling. (Scale bar, 20 μm.)

and characterization of the maize variety, as was the case for the ceramic residue starches. Twenty-one (60%) of the starch granules were consistent with a soft endosperm maize variety, whereas nine (40%) were characteristic of a hard endosperm variety. Thus, the cooking-pot residues and grinding stone tool residues both indicate that both hard and soft endosperm varieties of maize were grown at Loma Alta, similar to the maize starch results from Real Alto (31). Damage from grinding on ≈50% of the maize starch recovered (Fig. 2*F*) supports the inference that the association of the starch with the tools was the result of food processing. The maize starch granules present in the site sediments likely derived from such food processing activities.

Three separate cooking-pot residues were dated directly by accelerator mass spectrometry (AMS) radiocarbon measurement (see *SI Materials and Methods*, Table 1, and Table S2), yielding a tight association of dates. Dates from charcoal associated with the other sherds and with grinding stones (Table 1) show a compact clustering of dates in concert with the AMS-dated pottery residues.

Table 1. Starch granules, source, and radiocarbon dates from Loma Alta, Ecuador

Sample	Source	*Canavalia* spp., *n*	*Capsicum* spp., *n*	*Manihot esculenta*, *n*	*Maranta arundinacea*, *n*	*Zea mays*, *n*	SA, *n*	Unidentified/ damaged, *n*	Date, cal B.P.	M	Lab no.
FS153, SS275	G					1			6250–5050	AC	SFU-123
FS153, SS275–2	G					7			6250–5050	AC	SFU-123
FS380, SS278–2	G					1			5950–5050	AC	SFU-110
FS689, SS281	G					2			5650–4850	AC	GX-7699
FS689, SS281–2	G					2			5650–4850	AC	GX-7699
FS1051, SS292	G					17			6050–4550	AC	GX-9460
FS1016, sample 13	C		2			10	1		5300–4960	CR	Beta-198623
FS1041, sample 6	C	1		2		3	1	1	5300–4960	CR	Beta-198621
FS860, sample 7	C	2	1			5		1	4410–4040	AC	Beta-9561
FS860, sample 37	S			1					4410–4040	AC	Beta-9561
FS884, sample 11C	C				1	4	1		6250–5050	AC	GX-9458
FS1056, sample 12	C				2	6	1	2	5310–4990	AC	Beta-9564
FS1056, sample 148	S		2			3			5310–4990	AC	Beta-9564
FS1052, sample 11	C	3	1		1	11	2		5290–4950	CR	Beta-198622
FS1052, sample 130	S					1			4860–4520	AC	Beta-9566
FS1063, sample 10	C		1			9	3		5310–4990	AC	Beta-9564
FS1063, sample 156	S	1	2			2			5310–4990	AC	Beta-9564
FS1050, sample 9	C	1	1	1		25	1	3	5310–4990	AC	Beta-9564
FS1050, sample 108	S	0	1			5		1	5310–4990	AC	Beta-9564

SA, starch aggregates; M, material dated; G, grinding stone tool; C, ceramic; S, sediment sample; AC, associated charcoal standard radiocarbon date, 2-sigma calibrated result; CR, AMS radiocarbon date on charred ceramic residue (Interior), 2-sigma calibrated result.

Phytolith Analysis

The interior charred residues from seven cooking-pot sherds and the grinding stone residues were processed for phytolith recovery (see *SI Materials and Methods* and Table S3). Maize wavy top and ruffle top rondel phytoliths were recovered from four grinding stones (Table S3), for a total of six of eight grinding stones with phytolith and/or starch evidence for maize. Only one to three maize rondels occurred per tool ($n = 8$), which is lower overall than the numbers of starch grains recovered (1–17 per tool; $n = 30$). Phytoliths recovered from the grinding stone tool residues also present a more diverse variety of taxa, including *Cucurbita* spp., *Calathea* spp. (llerén), Zingiberales, Fabaceae (*Phaseolus* spp.), and Marantaceae/Zingiberales/Bombacaceae nodular spheres. In addition, Fabaceae fibrous mesh phytoliths and root and fruit transport tissue phytoliths were also identified. Ceramic residues, by contrast, contained no *diagnostic* maize wavy top or ruffle top rondels, whereas maize starch was present in all (total count: 70 maize granules in 7 ceramics examined for both starch and phytoliths). Rondels and complex short cells that are predominantly rondel-based are present in all Loma Alta samples, and moderate to common in most ceramic residues (Table S3). Although we cannot state that this pattern of phytolith occurrence identifies maize in the ceramic residues, it is certainly consistent with maize cob residue, which consists predominantly of rondels (32). Other economic plant taxa phytoliths in the cooking-pot residues include Aracaceae (Palm family) and nodular spheres consistent with Marantaceae/Zingiberales/Bombacaceae and an arrowroot (*Maranta* spp.) seed epidermis phytolith from residue FS1052, from which *Maranta arundinacea* starch was also recovered.

Discussion

The recovery of maize starch directly from the charred residues of each utilitarian cooking vessel and four grinding stones tested indicates a common, domestic use of maize by at least 5300–4960 cal B.P. at Loma Alta, and conceivably earlier. Direct dating of cooking-pot residues is equivalent to the direct dating of macroremains (13, 33), and thus provides a firm chronology for the presence and consumption of foodstuffs identified in the residues, including the maize remains. The dates reported in Table 1 for the grinding stone tools are based on charcoal found in the same 10-cm arbitrary level as the artifacts. Thus, although maize is securely present at Loma Alta by 5300 cal B.P. based on direct dates (see *SI Materials and Methods* regarding a possible freshwater reservoir effect on charred-residue AMS dates), maize may well be present as early as 6250 cal B.P.

Importantly, although we do not deny that maize played a significant role in Andean ceremonial life, our results show that it was indeed consumed as food as part of a diverse subsistence system. Our results indicate that a greater percentage of hard endosperm versus soft endosperm maize was cooked in the pots analyzed from Loma Alta. The higher percentage of soft endosperm maize present on the grinding stones may indicate extensive milling of soft endosperm maize to produce flour, resulting in a higher recovery rate from those artifacts. Other starches identified in the ceramic residues show that maize was one of a complex of crops exploited. Domesticated plants identified (Table 1) by starch included manioc (*Manihot esculenta*), arrowroot (*M. arundinacea*), chili peppers (*Capsicum* spp.) (34), and *Canavalia* spp. These data are supported by previous *in situ* and flotation analysis of Early Valdivia sediments from Loma Alta where maize and arrowroot phytoliths and jack bean (*Canavalia* spp.) cotyledon fragments were recovered (16).

Results of the phytolith analyses from the cooking-pot sherd and grinding stone residues also attest to the diversity of plants used, and support the starch analysis results in the case of arrowroot and maize. Although diagnostic maize phytoliths are not well represented in the cooking pots or grinding stones tested, our approach to identifying maize phytoliths is highly conservative and relies on a small number of diagnostic forms that have been tested against wild grasses from the lowland tropics (31). This difference in microfossil abundance between maize phytoliths and starch is similar to that observed on grinding stones from Real Alto (31), and may be caused, in part, by differences in how microfossils are deposited on this type of tool (i.e., starch is ground into surfaces directly, phytoliths must be released by decay). Although precise diagnostic maize phytoliths were absent from the cooking-pot residues, maize is likely represented by other rondel forms.

Stable isotope measurements of human skeletal remains from Loma Alta, although inconclusive because of poor preservation, also indicate a broad-based diet with a slight inclusion of maize (15, 35). The $\delta^{13}C$ measurements from the AMS-dated ceramic residue samples show values of −24.8, −24.9, and −25.0‰ (see Table S2) indicating that, although a variety of C3 and C4 foods contributed to the residue $\delta^{13}C$ signatures, maize may have represented 10–20% of the overall dry volume of foods cooked in the pots (36). More recent research into the interpretation of stable carbon analysis of cooking residues indicates that systematic underrepresentation of maize will result from not knowing the C3 and animal content of the residues, making any interpretation difficult without comparison to experimental cooking residues (37). The stable isotope ratios are a reflection of all foods that were cooked in the pots throughout their use-life (38), including C3 plants such as beans, arrowroot and manioc and animal protein sources that were not reliant on C4 grasses, with this then masking the maize signature.

This picture of a diverse Valdivia subsistence base is mirrored at the Real Alto site, where maize was ubiquitous in domestic contexts by 4750–4300 cal B.P. in association with roots and tubers, legumes, and fruits (10, 16, 28, 34). Maize was introduced to Ecuadorian coastal populations already familiar with plant cultivation. At the preceramic Vegas site (OGSE-80), phytolith assemblages, which included bottle gourd (*Lagenaria* spp.), the root crop llerén (*Calathea* spp.), and domesticated-size squash phytoliths, were directly dated to 11,210–9,900 cal B.P. (4, 6), with maize present in directly dated phytolith assemblages to ≈7500 cal B.P. (4–6).

Because of the paucity of research on starch granules from charred pottery residues, the possible mechanisms of starch preservation have not previously been addressed. As noted earlier, changes observed on some starch granules in the cooking-pot residues, such as granular swelling, partial loss of the extinction cross, and starch aggregates are all associated with boiling starch in water, as opposed to dry-heat cooking, which results in dextrinization (39). Because most starches are completely gelatinized over a temperature range below the boiling point of water, it is apparent that food processing and cooking techniques, and the physiochemical properties of starches from different botanical sources, are all potential factors involved in starch survival. These factors likely bias the number and types of starches recovered and thus future research should focus on experimental cooking studies (28) to assist in interpretation and quantification of both starch granule and stable isotope analyses. For example, and with respect to the maize starches (soft versus hard endosperm) recovered from the cooking-pot residues, if ground soft endosperm (flour) maize and hard endosperm (flint/pop) kernel maize were both cooked in the pots, the indurate aleurone of the flint/pop maize kernels may have provided protection to the endosperm starch, delaying or eschewing gelatinization of flint/pop maize starches resulting in a higher recovery rate from the pot residues compared with flour maize.

Food processing and cooking techniques can modify starch granules, augmenting granule stability and increasing gelatinization temperatures, resulting in the preferential survival of starches (26). One such method of modifying starch granules to increase the gelatinization temperature is annealing, whereby starch is cooked at low water contents and low heat (below gelatinization temperature), resulting in increased gelatinization temperatures, decreased granular swelling, and restricted leaching (40). A similar method would be heat-moisture treatment, which is used to describe low-water, high-heat treatment (40). Alkali cooking techniques [the addition of lime (calcium hydroxide) $Ca(OH)_2$, lye (sodium hydroxide) NaOH, or wood ash (potassium hydroxide) KOH] will also increase the temperature at which starches gelatinize, as does the addition of salts and/or sugars to the water (41–43). The identification of jack bean cotyledon fragments and starch granules consistent with *Canavalia* spp. at Loma Alta demonstrates that saline cooking techniques were used at Loma Alta. To detoxify *Canavalia* spp. seeds, which contain the toxic lectin concanavalin A, jack beans must be cooked in a saline solution (44). The use of a saline cooking technique may also explain the low frequency of root and tuber starches in the charred cooking-pot residues compared with maize, jack beans, and chili pepper starches (Table 1). If root crops, such as arrowroot and manioc, were not cooked with maize, beans, and chili peppers in a saline solution then the starch granules of these species are more likely to be gelatinized and not preserved in the pottery residues. There are dietary reasons why maize, beans, and chili peppers would be cooked together. Whereas maize is deficient in the essential amino acids lysine and tryptophan, and in niacin, legumes contain these essential dietary components and the consumption of maize and beans together complement each other and are nutritionally complete; chili peppers are high in vitamin C, which increases the absorption of iron (44, 45).

Loma Alta and the Antiquity of Maize in Northwestern South America

Questions regarding the subsistence base have occupied the attention of investigators since the discovery of early village sites in southwestern Ecuador >40 years ago. Although high levels of agricultural productivity eventually emerged in Mesoamerica and the Central Andes, the two areas of the Americas where civilizations developed, social and economic complexity in the form of settled village life and sophisticated food production began much earlier in coastal Ecuador from the outset of the Valdivia Period. As noted earlier, the AMS dates obtained from the charred cooking-pot residues overlap with and support the charcoal dates associated with the grinding stone tools from Loma Alta. Our results confirm previous research demonstrating that when the people of southwestern Ecuador made the transition to settled village life, maize was an established part of a well developed, diverse agricultural base. Moreover, the identification of starch from both flint/pop and flour races indicates that more than one maize variety was being cultivated, with this then suggesting that maize played a complex role in the overall broad-based cuisine of the Valdivia people. Our results also show that sophisticated food processing techniques were used at Loma Alta to detoxify an otherwise inedible plant food—jack beans—possibly accounting for the high relative frequency of maize, jack bean, and chili pepper starches in the cooking-pot residues. Forthcoming research here, as in other regions, should include experimental cooking studies to clarify issues of differential starch and phytolith preservation and to better interpret stable isotope measurements of food residues. These findings should erase any doubt that maize was cultivated, processed, and consumed in domestic contexts throughout the Ecuadorian Formative. By firmly establishing that maize was part of a well developed agricultural base and that sophisticated food processing techniques were being used by at least 5,300 calendar years ago, we contend that maize would have been introduced to Ecuador earlier than the Formative Period. Thus, our data also support previous research indicating that maize was present in southwestern Ecuadorian mobile hunter-gatherers/cultivators much earlier (4–6). Indeed, there is now a convincing body of evidence demonstrating the early mid-Holocene dispersal of maize from west Mexico (see ref. 46 for a recent review of this debate).

The recovery of maize starch granules from charred residues on pottery, grinding stone residues, and sediments provides key evidence of early agriculture in northwestern South America, a region where information from macrobotanical and human remains is lacking because of poor preservation. Most importantly, the ability to obtain AMS dates directly from the charred cooking-pot residues that contained maize starch was crucial to our ability to confirm the cultivation and consumption of maize in the ancient villages of southwestern Ecuador. In regions where pottery was used, it is often the most abundant artifact class recovered because of its resistance to depositional destruction. Our results demonstrate that it is possible to recover, identify, and directly date starchy foods from charred pottery residues. Throughout the world where pottery is present, this technique then has critical potential for future archaeological research to expand our knowledge about past human–plant interactions.

Materials and Methods

Eight sherds of ceramic cooking vessels, eight grinding stones, and seven sediment samples were selected for analysis. Charred residues were removed from the interior surfaces of the sherds with a sterilized dental pick, pretreated with mild oxidation, and the starch isolated between 1.3 and 1.7 specific gravity (sg) by heavy-density liquid separation. The >1.7 sg fraction was then processed for phytolith recovery that used stronger oxidation pretreatment followed by heavy-density liquid separation. Stone tool residues were removed with dry brush, wet brush, and sonication with each sample, then processed for combined starch and phytolith recovery. Sediment samples were processed for starch recovery only. For more details, including the full procedure for recovering starch from charred ceramic residues, see *SI Materials and Methods*.

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