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Diagenesis in freshwater mussel shell and its implications for provenance determination – Evidence from the Kinlock Site, 22SU526 (Yazoo Basin, Mississippi, U.S.A.)

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ABSTRACT

Freshwater shells from archaeological contexts hold the potential to allow sourcing of shell-tempered ceramics on the basis of their chemical composition. This application, however, requires understanding chemical interaction of shell with the burial environment. Here, we use material recovered at Kinlock (22SU526), a Late Woodland - to Mississippian-period site located in the Yazoo Basin, Mississippi, U.S.A. as a case study to evaluate the presence and impact of diagenesis on Unionid shells. Twenty whole shells recovered from the plow zone and the sub-plow zone are analyzed using a combination of thin sections, Scanning Electron Microscopy, and Inductively Coupled Plasma-Mass Spectrometry. Results show that, contrary to what might be expected, shells from the sub-plow zone are more affected by diagenesis than samples from the plow zone. The chemistry of the shells from the sub-plow zone is affected by modern human contaminants (fertilizers) within a perched water table, and is no longer representative of the original composition of these samples, compromising their use in provenance research. Shells from within the plow zone are less affected by contamination, making them potentially more useful to generate background data for provenance studies.

1. Introduction

Shell-bearing sites, including freshwater mussel (Unionidae, Margaritiferidae) shell middens, have received a great deal of attention in recent years, being the focus of research on paleoenvironments, biogeography, seasonality, economics, settlement patterns, social stratification, ceremonialism, and more (e.g., Bērziņš et al. 2014; Claassen 2010; Collins et al. 2020; Johnson and Plew 2016; Mitchell and Childress 2021; Peacock and Jenkins 2010; Peacock et al. 2011; Theler and Hill 2019). A relatively new pursuit, but one with great promise, is sourcing of freshwater shell artifacts and shell-tempered ceramics via the chemical composition of the shell. The premise is that freshwater mussels, being essentially sessile filter feeders, build local water chemistry signatures into their shells; if those signatures (elemental and/or isotopic) remain stable over time, then shell can be used as a sourcing agent.

Freshwater mussel shell is an “exoskeleton” (Claassen 1998:16) secreted by the mantle and taking the form of aragonite (Checa 2000; Checa and Rodríguez-Navarro 2001; Compere and Bates 1973), a calcium carbonate polymorph metastable at Earth surface temperatures and pressures and susceptible to dissolution in geological settings (e.g., Chafetz et al. 2008; James et al. 2005; Wright and Cherns 2008). Freshwater mussel shell contains both inorganic and organic components. The latter are comprised of both soluble (organic protein or glycoprotein, a.k.a. conchiolin) and insoluble (hydrophobic protein) components that together make up ca. five percent of the shell by weight (Carroll et al. 2006; Petit et al. 1980; Wheeler 1992). Shells have three layers. Organic matter is most prominently represented by outermost layer, the periostracum, an external, proteinaceous “skin” that is uncommonly preserved on archaeological specimens. No periostracum was present on the Kinlock specimens analyzed. $CaCO_3$ crystal growth begins on the inner surface of the periostracum (Checa 2000; Checa and Rodríguez-Navarro 2001) and is expressed in two layers, the prismatic

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and the nacreous, both of which are comprised of nanometer-sized, organic membrane-coated granules or "spherules" of $CaCO_3$ (Checa 2000; Checa and Rodríguez-Navarro 2001; Jacob et al. 2009; Petit et al. 1980). The outer, prismatic layer accounts for ca. ten percent of total shell thickness (Checa and Rodríguez-Navarro 2001), with the bulk of the shell being comprised of the inner, nacreous layer. In the absence of periostracum, the prismatic and nacreous layers are represented in digested samples. The crystal structure of aragonite allows for inclusion of a variety of trace elements. Calcium, magnesium, and strontium have been the elements most widely used in paleoenvironmental reconstruction (Claassen 1998:138). A host of other trace elements is present, some of the most common being sodium, manganese, and barium; iron, copper, potassium, chromium, tin, zircon, aluminum, and other minor elements that are consistently detected (e.g., Carroll and Romanek 2008). In the study of the chemical composition of fresh water shells of the genus *Margaritifera* spp. from modern and uncontaminated sites across Eurasia the concentration in 45 trace elements was measured in addition to Ca and Na (Bolotov et al. 2015).

General environmental characterization of modern (non-archaeological) shell using a variety of spectrographic methods has become common (e.g., Barats et al. 2009; Lazareth 2000; Lazareth et al. 2000, 2003; Lorrain et al. 2003; Vander Putten et al. 2000), with growing attention to the shells of freshwater mussels (e.g., Carroll and Romanek 2008; Geeza et al. 2019; Izumida et al. 2011). The uptake of chemicals by freshwater mussels mostly has been studied from the perspective of pollution monitoring (e.g., Das and Jana 2003; Jacomini et al. 2003; Markich et al. 2002; O'Neil and Gillikin 2014; Wilson et al. 2018). In such studies, elements typically recorded include manganese, magnesium, calcium, strontium, and barium. Significant differences in trace elements between study sites (e.g., Lazareth et al. 2003) imply utility for archaeological applications. As of yet, chemical study of archaeological specimens remains limited. In a study using LA-ICP-MS (laser ablation – inductively coupled plasma – mass spectrometry), Carroll (2006:395) notes an increase in manganese in post-mortem mussel shells over time, but also notes that the effect is most pronounced on shell exteriors and concludes that trace elements retained in shells could be used to help reconstruct continental paleoenvironments. Carroll et al. (2008) compared ca. 2,000 year-old midden specimens from South Carolina with modern mussel shells via LA-ICP-MS and found similar concentrations of manganese, strontium, barium, and copper. Boulanger and Glascock (2015), Peacock (2017), Peacock et al. (2010), and Peacock et al. (2012) report chemical groups in archaeological Unionid shells related to drainage. These preliminary studies suggest that the "provenience postulate" applies, at least where the shells themselves are concerned. Testing of shell temper also has produced distinct chemical groups for ceramics (Peacock et al. 2007). Importantly, neither burning nor metabolic differences related to species appear to be significant sources of variation in Unionid shell trace element content (Boulanger and Glascock 2015; Cogswell et al. 1998; Collins 2012), although the proportions of some elements obviously can be altered by leaching or burning of shell (e.g., relative elevation of Ca as carbon burns out - Claassen 1998).

The promise of using freshwater shell chemistry for sourcing shell artifacts and, in particular, shell temper in ceramics, is clear, and the authors currently are engaged in analyzing shells and shell temper from numerous sites in two major river basins in eastern North America. However, as it is with any chemical sourcing method, diagenesis is a potential issue that has to be examined. In general, shell preservation varies greatly depending on soil pH, soil mechanical action, and other factors. Post-depositional chemical alteration due to burial environment may or may not be signaled via physical changes (e.g., the conversion from aragonite to calcite, or the development of "cement" between aragonite crystals – Morrill and Koch 2002; O'Conner et al. 2014; Webb et al. 2007) observable via SEM (scanning electron microscope) or other methods. Physical alteration of shell has been noted via SEM in one instance, a ca. 5,000-year-old assemblage from the Tombigbee River in eastern Mississippi (Peacock et al. 2020) that also shows significant chemical differences with shells from a ca. 1,200-year-old stratum at the same site (Peacock and Seltzer 2008). Whether those chemical differences are attributable to diagenesis or changed river conditions is under investigation (Peacock et al. 2020), but the larger point is that studies are needed to evaluate the extent to which diagenesis is a factor to be considered in shell sourcing research in different environmental settings.

The objectives of this manuscript are: 1) to provide the results of a case study designed to evaluate the physical and chemical alteration of freshwater shells related to burial environment; and 2) to determine the extent to which the samples can be used to establish a local signature for future provenance studies. For this purpose, samples were selected from two layers of a prehistoric site in the Yazoo Basin of Mississippi (southeast US).

2. Site and material

The samples selected here are from the Kinlock site (22SU526), a Late Woodland - to Mississippian-period shell midden located on the Sunflower River in the Yazoo Basin of Mississippi (Fig. 1). Shell middens are common in the basin, including many "shell rings", a general term referring to middens taking roughly circular to arcuate forms with an interior "plaza" relatively free of artifacts (Carlock 2015; Peacock et al. 2011; Phillips 1970). Kinlock is one such shell ring. Shell middens in general, and especially the ring forms, appear mostly to date to the Late Woodland-period Deasonville phase (400–600 CE) in the basin (Buchner 2015; Peacock and Jenkins 2010; Peacock et al. 2011; Phillips 1970). There is no evidence to suggest that shell was intentionally used as a building material at the Yazoo Basin middens; rather, it was simply one constituent of general refuse deposits rich with ceramic sherds, stone tool debris, animal bones, etc. (Carlock 2015; Gilleland 2016; Raymond 2016). That domiciles existed on top of the middens is evidenced by

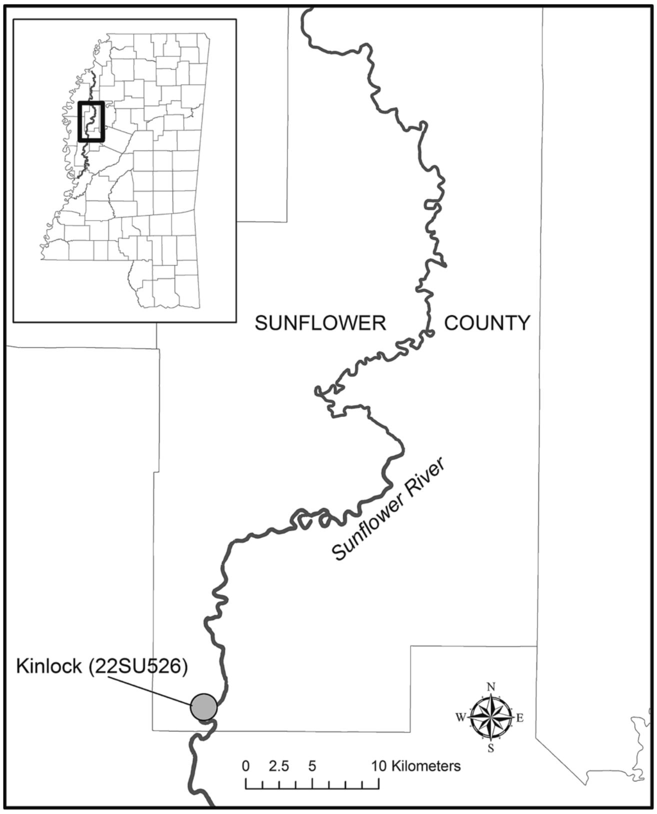

Fig. 1. Location of the Kinlock site (22SU526), Sunflower County, Mississippi (from Mitchell and Peacock (2014), used with permission).

postholes penetrating into the sterile subsoil that contains shell (Buchner 2015; Carlock 2015; Raymond 2016).

Field work conducted at Kinlock by Carlock (2015) included controlled surface collection in 2 × 2 m units over a large area of the site and excavation of two 1 × 1 m units and one 0.50 × 0.50 m unit. One 1 × 1 m unit and the 0.50 × 0.50 m unit were placed on the ring midden. Materials discussed here were obtained from quarter-inch mesh following water screening. Units were excavated by natural levels with arbitrary subdivisions of 10 cm or less within levels. Excavations in each unit reached sterile subsoil. The ring midden is a Deasonville-phase deposit, as indicated by the predominance (70 percent) of grog-tempered ceramics (Carlock 2015: Table 8.2) and a radiocarbon date of 1230 ± 30 BP (two-sigma calibrated intercepts of AD 715–745 and AD 765–890) (Carlock 2015). Stratigraphy at the site is simple, with the shell midden overlying a stiff clay subsoil (Fig. 2). A ca. 20-cm thick plow zone is marked by fragmented shells, with an abrupt transition to ca. 20 cm of undisturbed deposits marked by large numbers of whole mussel valves, large sherds, animal bones, and other artifacts. The midden matrix is silty clay, as is the subsoil, although it has a much higher clay content with no visible organic matter.

Over 47,000 mussel valves from Kinlock have been analyzed from both plow zone and sub-plow zone contexts, with 33 species being identified (Mitchell and Peacock 2014; Mitchell et al. 2016). Preservation varies between the two contexts, with ca. 30 percent of the plow zone shells (valves retaining the umbo) being unidentifiable to species as compared to ca. 15 percent of the sub-plow zone shells (Mitchell et al. 2016). Differential preservation is reflected in taxonomic richness, with eight breakage-prone species being identified only in the sub-plow zone assemblage (Mitchell et al. 2016). Most shells are broken along the posterior-ventral margin, a pattern interpreted to represent breakage for meat extraction. Very few shells are burned, further indicating that in-the-shell food preparation (steaming, baking, roasting) does not seem to have been practiced.

For this study, ten shells from the plow zone and ten from the sub-plow zone were selected from among the species most commonly found at the site. Five species per stratum and two specimens per species were selected. To avoid sampling the same individual twice, only left or right valves of any particular species were used. The following species were sampled: *Plectomerus dombeyanus*, *Pleurobema rubrum*, *Amblema plicata*, *Reginaia ebenus*, and *Cyclonaias pustulosa* (Table 1).

3. Methods

Valves were cut in half using a diamond saw, rinsed with deionized water, and air dried. One half was used for thin-sectioning and SEM, with valve remnants being archived, while the other half was used for chemical analyses.

3.1. Thin sections

For petrographic analysis, a strip of the whole shell was cut from umbo to posterior margin using a fine blade wet-saw to fit a 27 × 46 mm glass slide. The strips were shipped to Spectrum Petrographics for impregnation with standard blue-dyed Epoxy, thin sectioning, and surface polishing. Thin sections were analyzed and photographed using an Olympus BS50 Petrographic microscope.

3.2. Scanning electron microscope

Scanning electron microscopy (SEM) imaging and analysis were carried out primarily using a JEOL JSM-6500F Field Emission Scanning Electron Microscope; some images were taken on a ZEISS EVO-50 Variable Pressure SEM. Samples were broken by hand from an accessible portion of the outer edge of shells and were attached to the stub using a hot-glue gun, with the freshly broken surface facing upward for imaging. For many of the samples, all but the surface to be imaged was covered in carbon-based paint to minimize charging and reduce drift (static) from the instrument. A target magnification of 20,000 X reveals the nanometer scale microstructure of the shell and was the most useful level of magnification to pinpoint visual diagenetic alteration. Because many of the shells were prone to charging, images ranging between 5,000—30,000 X magnification were used for assessment of diagenetic alteration. Images were taken in the same part of the shell structure where parallel layers were clearly visible.

3.3. Elemental chemistry

The surface of the half valve was mechanically cleaned using a micro drill equipped with a silicon carbide bit to remove any trace of sediment/material attached to the shell. The half valve was then rinsed with mQ water, air dried, and powdered using an agate mortar and pestle. The powders were dried at 105 °C for 24 h and an aliquote of about 250 mg was digested in PFA Savillex® vials using 4 ml of 14 N Optima grade HNO_3. The closed vials were place on a hot plate and gradually heated up to 120 °C. Solutions were then prepared for analyses by ICP-MS and brought up to 3 % HNO_3 with addition of internal standard of Sc, In, and Tl. The instrument used for analyses is a PerkinElmer NexION 300 X operated in KED (kinetic energy discrimination) mode. The instrument

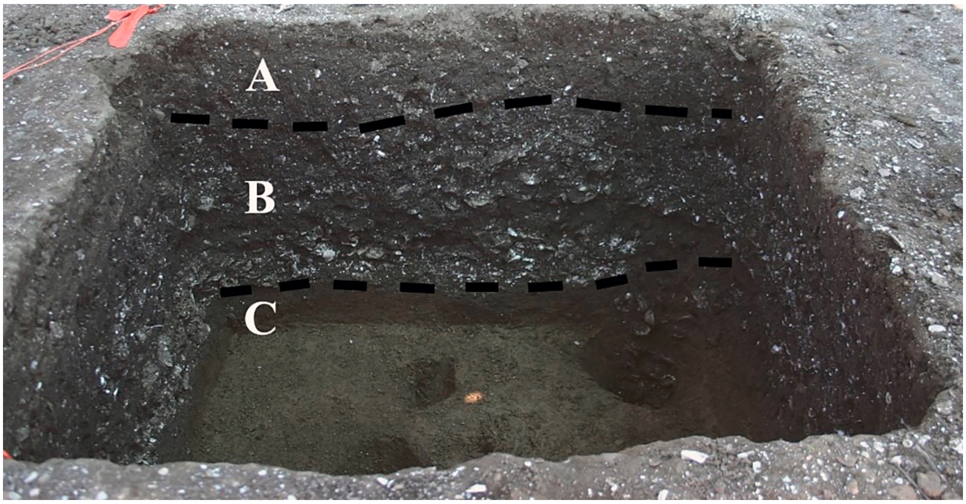

Fig. 2. North profile of 1-x-1-m unit 14S26W, Kinlock site. Adapted from Carlock (2015: Figs. 8.13 and 8.14). A – plow zone; B – undisturbed shell midden (sub-plow zone); C – subsoil.

Table 1
Sample ID, context (pz for plow zone and spz for sub-plow zone), shell species, valve orientation (R for right and L for left), and elemental concentrations (LOD for limit of detection, * for duplicate).

Sample ID	Context	Species	Valve	Li	Na	Mg	Al	P	K	Ca	Ti	V	Cr	Mn	Fe
				ppm	%	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm
LOD				0.005	0.001	0.048	0.150	9.80	3.70	0.024	0.023	0.002	0.007	0.250	0.190
EPS001	pz	*Plectomerus dombeyanus*	R	0.119	0.202	17.6	1.54	148	18.7	38.8	0.307	0.113	0.427	162	2.68
EPS002	pz	*Plectomerus dombeyanus*	R	0.096	0.203	14.7	11.7	160	29.7	38.7	0.513	0.112	0.357	326	7.55
EPS003	pz	*Pleurobema rubrum*	R	0.116	0.197	18.0	0.970	120	25.5	38.9	0.319	0.047	0.124	354	2.25
EPS004	pz	*Pleurobema rubrum*	R	0.113	0.186	24.0	1.34	125	31.0	38.2	0.327	0.056	0.117	422	3.88
EPS005	pz	*Amblema plicata*	L	0.093	0.208	13.7	0.930	131	26.1	38.9	0.320	0.075	0.204	237	3.96
EPS006	pz	*Amblema plicata*	L	0.096	0.202	9.85	3.13	187	17.7	38.7	0.450	0.098	0.361	324	5.63
EPS007	pz	*Reginaia ebenus*	R	0.148	0.192	20.1	1.19	122	15.5	38.5	0.311	0.046	0.083	636	1.31
EPS008	pz	*Reginaia ebenus*	R	0.130	0.193	16.4	1.00	154	14.8	39.6	0.313	0.048	0.185	730	4.21
EPS009	pz	*Clyclonaias pustulosa*	L	0.102	0.198	11.7	1.07	135	19.1	39.4	0.259	0.066	0.329	343	1.95
EPS010	pz	*Cyclonaias pustulosa*	L	0.125	0.209	13.8	0.670	95.4	22.9	39.4	0.316	0.051	0.094	231	1.11
EPS031	spz	*Plectomerus dombeyanus*	R	0.081	0.193	12.3	1.99	488	12.1	39.2	0.497	0.087	0.068	359	4.67
EPS032	spz	*Plectomerus dombeyanus*	R	0.082	0.200	10.7	2.45	600	10.3	39.0	0.525	0.099	0.112	256	6.52
EPS033	spz	*Amblema plicata*	L	0.084	0.201	15.7	2.39	893	11.5	39.1	0.688	0.158	0.118	350	13.9
EPS034	spz	*Amblema plicata*	L	0.107	0.193	18.2	1.45	414	10.1	39.6	0.455	0.078	0.060	442	7.48
EPS035	spz	*Pleurobema rubrum*	R	0.107	0.196	15.5	2.13	826	13.0	38.7	0.571	0.117	0.095	526	3.17
EPS036	spz	*Pleurobema rubrum*	R	0.115	0.206	15.8	2.48	384	14.0	39.7	0.526	0.127	0.091	536	4.16
EPS037	spz	*Cyclonaias pustulosa*	L	0.121	0.202	18.6	2.55	1450	13.1	38.8	0.709	0.194	0.143	485	4.44
EPS038	spz	*Cyclonaias pustulosa*	L	0.125	0.205	15.4	3.46	975	13.4	38.7	0.580	0.142	0.112	290	2.46
EPS039	spz	*Reginaia ebenus*	L	0.102	0.202	16.4	2.84	848	12.9	39.5	0.561	0.156	0.123	446	3.94
EPS040	spz	*Reginaia ebenus*	L	0.137	0.192	13.7	2.13	345	13.5	38.9	0.395	0.085	0.105	413	2.88
EPS001 *				0.100	0.201	17.1	1.40	157	20.4	38.9	0.277	0.115	0.424	154	2.80
EPS031 *				0.087	0.194	12.8	2.24	495	11.8	39.0	0.528	0.091	0.069	359	4.84
Bone Ash				0.715	0.651	6740	252	162,000	158	38.8	9.64	0.636	0.698	13.7	383
Bone Ash				0.731	0.646	6580	257	165,000	154	38.6	8.67	0.639	0.700	13.6	383

Sample ID	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb	Mo
	ppb	ppm	ppm	ppm	ppb	ppb	ppm	ppb	ppm	ppb	ppb	ppb	ppb
LOD	3.40	0.003	0.002	0.011	3.60	11.0	0.018	1.80	0.070	3.10	3.10	0.460	5.30
EPS001	3.80	0.105	0.211	1.33	8.00	15.0	0.093	7.50	294	3.30	<LOD	0.610	<LOD
EPS002	5.20	0.075	0.192	0.987	17.3	17.0	0.044	22.1	376	6.80	6.10	1.64	6.00
EPS003	<LOD	0.048	0.121	0.642	16.7	17.0	0.061	7.90	319	6.40	7.60	0.780	10.3
EPS004	8.50	0.114	0.186	0.972	17.3	14.0	0.038	10.7	319	8.50	30.9	1.25	10.5
EPS005	<LOD	0.063	0.125	0.642	13.7	21.0	0.189	7.90	297	4.30	5.40	0.690	7.30
EPS006	6.00	0.137	0.204	1.31	13.0	13.0	0.057	8.20	330	5.30	<LOD	0.940	10.6
EPS007	3.90	0.097	0.168	0.623	25.9	23.0	0.041	4.80	345	<LOD	<LOD	1.14	<LOD
EPS008	10.3	0.125	0.231	0.699	30.0	14.0	0.061	5.20	349	<LOD	52.3	1.20	<LOD
EPS009	4.70	0.093	0.150	0.869	14.5	18.0	0.439	5.60	308	4.90	<LOD	1.48	<LOD
EPS010	3.90	0.066	0.179	0.918	9.10	18.0	0.047	7.90	280	3.60	<LOD	0.620	<LOD
EPS031	13.6	0.356	0.375	2.49	18.2	19.0	1.60	4.50	293	22.7	17.5	1.94	10.6
EPS032	23.2	0.377	0.435	4.08	12.0	13.0	0.034	5.70	277	31.4	39.8	1.84	7.70
EPS033	32.6	0.623	0.446	4.59	15.9	17.0	0.059	5.00	274	28.5	31.8	2.71	17.2
EPS034	19.5	0.319	0.306	1.99	17.8	20.0	0.037	2.70	308	16.8	20.6	1.61	9.90
EPS035	15.3	0.447	0.386	4.26	20.7	15.0	0.123	2.40	295	12.1	6.00	2.59	17.7
EPS036	29.9	0.696	0.387	3.93	23.2	17.0	0.036	6.70	290	8.00	15.7	2.44	25.2
EPS037	20.3	0.700	0.571	6.51	25.9	16.0	0.047	6.20	271	17.2	8.90	2.68	20.7
EPS038	14.1	0.446	0.449	5.39	12.1	12.0	0.257	5.10	245	13.0	8.90	3.03	16.8
EPS039	18.9	0.729	0.551	4.90	21.0	15.0	0.123	5.60	251	5.80	5.80	2.63	25.0
EPS040	9.00	0.327	0.410	2.84	20.7	26.0	2.00	5.50	269	5.10	<LOD	0.620	12.7
EPS001 *	4.30	0.115	0.200	1.27	7.70	11.0	0.097	7.20	288	3.20	3.20	0.690	<LOD
EPS031 *	16.3	0.361	0.367	2.50	15.6	18.0	1.54	5.00	294	22.6	28.7	2.13	11.0
Bone Ash	89.2	3.53	2.38	129	173	85.0	0.431	456	238	239	684	45.2	243
Bone Ash	103	3.58	2.29	126	194	97.0	0.406	457	238	235	668	40.2	239

Sample ID	Ag	Cd	Sn	Sb	Ba	La	Ce	Pr	Nd	Eu	W	Pb	U
	ppb	ppb	ppb	ppb	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
LOD	1.40	7.30	3.50	2.60	0.150	0.840	1.40	0.340	2.80	0.760	4.10	0.860	0.300
EPS001	1.70	13.6	<LOD	2.70	118	3.26	3.60	0.810	<LOD	1.82	10.4	12.6	24.9
EPS002	2.20	<LOD	4.80	3.00	151	11.2	15.1	1.93	7.60	2.37	10.1	9.35	35.3
EPS003	1.70	14.7	<LOD	2.70	124	6.02	5.80	0.870	3.00	1.93	12.8	7.26	20.4
EPS004	2.60	21.1	3.50	2.60	121	8.16	9.20	1.05	3.30	2.47	20.5	38.2	25.8
EPS005	2.50	11.9	<LOD	<LOD	108	3.49	4.50	0.710	<LOD	1.78	11.0	5.48	28.6
EPS006	2.40	26.9	180	<LOD	157	7.36	6.90	1.2	3.40	3.06	13.5	7.27	49.4

(*continued on next page*)

Table 1 (*continued*)

EPS007	1.50	12.8	17.5	<LOD	159	2.00	<LOD	<LOD	<LOD	3.29	14.9	3.20	19.2
EPS008	<LOD	19.4	12.3	<LOD	180	1.68	<LOD	0.420	<LOD	2.75	11.0	1.81	36.2
EPS009	2.50	10.4	<LOD	<LOD	122	5.52	1.70	0.630	3.20	2.28	11.5	7.34	41.6
EPS010	2.60	10.2	52.0	3.90	102	5.32	2.00	<LOD	<LOD	2.02	13.5	680	36.1
EPS031	6.00	56.1	13.1	<LOD	115	49.9	17.1	6.40	22.8	4.27	16.8	16.1	31.2
EPS032	7.50	102	<LOD	3.40	107	26.6	12.3	4.12	20.3	2.78	14.1	25.4	50.5
EPS033	5.20	123	5.80	4.30	110	17.6	8.3	2.55	13.2	3.15	12.2	20.7	50.5
EPS034	2.40	57.1	13.9	3.60	130	14.2	6.00	2.41	11.7	2.94	14.9	14.7	20.5
EPS035	3.30	89.0	6.20	2.70	125	9.58	4.90	1.34	6.20	2.32	13.1	16.9	39.3
EPS036	2.40	96.3	4.50	10.7	132	6.07	5.40	0.930	6.20	3.46	11.3	16.7	24.6
EPS037	4.50	158	4.90	6.80	148	17.0	8.20	2.46	11.9	3.28	12.6	21.9	56.0
EPS038	3.30	114	5.70	3.20	105	17.4	8.40	2.87	9.50	1.74	13.4	18.3	32.9
EPS039	3.10	115	4.10	<LOD	119	4.28	2.20	0.390	2.80	2.33	14.0	12.9	38.0
EPS040	3.30	56.4	8.50	2.90	131	4.59	3.50	0.520	3.00	3.22	11.5	7.70	17.7
EPS001 *	3.60	15.2	4.70	3.70	121	3.20	4.50	0.650	<LOD	1.17	9.30	13.6	26.6
EPS031 *	5.90	63.4	9.60	7.00	114	47.6	20.7	6.18	25.4	2.97	14.5	16.7	32.6
Bone Ash	4.10	26.1	271	608	233	333	652	67.0	0.241	0.012	142	8540	59.7
Bone Ash	4.90	20.6	279	599	233	317	643	64.6	0.252	0.013	134	8460	60.2

was calibrated for each analyte using five standard series with four or five linearity points each; all standards were gravimetrically diluted from commercial High-Purity Standards (North Charleston, SC) single- and multi-element stock solutions. Internal standards Sc, In, Tl were added to all linearity standard solutions at known levels. Instrument Limits of Detection (LOD's) were estimated for each element as three times the standard deviation of the elemental concentrations measured in ten analyses of a zero point standard (blank 3 % HNO3 with internal standards). Sample limits of detection were determined for each element and sample as the multiplicative product of the instrument LOD and the total gravimetric sample dilution factor. The concentrations in the following elements (50) were measured: Li, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Hf, Ta, W, Pb, Th, and U. Two aliquots of a reference material with Ca-rich matrix (SRM1400 Bone Ash) were analyzed together with the samples (Table 1). Two duplicates (i.e., entire procedure applied twice to the same sample) were also analyzed to evaluate the reproducibility of the measurements (Table 1).

4. Results

4.1. Thin sections

Little evidence of dissolution was readily visible in the majority of the standard thin sections from this site. Under the petrographic microscope, shells from both the plow and sub-plow zone appear largely pristine other than a few fractures between shell layers. However, two shells from the plow zone contained large pores with sharp, curved margins typical of pores created by boring organisms (Fig. 3a). In these samples from the plow zone, edges of the tunnel-like cavities appear to cut sharply across otherwise pristine shell structure (Fig. 3a). The cavity shown in Fig. 3a is described as empty based on sequentially focusing on a series of planes at high magnification. A pronounced variation in refractive index as the stage rotated suggests that the interior of the cavity is also aragonitic. Examination with reflected light and a variety of colored backgrounds did not reveal any organic matter in this cavity (Folk 1987), and no clay minerals were observed. A few of the shells from the plow zone have small accumulations of brown organic matter or clay minerals in spots between layers or in cavities near the edges of the shells. Two shells from the sub-plow zone showed dissolution near an open space between shell layers (Fig. 3b). In these shells from the sub-plow zone, dissolution cuts both above and below the boundary between the two layers, cutting into each layer, showing that dissolution occurred after creation of each layer. In the sub-plow zone sample shown in Fig. 3b, the pore space created by dissolution was not

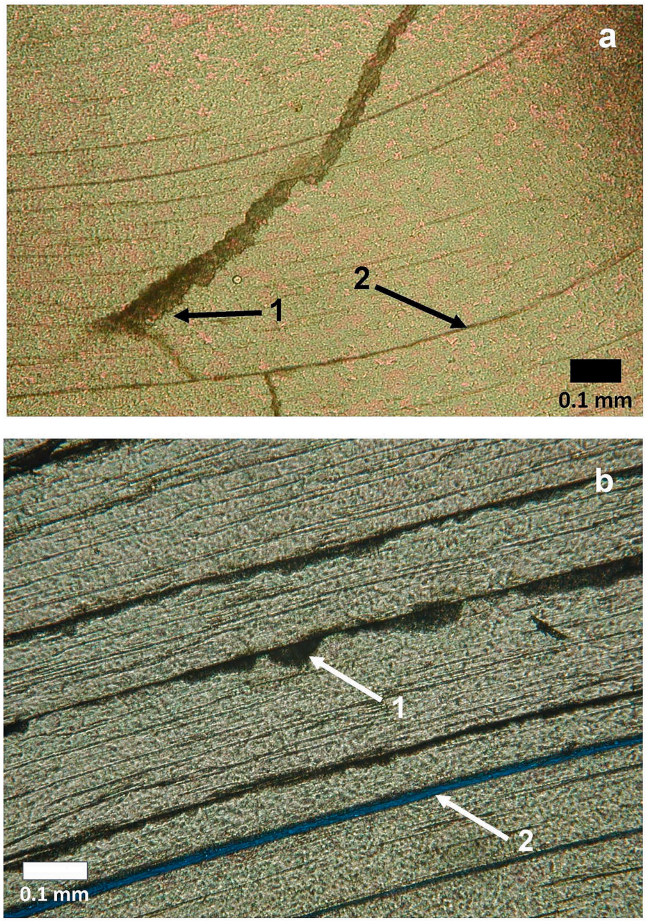

Fig. 3. A) images photomicrograph of sample EPS007 *Reginaia ebenus* from the plowzone showing a tunnel-like structure with a margin characteristic of boring organisms (arrow 1) and a slight open space between growth layers (arrow 2). The rest of the shell structure appears pristine. b) Images Photomicrograph of sample EPS037 *Cyclonaias pustulosa* from the sub-plow zone showing dissolution along a fracture between shell layers (arrow 1) and an open space between shell layers showing the blue dyed epoxy used for impregnation of open shell pore spaces as part of the process of making the thin section (arrow 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

impregnated by blue-dyed Epoxy. The process of making the thin section includes immersing the shell in blue-dyed Epoxy, heating it to decrease viscosity of the Epoxy, and placing the shell and Epoxy under vacuum. The presence of blue Epoxy indicates an open pore space connected to the outer part of the shell; the lack of Epoxy in a pore space suggests that pore space was either isolated or that the pore network was not pervasive enough to allowed Epoxy to impregnate throughout the shell. Most of the sub-plow zone shells had a few thin layers of brown organic matter or clay minerals filling fractures between layers and one sample had small fractures along one edge of the shell. Fractures between layers were common in the thinner parts at the edges of the shell but rare in the thicker portion of the shell, which was used for geochemical analysis.

4.2. Scanning electron microscope

Imaging with a scanning electron microscope allowed for visual assessment of many more details showing alteration of the shells by diagenesis. The degree of diagenetic alteration is observable in a spectrum of features visible in SEM images. To organize these observations, six qualitative categories were defined: - little to no evidence of diagenesis; - rare or minor pitting; - possible dissolution between layers; - dissolution with holes larger than the shell nanoscale structure; - major pitting with large and abundant holes or large areas of dissolution; - presence of dissolution and nanometer-scale lumps of organic proteins. Each piece of shell was imaged in multiple places on the individual sample. A variety of types of alteration could be seen on any one sample and the degree of alteration varied to some extent across each sample, but the degree of alteration was more often consistent from place to place on the same sample. These categories are illustrated in Fig. 4 and the types of alteration observed in each sample is reported in Appendix A.When they present little to no diagenesis (Fig. 4a), the samples show planar boundaries formed by flush parallel layers composed of spherical to subspherical granules, spheruliths (see Checa 2000; Checa and Rodríguez-Navarro 2001) or macromolecules of the protein matrix (Marie et al. 2017). Samples with rare to minor pitting (Fig. 4b) show the presence of very small (10 s of nanometers in diameter), typically diamond- to triangular-shaped holes between the spherical to sub-spherical forms characterize the natural, intact structure of the shell. More advanced diagenesis is shown in Fig. 4c, which illustrates that dissolution appears to begin between shell layers and proceeds in the formation of arcuate curves (instead of perfect planes) between layers. In contrast to pristine samples where layers maintain a consistent thickness, layers thin above and below the arcuate openings suggesting loss by dissolution. Fig. 4d illustrates continued diagenesis resulting in dissolution with holes larger than the shell nanoscale structure. It shows shells having undergone more dissolution have larger, deeper arcuate shapes, and holes within the lamellae have begun to form. As diagenesis progresses, shells show major pitting (Fig. 4e) and zones of large holes that sometimes cross lamellar boundaries. These samples are considered to have undergone the greatest dissolution and have clearly visible abundant

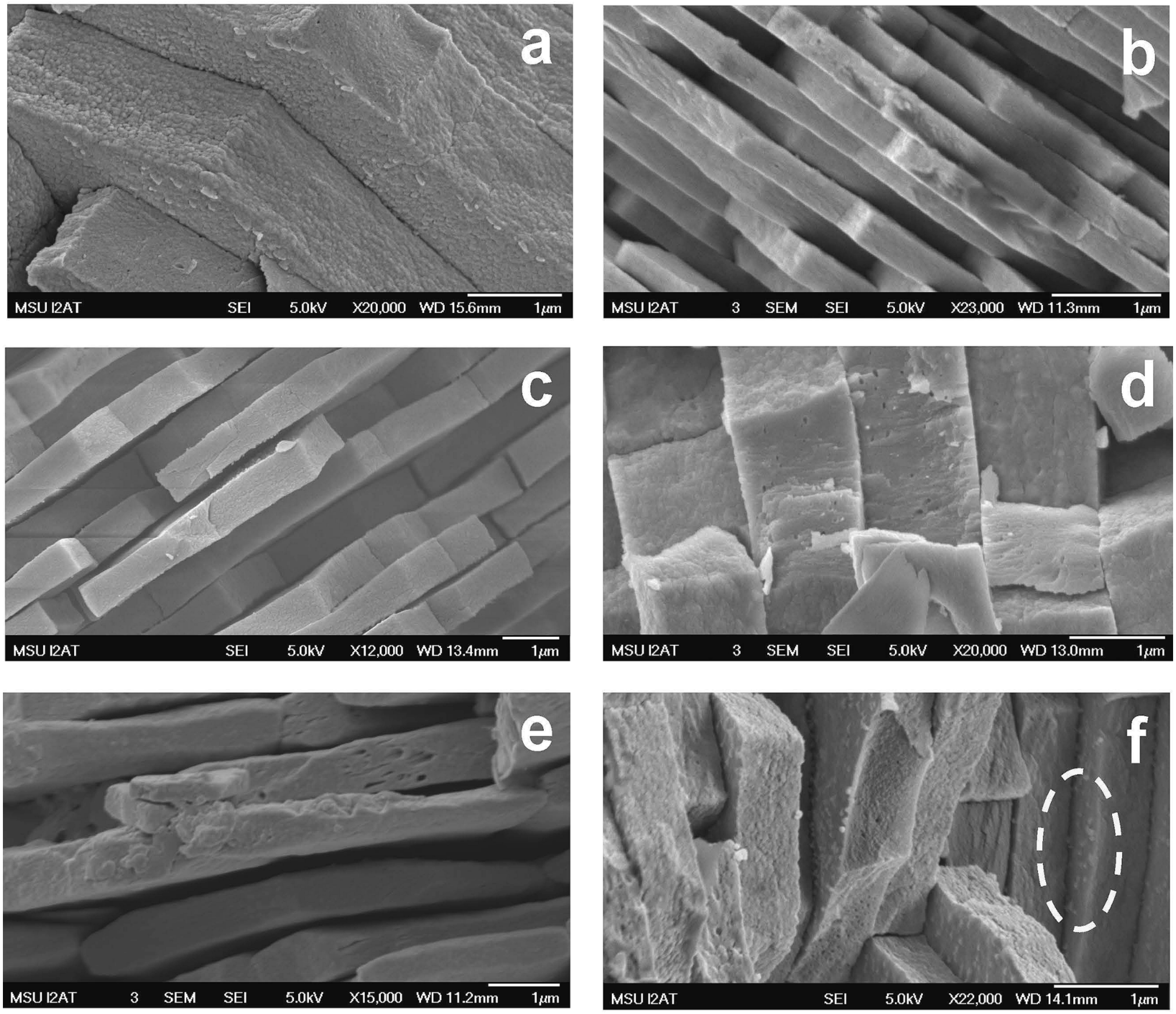

Fig. 4. SEM photomicrographs showing the different types of alteration observed in the shells.

holes with sharp-edges ranging in size from 0.1 to 0.4 μm as shown in Fig. 4e. Holes were up to 1 μm and arcuate gaps between layers up to 0.1 μm high by 3 μm long. Finally, in some cases (Fig. 4f), the dissolution of the aragonite reveals nanometer-scale sub-spherical forms that may be remnants of macromolecular protein matrix (see Marie et al. 2017). In the sub-plow zone, the majority of the shell samples (7/10) show this type of relatively pronounced dissolution between prismatic layers along with zones of large, sharp-edged holes that in some cases cross over prismatic layers. In the plow zone, only three samples are affected by these two types of diagenetic alteration. The evaluation of diagenetic alteration by SEM indicates that the samples from the sub-plow zone are all affected by some form of diagenetic alteration, in particular by dissolution that, in some cases, has subtly removed a potentially geochemically significant volume of the shell between lamellae. Visual estimates suggest that, in the most pronounced cases, 1–3 % of the shell has been dissolved.

a. little to no evidence of diagenesis; b. rare or minor pitting; c. possible dissolution between layers; d. dissolution with holes larger than the shell nanoscale structure; e. major pitting with large and abundant holes or large areas of dissolution; f. presence of dissolution and nanometer-scale lumps of organic proteins. The area highlighted in Fig. 4f shows examples of white clumps corresponding to the organic proteins.

4.3. Elemental chemistry

The concentrations in twelve elements were below LODs (limits of detection) (Cs < 2.10 ppb, Sm < 1.80 ppb, Gd < 0.99 ppb, Tb < 0.55 ppb, Dy < 1.50 ppb, Ho < 0.46 ppb, Er < 1.40 ppb, Tm < 0.21 ppb, Yb < 2.10 ppb, Hf < 2.60 ppb, Ta < 0.47 ppb and Th < 0.99 ppb) in most samples and were not further investigated. The concentrations of the remaining 38 elements (Table 1) were used and 37 of them were normalized to Ca and multiplied by a factor of 1000. A PCA was conducted using the resulting values to conduct a first exploration of the data. The details on the PCA are provided in Appendix B. PC1 explains 41.9 % of the variance and PC2 explains 14.2 % (Fig. 5). The elements that are mainly driving PC1 towards positive scores are Cd, Ni, P, Zn, Cu and V, as well as Y, Nb and some of the REEs (La, Pr, Nd). Positive scores on PC2 are mainly related to Pb and negative ones to As. The influence of lead is mainly related to the higher concentration in one sample from the plow zone (EPS010).

The samples are distributed between two distinct groups, with one group corresponding to the samples from the plow zone and the second one corresponding to the samples from the sub-plow zone (Fig. 5). The two groups are mainly separated according to their PC1 scores. The relation between the elements was then further examined using biplots (still using ratios to Ca). Samples from the sub-plow zone present higher P, V, Ni, Cu, Zn, and Cd concentrations and also larger ranges of variation than the samples from the plow zone. Concentrations in P, V, Ni, Cu, Zn, and Cd in the samples from the plow zone are 95.4–187 ppm, 0.0463–0.113 ppm, 0.048–0.137 ppm, 0.121–0.231 ppm, 0.623–1.33 ppm, <LOD (0.0073)-0.0269 ppm, respectively. The concentrations in P, V, Cu, Zn, and Cd in the samples from the sub-plow zone are higher with the following ranges of values, respectively: 345–1450 ppm, 0.0777–0.194 ppm, 0.319–0.729 ppm, 0.306–0.571 ppm, 1.99–6.51 ppm, 0.0561–0.158 ppm. In the samples from the sub-plow zone, moreover, V, Cu, Zn, and Cd concentrations are positively correlated to the concentrations in P, with this trend being less pronounced for Ni (Fig. 6). This relation between P and V, Ni, Cu, Zn, and Cd is not present in the samples from the plow zone (Fig. 6). Similar results are observed when using the elemental concentrations instead of the ratios to Ca.

A systematic comparison between the two layers shows that most elements have higher concentrations in the samples from the sub-plow zone than in those from the plow zone. The average of the concentrations normalized to calcium is higher in the sub-plow zone than in the plow zone for the following elements: P, Ti, V, Fe, Co, Ni, Cu, Zn, Ga, As,

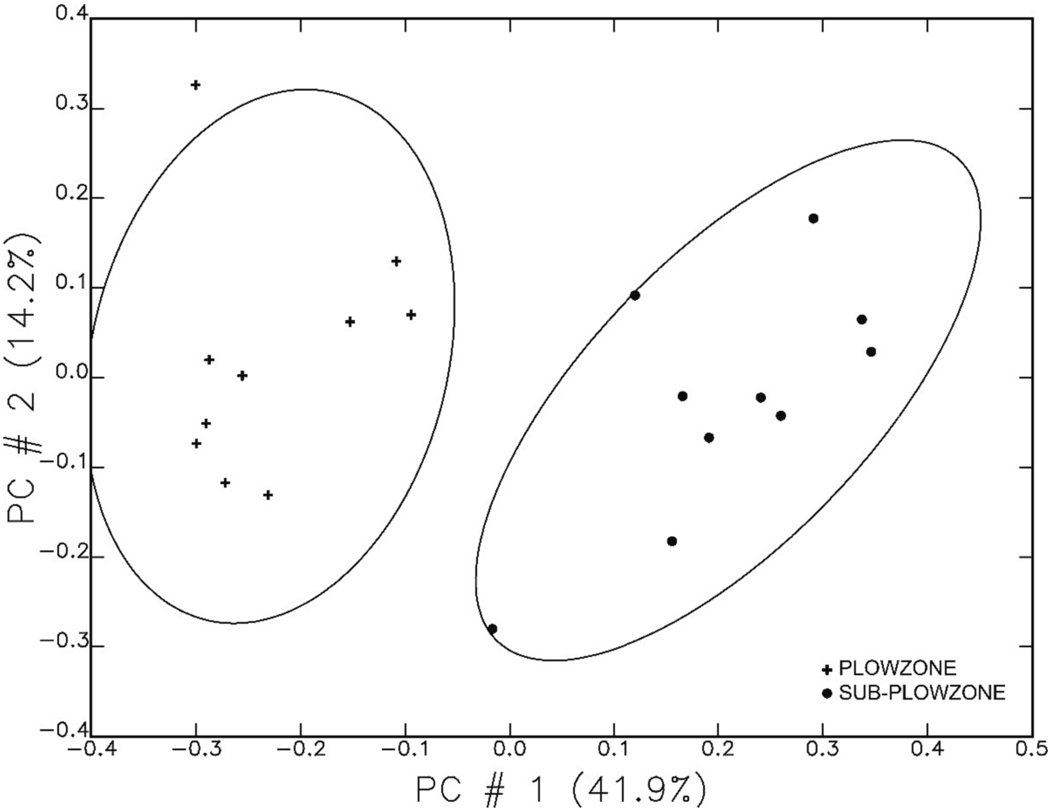

Fig. 5. PC1 scores vs PC2 scores for shell samples from the plow and sub-plow zones. Results of elemental composition with all elemental concentrations normalized to calcium and multiplied by a factor of 1000.

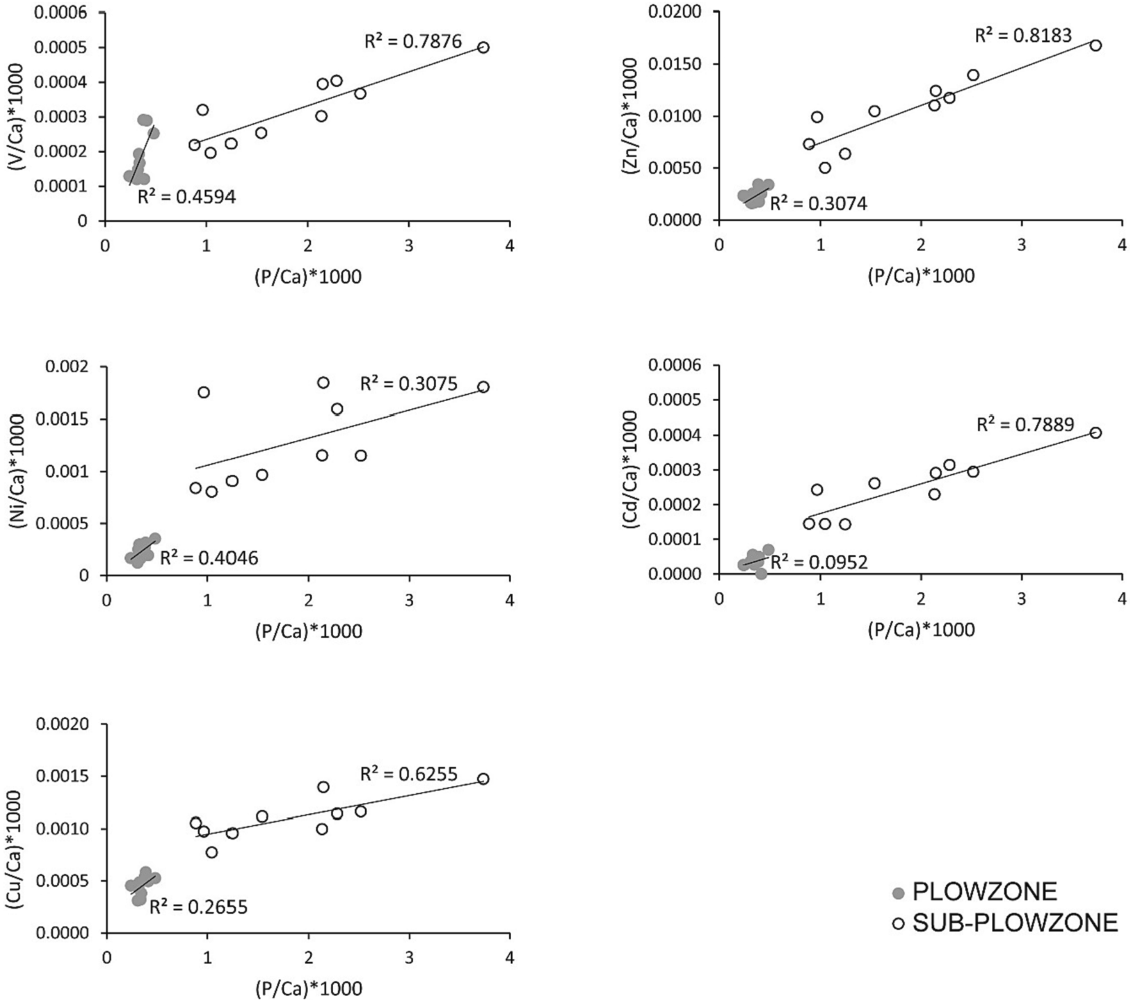

Fig. 6. Biplots of a selection of elements (V, Ni, Cu, Zn, and Cd) vs phosporus. All concentrations measured in ppm were normalized to calcium and multiplied by a factor of 1000.

Y, Zr, Nb, Mo, Ag, Cd, Sb, U and the REE's. Some elements have largely overlapping values (average ± 2SD): Na, Mg, Al, Ba, Li, Ge, Rb and W. The values for four elements, K, Cr, Sr, and Sn are higher in the samples from the plow zone than in those of the sub-plow zone. The average of the Pb/Ca is higher in the plow zone because of one outlier in the plow zone. If the outlier is removed, then the average of Pb/Ca is lower in the plow zone than in the sub-plow zone.

5. Discussion

Characterization by SEM shows that samples from the sub-plow zone are more affected by dissolution than the samples from the plow zone, and chemical alteration is higher in the sub-plow zone as well. The difference in elemental chemistry between the samples from the two zones is unlikely to represent different sources for the shells, which, based on similarities of taxa, midden context, presumed processing damage, and similarity to other, contemporary assemblages in the area in all such regards (Gilleland, 2016; Mitchell and Childress 2021; Mitchell and Peacock 2014; Peacock et al. 2011) reflect consumption of local resources. The discrepancy observed here is most likely the result of the alteration of the chemical signature of the shells by their burial environment, with samples from the two zones being affected differentially because of the different conditions in the two layers (plow zone vs sub-plow zone).

The concentrations and distribution patterns of V, Ni, Cu, Zn, Cd, and P in the shells from the sub-plow zone indicate not only contamination of the samples from these elements but also that the contamination is, at least in part, coming from a common source. The Yazoo Basin is today an area largely used for intensive agriculture to grow crops such as soybeans, cotton, corn, rice, and sorghum (Shields et al. 2009), which involves the application of livestock manure and fertilizers, including high-phosphate fertilizers (Ochs and Milburn 2003; Walker et al. 2003). The estimated annual average loading in P in the Yazoo Basin-wide is 0.43 t/km^2 (Shields et al. 2009:275), with consequent P enrichment of soils (Shields et al. 2009:276 and ref therein). In the context of the Kinlock site, the high level of P observed in the samples from the sub-plow zone likely derives from contamination of the shells by modern phosphate fertilizers. Phosphate fertilizers can present high concentrations of elements derived from the phosphate rocks used for their production (Lottermoser 2009). The five elements showing a correlation with P in the shells have been measured in phosphate fertilizers (e.g., McLaughlin et al. 2000; Otero et al. 2005; Lottermoser 2009; McBride and Spiers 2001) and enrichments in Cd and Zn, for example, have been measured in soils where phosphate fertilizers are recurrently applied (e.g., Lottermoser 2009). The relatively high accumulation of contaminants in the sub-plow zone layer at Kinlock is likely related to the clay subsoil forming a water barrier. Contaminants moving through the soil column, including elements leached from the surficial plow zone, accumulate in the perched water, increasing their contact with the sub-plow zone shells for longer periods of time.

That shells from the plow zone present a smaller range of chemical composition, i.e., are less affected by contamination than those from the sub-plow zone, is a somewhat unexpected result, given the greater physical alteration of the shells in the plow zone and standard conceptions of "disturbance" in archaeology. From a diagenesis perspective, however, these results make sense both in logical and comparative terms. Water perching on the clay subsoil at the site saturates the deeper, sub-plow zone shell for longer periods, providing a mechanism for greater chemical alteration with depth. In a discussion of freshwater shell middens, Stein (2005) notes that leaching typically begins at a site's surface as meteoric water percolates through the deposits, leading to a standard profile showing less leaching with depth. However, with perched water tables, this situation can be reversed, as was found to be the case with the "light zone-dark zone" phenomenon noted for marine shell middens on the Northwest Coast of North America. As Stein et al. (2008) demonstrated, the basal "dark zone" consistently observed at middens in that area is the result of brackish water saturating the lower parts of sites and leaching out carbonates. The water tables, even the perched water tables, in the Yazoo Basin have surely varied through time with seasonal rain fall, climate changes related to global variation, changes in native vegetation due to agriculture, or disruption of drainage patterns. With time, dissolution could have increased the surface area of the shell in contact with water, increasing in turn sites for chemical exchanges.

While the plow zone shells appear to be relatively uncontaminated at Kinlock, the degree to which they, too, may have been chemically altered by anthropic activities remains to be determined. Strontium, one of the few elements showing higher concentrations in the samples from the plow zone, may reflect disturbance by the input of fertilizers in the soil (e.g., Lottermoser 2009). Its concentrations do not display correlation with P in the plow zone or the sub-plow zone. But with elements in such high concentrations, the possible input of fertilizers may be present but more difficult to detect. Strontium is known as a trace element easily caught into the structure of the aragonite molecule and found in a wide range of organisms that produce aragonitic by biomineralization (Kinsman 1969; Tucker and Wright 2002; Marcano et al. 2015). The lower concentration in strontium observed in the samples from the sub-plow zone could also be explained by a loss of this element because of dissolution. In the samples from the plow zone, the concentrations of Cr, Ni, V and Pb may also be affected by anthropic activities, as these elements can be associated with fertilizers, even if they, too, do not display a clear pattern of correlation with P. In addition, leaching processes could also affect the concentrations of the more mobile elements. It is therefore difficult to know to what extent samples from the plow zone have preserved their initial elemental concentrations and can or not be confidently used as a representative signal for their provenance. One way to ascertain this would be to look for large-scale spatial patterns in shell chemistry that can be confidently related to drainage locale. If chemical patterns consistently map onto stream of origin, it can be assumed that chemistry related to home waters outweighs the effects of diagenesis and/or contamination; i.e., that the provenience postulate holds (e.g., Peacock 2017; Peacock et al. 2007; Peacock et al. 2010). Regardless, pre-sourcing work to identify the presence and degree of physical and/or chemical alteration will be useful.

Employing a similar approach to comparing plow zone and sub-plow zone shells from other middens would be a good start. The pattern of less chemical alteration in the upper portions of sites need not, of course, be limited to the Yazoo Basin, but might be expected in any environmental setting where water perches, even intermittently, such that the lower parts of site deposits are saturated for longer periods of time. One important implication is that stripping the plow zone off sites to expose "undisturbed" deposits and features, a standard practice in cultural resource management (CRM) in the United States and elsewhere, has unintended deleterious impacts on what can be learned from those sites. Site stripping as a rote practice has been criticized from a number of perspectives (e.g., Peacock and Rafferty 2007). Without proper sampling of plow zone deposits, stripping also may be compromising our ability to conduct sourcing studies using shell and, by extension, other biotic materials whose chemical signatures may, ironically, hold more fidelity in the upper parts of sites, even when plowing has occurred. This possibility can be explored via the targeted expenditure of CRM funds.

6. Conclusions

This research demonstrates the necessity to conduct a careful evaluation of material for diagenesis prior to the use of elemental chemistry as a tool for sourcing fresh water shells. It shows the importance of evaluating the impact of modern activities in the area of the site. These results also have implications for best practices to use on the field when deciding when collecting material for future analyses. It provides guidelines to examine material and raises the issue of diagenetic impact on elemental chemistry of shells.

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CRediT authorship contribution statement

Virginie Renson: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Simon P. Sherman III:** Formal analysis, Investigation, Writing – review & editing. **Brenda L. Kirkland:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Michael D. Glascock:** Formal analysis, Writing – review & editing, Visualization. **Evan Peacock:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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