Here Today, Gone Tomorrow? Integrated Experimentation and Geochemical Modeling in Studies of Archaeological Diagenetic Change

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ABSTRACT

The factors which influence the survival or otherwise of archaeological materials in the burial environment must be understood to allow systematic interpretation of the archaeological record. Studies of postdepositional change, or *diagenesis*, are therefore essential. The dynamic nature of terrestrial burial environments and the complexity of aqueous fluid-mediated transformation mechanisms have hindered detailed diagenetic research to date. The novel use of integrated experimental and geochemical modeling strategies has the potential to make progress toward a quantified understanding of the diagenesis of inorganic and bioinorganic archaeological materials. We describe current work that is attempting to develop this approach.

Introduction

Most archaeological knowledge comes from a study of objects which have survived for a considerable time in the ground. Many of these objects are altered in some way, and unknown proportions do not survive at all. Survival rates depend partly on the nature of the material—for stone, survival is close to 100%, whereas, for biological materials, such as skin, survival is virtually zero other than in exceptional circumstances. We need to understand these processes of alteration and survival if we are to interpret the archaeological record in a systematic manner, and chemistry has a substantial role to play in generating this understanding.

In archaeology, *taphonomy* is research which "defines, describes and systemises the nature and effects of processes that act on organic remains after death".[1] *Biostratinomy* and *diagenesis* are separate elements of taphonomy,[2] with biostratinomy being those factors which "affect organic remains between death and final burial", while diagenesis refers to "transformations occurring after final deposition". As originally conceived, these concepts only apply to the remains of living organisms, but since components of these (e.g., bone mineral) are inorganic, the "diagenesis" of inorganic material is a valid concept. We wish to broaden the concept further to include those transformation processes which act on any material of archaeological interest after final deposition, which might be described as causing *postdepositional change*. Diagenesis is therefore the cumulative physical, chemical, and biological processes that alter all archaeological materials in the burial environment and is consequently a fundamental characteristic of the archaeological record. These processes will modify an inorganic object's original chemical and/or structural properties and will govern its ultimate fate, in terms of preservation or destruction.

It is useful to think of diagenesis in thermodynamic terms. An object, once it reaches its "final depositional environment", seeks to reach equilibrium with its environmental conditions, with the net rate of change slowing down as equilibrium is approached. This gives the concept of an object being "stable" in its burial environment (providing it is possible for a particular material to survive in a particular environment). Strictly it is only metastable, since any alteration to that environment through natural (e.g., climate change) or anthropogenic (e.g., excavation) agency will cause the object to move toward a new position of equilibrium, resulting in further change. Although the physical location of a buried object might be fixed over archaeological time, it is unlikely that the local physical, chemical, or biological conditions will be similarly constant (hence the cautious use of "final depositional environment"). Thus an object might be expected to experience a sequence of metastable conditions throughout its postdepositional existence. We can visualize this postdepositional history as a series of *diagenetic trajectories* or *pathways*. In a stable burial environment, the diagenetic pathway is in principle predetermined by the nature of the object and of the burial environment, and the interaction between them. This trajectory might lead to perfect preservation or complete destruction but more often to some intermediary state. If the burial conditions change, the object will set off on a new trajectory but always toward a more altered state (in other words, as entropy dictates, it cannot spontaneously recover its original state!). Naturally, the complexity of the burial environment makes these simplistic views difficult to interpret in practice. In particular, the concept of noncommutativity is important—the order in which things happen has an influence on the final outcome (e.g., the sequence of insect or microbial colonization on a carcass). Overall, the situation is similar to the familiar conflict in chemistry between thermodynamics determining which reactions are possible and kinetics determining which will actually happen.

Although in archaeology diagenetic change is usually regarded as detrimental to analytical studies of artifacts, such effects are often neglected or considered negligible.

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Some postdepositional change can actually be beneficial in that it protects objects (e.g., an oxidized layer acting as a protective patina on metals[3]). More interestingly, it can also reveal information about the burial history of an artifact (e.g., in bones,[4] or more generally "the object as historic document"[5]). It has sometimes been said that the removal of the corrosion layer on a metal artifact is actually throwing away the most interesting part of the object!

For most archaeological and conservation purposes a qualitative understanding of diagenesis has thus far been sufficient. However, there is now a need for a systematic understanding of diagenetic processes and also to quantify the resulting changes. For example, analytical studies of all archaeological materials must be able to account for postdepositional chemical and mineralogical change to provide meaningful archaeological interpretations (e.g., in provenance, technological, and dietary/nutritional studies). At a larger scale, current planning policy in England and Wales[6] and elsewhere recommends in-situ preservation of archaeological remains wherever possible, but the scientific underpinning of this policy is at best empirical. Quantitative prediction is necessary to aid risk assessment and, in particular, to evaluate the damaging effects of changes in soil/groundwater conditions and soil chemistry following a disturbance (e.g., excavation/reburial). Conservation strategies for artifacts and heritage management plans for subsurface and standing monuments therefore need explicit diagenetic knowledge. In a wider context, archaeological materials have been used as analogues for understanding the long-term behavior of modern materials, e.g., glass for the stability of vitrified nuclear waste or the Inchtuthil Roman nails for the rate of release of iron into the environment.[7] Quantification of the archaeological data is essential to fully realize the value of these analogues.

Understanding Diagenetic Processes: Recent Research

Emphasis on the reburial of archaeological material as a means of preservation has necessitated an increased study of the burial environment. The issue of changes in oxic state following excavation and reburial and the potential damage to the archaeological record and its stratigraphy has recently been highlighted.[8] Similar problems are associated with disturbance of the aqueous equilibrium,[9,10] and collaboration between archaeological scientists and geotechnical engineers is essential for the prevention of further degradation in-situ.

Recent work in Sweden[11–13] has investigated the deterioration of archaeological metal artifacts in soils, examining the impact of atmospheric pollution and the resulting increased soil acidification on metal corrosion. Similar research has been conducted into the influence of declining groundwater tables and other soil parameters on metal corrosion and decay.[14–16] The issue of intensification of agricultural practices has been raised as a possible cause for the observed trend in increased decay of freshly excavated archaeological metals,[14,15] but the impact of mineral fertilizers has not yet been addressed in a systematic manner. The establishment of an international system which qualitatively defines the "preservation potential" of soil types for archaeological materials buried within has recently been proposed.[15] While attainment of this objective may lie some way in the future, it suggests the possibility of developing internationally comparable environmental impact assessment and heritage management strategies.

In-Situ Approaches. Archaeological diagenesis has been directly investigated in only a limited number of field cases. Inherent burial environment fragility and dynamics hinder in-situ measurements without disturbance of its metastable geochemistry and, therefore, its modification. However, one environment that has proved conducive to in-situ diagenetic studies is the cave system. Caves present a unique environment for this type of archaeological investigation, and innovative approaches have had remarkable success.[17,18] The series of diagenetic reactions experienced by bones, ash, and carbonate rocks in-situ were studied in terms of mineralogical change.[17] Carbonate minerals were found to be preserved unaltered under certain conditions, while in other cases the minerals had either dissolved or dissolved and reprecipitated as a new form of carbonate mineral. The in-situ formation of these authigenic minerals is direct evidence for diagenesis and has allowed establishment of the sequence of diagenetic events in several cave sites.[17] Diagenesis appears to vary in severity within localized environments, although processes of degradation appear to follow "fairly specific common pathways" within cave contexts.[17] The use of authigenic minerals in assessing the completeness of the archaeological record in prehistoric caves has recently been proposed,[18] on the basis of previous concepts[19] which sought to theoretically estimate the completeness of the rock and fossil record using fossil soils. The current level of understanding of authigenic mineral properties is insufficient,[18] but with more research, these techniques can potentially be used to accurately *predict* diagenetic processes in cave environments over archaeological time scales.

"Ex-Situ" Approaches. Several laboratory analyses of degraded archaeological materials (especially metals) and their contextual soil samples have been carried out in an attempt to characterize diagenetic change. Calculated correlation coefficients indicate the relationship between soil properties and the degree of artifact corrosion.[11,13,14] In the most in-depth study to date, corrosion products on bronze artifacts have been analyzed in conjunction with soil samples from their corresponding burial stratigraphy.[11] Bronzes were taken from aerobic sites with a variety of environmental and geological conditions and subjected to mineralogical analyses. Soils were characterized in terms of their chemical and physical attributes, and concentrations of water-soluble ions were also measured. Thermodynamic predictions of corrosion compositions were made following an analysis of soil water composition and interpretation via stability diagrams.

Statistical treatment of the resultant data showed a clear correlation between soil chemistry and corrosion products formed.[11]

"Single Element" Approach. The "single element" approach to understanding diagenetic change has been explored in terms of bone alteration in terrestrial burial environments.[4] The geochemistry of one element is considered, its interaction with soil and bone and transport mechanisms. Uranium uptake has been most extensively studied to date because of its importance in a number of dating techniques,[20] although the method has recently been applied to arsenic in bone using identical principles.[21] On the basis of experimental findings,[4] trace element uptake by archaeological bone is considered to be dominated by diffusion and adsorption mechanisms. Trace elements transfer from soil to groundwater and, once mobile, move along a concentration gradient into bone porewater, where they are fixed by adsorption and become incorporated into bone mineral. The single element method involves laboratory measurements of partition coefficients among soil, groundwater, and bone mineral. Because of the high coefficients involved, elemental concentrations in bone can be considerably higher than those of the surrounding soil and groundwater, negating the value of conducting a simple "soil analysis" for a particular element to indicate the likely amount of postdepositional uptake. This approach does have limitations, however. By definition, it is noncomprehensive and site-specific. While potential exists for quantification of diagenetic uptake, the method can, at best, only offer "order of magnitude estimations" of elemental uptake.[21]

The factors influencing diagenesis are complex and interdependent. We envisage a series of simplifications which will enable an experimental approach to simulate aspects of the behavior in the natural environment. Here we consider only geochemical reactions, neglecting physical and biological processes. It might be argued that it is impossible to separate these three regimes, since many natural chemical processes (e.g., sulfate reduction) are microbially mediated. The approximation becomes more tolerable if, however, we restrict ourselves to inorganic materials. Ultimately, all these disciplines must be integrated to generate a holistic approach to archaeological diagenesis, but we believe that such simplifications provide a useful step along the road. We therefore describe a combined protocol incorporating laboratory experimentation and computer-based geochemical modeling to investigate the behavior of inorganic and bioinorganic material in terrestrial burial environments where diagenetic reactions are mediated by aqueous fluids.

Geochemical Modeling and Experimentation: Concepts and Applications

Terrestrial Burial Environments. In terrestrial deposits above the water table, the burial medium is typically a soil or sediment, which is a dynamic three-dimensional
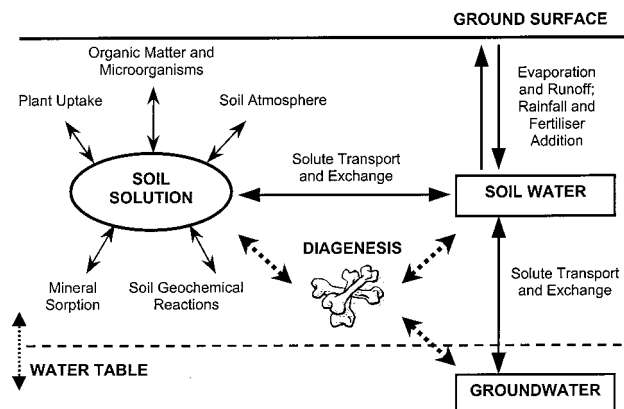

FIGURE 1. Dynamic equilibria in soils and influence of fluids on archaeological diagenesis. (Adapted from Lindsay, 1979, p 3.)

environment,[22] varying spatially and temporally.[23] It is geochemical interactions between solids, water, and solutes (and to a lesser extent gases) in aqueous soil systems which predominantly threaten the survival of inorganic and bioinorganic material. Diagenetic processes are driven by thermodynamic instability, and reaction kinetics predict the extent of diagenesis and the rate at which degradation will occur until equilibrium is reestablished. Furthermore, pH and redox potential define threshold conditions beyond which archaeomaterials are unstable.[24] The prediction of diagenesis therefore requires a quantitative description of biogeochemical and hydrological processes and their interaction.

Soil Solution. Above the water table, in the *vadose zone*, oxygenated *soil water* fills pore spaces between soil particles (Figure 1). Below, in the zone of saturation, anoxic *groundwater* flows. Either soil water or groundwater (or both, if the water table fluctuates) will interact with buried archaeological material. For the geochemical modeling of diagenetic trajectories, therefore, this soil water or groundwater should be sampled and its chemistry determined. However, direct measurement of their composition in the field is difficult, since it will fluctuate,[25] for example, with the amount of rainfall. In addition, we would like to develop a method whereby stored soil samples from archaeological sites may be used to directly generate the necessary information for predicting the preservation potential of a particular context or the likely accumulation/depletion of particular trace elements in an archaeological sample. To address these issues, we propose experimental sampling of the *soil solution* from field moist soil samples, following standard laboratory protocols for extraction and analysis.[26] Soil solution is different from soil water and is defined as "the aqueous liquid phase associated with soil",[27] at or below field capacity.[26] Soil solution composition reflects the processes that depend on the aqueous phase: biological activity; mineral dissolution/precipitation; adsorption/desorption; physical transport; anthropogenic inputs.[27]

Although separate entities, a fundamental and interdependent relationship exists between soil solution and soil water.[26,28] Inevitably, a portion of soil water is sampled

during soil solution displacement experiments and therefore directly influences soil solution composition.[26] Like soil water, soil solution varies temporally and spatially, but general compositions can be determined.[27] Soil water obtained by field lysimetry is of unknown origin and may represent recent rainfall or irrigation events, resulting in ambiguous interpretations.[26] Analyses of displaced soil solutions have been shown to exhibit seasonal variations in nutrient ion compositions, a trend absent from comparable soil waters.[26] Soil solution retains a more tangible record of formative events within its chemistry than soil water. On this basis, the chemical composition of soil solution, expressed at local equilibrium, best represents the fluid which interacts with buried archaeological material in terrestrial vadose zones (Figure 1).

Numerous dynamic parameters and processes constrain the composition of soil solution and so indirectly influence diagenesis. *pH, Eh, conductivity,* and *suspended colloidal materials* manipulate the chemical concentration, speciation, and activity of soil solution.[26] Temperature, pressure, and soil moisture content contribute further to the observed soil solution composition. *Ion speciation* is an important concept in the chemistry of natural aqueous systems.[29,30] Although soil solution is inherently dynamic, geochemical modeling requires all aqueous systems to be expressed at equilibrium. The model establishes equilibrium conditions on the basis of the given fluid's temperature and compositional information and subsequently traces the influence of mass entering and leaving the system and temperature changes on the system's equilibrium state.[31] The model anticipates natural fluctuations in soil solution composition and parameters, as it proceeds along the reaction pathway, partially compensating for historical changes. Using all available system and database information, the model predicts and quantifies thermodynamically feasible reactions as "virtual diagenesis" occurs.

Geochemical Modeling. Geochemical models can simulate numerous reactions, but from an archaeological perspective, modeling of water–rock (i.e., mineral(s)) interactions have the greatest value. Terrestrial and aqueous burial environments (e.g., marine, lacustrine, riverine) are fluid systems involving interactions between artifact, soil, or sediment and "water". Geochemical modeling is therefore suitable for visualizing diagenesis of archaeological materials with a mineral composition, in aqueous burial environments, at an assumed local thermodynamic equilibrium.[32] Geochemical modeling principally considers reaction thermodynamics. Ion speciation and mineral solubility are taken into account as aqueous solutions are manipulated and, thus, expressed at local equilibrium. Species are expressed as the most common form for the environmental conditions (primarily pH and Eh) prevalent at any particular point in the reaction. Determination of the rate of postdepositional change will necessitate the introduction of reaction kinetics, but initially, diagenetic quantification can be achieved without this temporal element.[33]
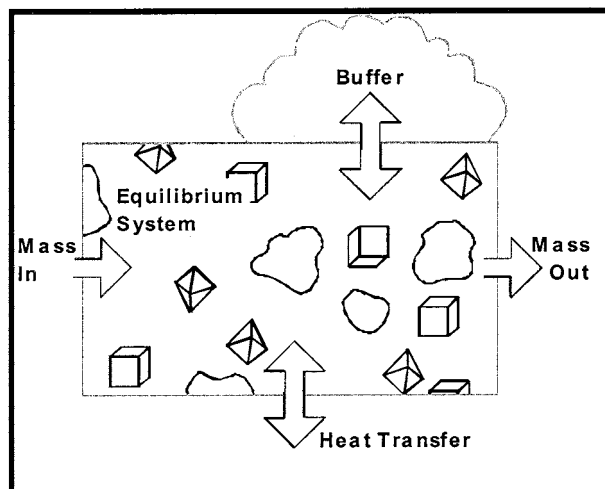

FIGURE 2. Schematic diagram of a conceptual reaction model. (From C. Bethke, *Geochemical Reaction Modeling*, 1996, p 10, by permission of Oxford University Press).

For successful geochemical modeling, a *conceptual model* of the reactants, reaction processes involved, and products must first be visualized (Figure 2) with strict controls over input values.[31] The initial system must be carefully defined, using experimentally generated data on solution chemistry and environmental parameters. Mass and chemical composition of solute, temperature, quantity of minerals present, fugacities of any gases, and pH and Eh values are required. Conditions must be expressed at equilibrium (achievable through mass balance calculations). The more complete the solute analysis, the closer to reality the result. Modeling assumes natural aqueous media are homogeneous, although they are, in fact, generally heterogeneous from a geochemical and hydrogeological perspective.[32] Furthermore, the dynamic (nonequilibrium) nature of soils limits the application of geochemical models to soil solutions.[27] However, nonequilibrium conditions can be overcome by the passage of time,[27] and with optimization of the modeling program, natural geochemical processes can be conceptualized at near-field scale[32] through informed interpretation.

Geochemical modeling has rarely been used in archaeological research to date. The investigation of metal corrosion, including copper[34] and lead minerals,[3] has been aided by thermodynamic modeling using very simple commercial packages. The potential use of geochemical models in the study of bone diagenesis has been actively promoted,[4,35] but no studies on the inorganic phase have yet been published.[36] Hydrological modeling of the bone–water system has received some attention,[20] and preliminary results suggest its beneficial use in the description of transport processes. Geochemical modeling packages have advanced significantly since these early applications, with current models capable of handling many geochemical processes simultaneously, correctly simulating dynamic laboratory experiments and field observations.[32] Microbiologically mediated processes can now also be tentatively investigated.[37]

Geochemical Modeling and Experimentation: Current Directions

By interpreting combined laboratory and geochemical modeling data, we believe a more holistic understanding of the geochemical aspects of diagenesis is achievable. As an initial prediction of archaeological material stability, *Eh−pH phase stability* (or *Pourbaix*) *diagrams* are useful, in which thermodynamic data are used to display mineral stability in aqueous soil matrices at equilibrium.[30,38] The geochemical modeling program we use (The Geochemist's Workbench (Act2 program)[37]) allows rapid generation of these diagrams.

Archaeologically Relevant Modeling Examples. Examples from some published experimental studies have been replicated by us using The Geochemist's Workbench (React program)[37] to demonstrate the potential and suitability of geochemical modeling in studies of archaeological diagenesis. A comparison of predicted and observed diagenesis is then possible. We give two examples—one indicating that the uptake of lead from groundwater into bone can be modeled and the other simulating the mineral alteration of archaeological ceramic in wet conditions.

(a) Lead Uptake by Hydroxyapatite. Recent research has investigated the uptake of lead by hydroxyapatite $(Ca_5(PO_4)_3OH)$ (HAP) as a strategy for contaminated land remediation.[39] HAP is similar to the inorganic mineral component of bone, and although the experiment was not developed with archaeological objectives in mind, it is directly relevant to understanding the chemical equilibration of bone with circulating water in archaeological contexts. In the published experiment, synthetic HAP was exposed to a 100 mg L^{-1} lead nitrate solution at pH 6 and at a constant temperature of 22 °C. This resulted in simultaneous dissolution of HAP and precipitation of hydroxypyromorphite $(Pb_5(PO_4)_3OH)$ (HPY), with complete removal of lead from the solution.[39]

To geochemically model this reaction using React, quantitative data was entered for the lead nitrate fluid and pH and temperature set at experimental conditions. HAP was then quantitatively reacted with the fluid. At theoretical completion, the majority of the synthetic HAP has been transformed to HPY, with only a fraction remaining unchanged (Figure 3). Geochemical modeling correctly predicted the experimental result. Aqueous lead was completely sequestered by halfway through the theoretical reaction (Figure 4), via uptake by HAP and transformation to HPY, following the overall reaction

$$HAP + 5Pb^{2+}(aq) \rightarrow HPY + 5Ca^{2+}(aq)$$
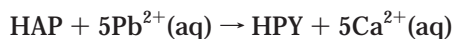
This simple example illustrates that even a material as complex as inorganic bone mineral is a suitable candidate for geochemical modeling approaches. Following on from hydrological modeling[20] and modeling of collagen diagenesis,[40] we suggest that more detailed geochemical modeling of the reactions of the inorganic mineral fraction is the necessary next step toward a better understanding of postdepositional alteration in archaeological bone. This
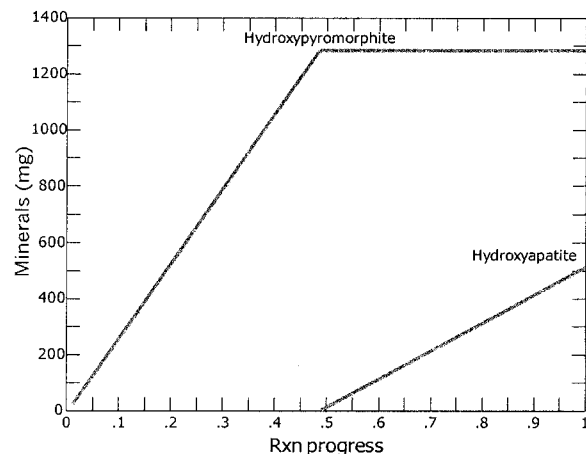
FIGURE 3. Transformation of synthetic HAP to HPY by lead uptake from surrounding environment (The Geochemists' Workbench: Gtplot output).
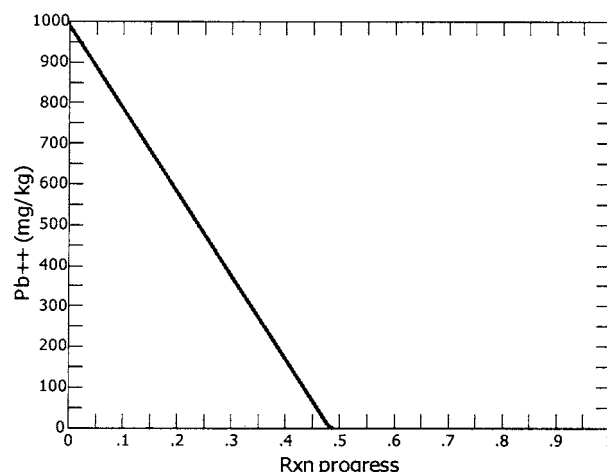

FIGURE 4. Removal of lead from aqueous solution (The Geochemists' Workbench: Gtplot output).

is an important issue, since much current work in archaeological biogeochemistry assumes that diagenetic alteration in bone can be ignored or dealt with by physical means.

(b) Alteration of Ceramic Mineralogy. Experimental work undertaken on calcareous ceramics in humid burial environments[41] examined the mineralogical change experienced by gehlenite $(Ca_2Al[(Al,Si)_2O_7])$. Powdered test sherds were subjected to solutions simulating natural aqueous burial conditions. In this case, hydrochloric acid (pH 1.0) was used to mimic natural soil solution. It was noted that gehlenite was altered to form authigenic minerals hydrogrossularite $(Ca_3Al_2[(Si,H)_4O_4]_3)$ and small amounts of $CaAl_2O_4 \cdot 10H_2O$ during prolonged exposure.[41]

In our geochemical modeling simulation, again using React, HCl fluid was created at 25 °C and expressed at equilibrium. By specification of the mineralogy of the ceramic material in realistic quantities (Table 1), a "rock" was created (N.B: only the mineralogy of the raw clay was given by the original authors[41] and so could not be directly used, as mineralogical change occurs during the firing process). The fluid was then reacted with the "rock", and the reaction continued until theoretical completion. The

Table 1. Ceramic Mineral Quantities Input into the Geochemists' Workbench (React Program) To Create Theoretical "Rock"

"rock" mineralogy	quantity reacted (mg)	"rock" mineralogy	quantity reacted (mg)
albite	12.2	amorphous silica	73.0
anorthite	49.4	hydroxyapatite	2.3
gehlenite	40.2	calcite	2.3
hedenbergite	14.4		
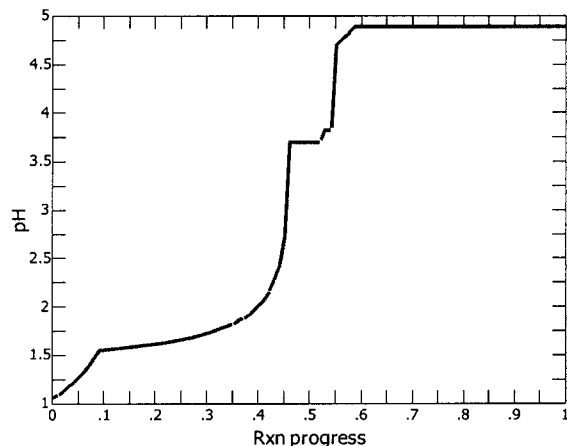
FIGURE 5. Alteration in reaction pH (The Geochemists' Workbench: Gtplot output).

thermodynamic database available did not contain information on the mineral hydrogrossularite. Instead, data from compositionally similar heulandite ($Ca_2(Al_4Si_{14})O_{36}\cdot 12H_2O$) was used, and so the program predicted the diagenetic formation of heulandite from the decomposition of gehlenite:

$$\text{gehlenite} + 5H_2O(l) + 6(\text{amorphous silica}) +$$
$$2H^+(aq) \rightarrow \text{heulandite} + Ca^{2+}(aq)$$
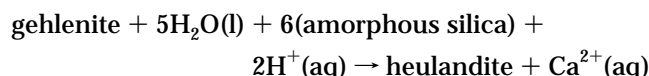
This is a feasible reaction, but by the inputting of some more relevant thermodynamic data, the results obtained experimentally[41] could have been better simulated. The pH of the aqueous medium shifts from strongly acidic toward neutral as diagenesis proceeds (Figure 5). Changes directly correspond to mineral formation and degradation evident in Figure 6. In our simulation, quartz is the only other principal end member, having remained relatively stable in the ceramic matrix throughout the diagenetic process.

These preliminary examples illustrate the potential of geochemical modeling strategies in studies of inorganic materials' diagenesis. They also illustrate the current shortcomings but serve to show that further work on constructing appropriate thermodynamic models will realistically contribute significantly toward understanding diagenetic alteration.

Methodology. Figure 7 outlines our overall methodology. The laboratory stage involves the extraction of soil solution from field-moist, unsterilized soils following established displacement procedures (saturated paste extracts and low-pressure centrifugation).[26,27] Practical derivation of "unaltered" soil solution is problematic, and ultimately, soil solution is operationally defined.[26] pH, Eh,
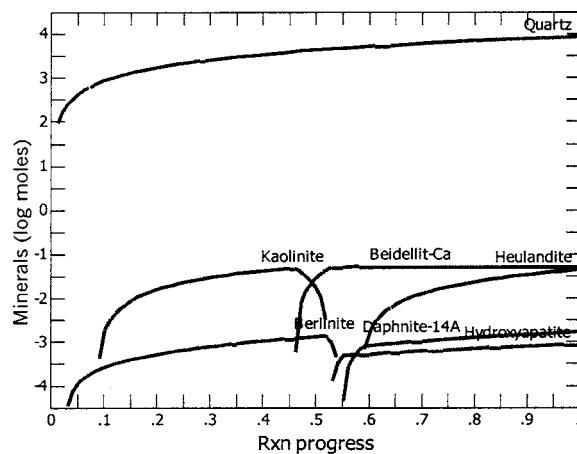
FIGURE 6. Alteration in ceramic mineralogy as diagenesis proceeds (The Geochemists' Workbench: Gtplot output).
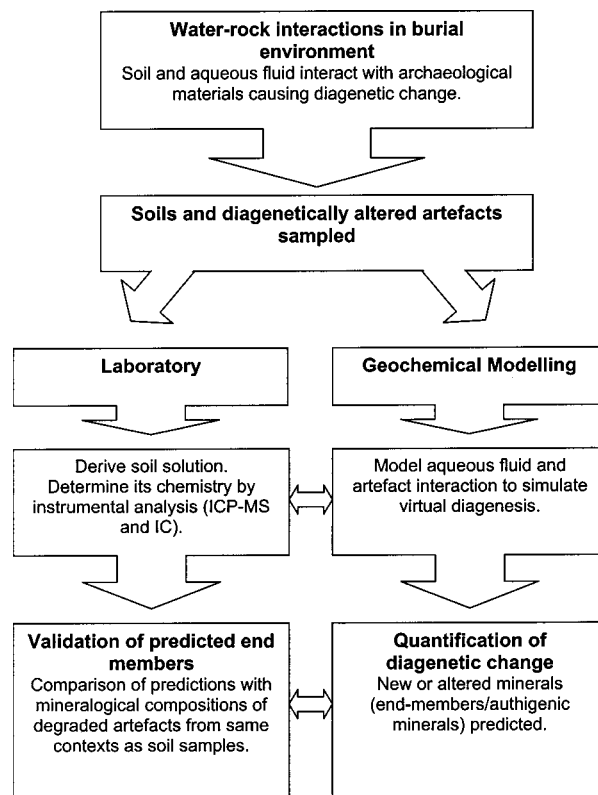
FIGURE 7. Philosophy of terrestrial burial environment diagenetic investigations.

conductivity, and other parameters are measured at this time. The soil solution obtained is analyzed by ion chromatography and inductively coupled plasma mass spectrometry, to obtain full solution chemistry. Some soil solution data from preliminary experiments are given in Table 2. On the basis of the hydrological assumptions detailed earlier, we propose the use of this soil solution, which incorporates elements of soil water composition (Figure 1), to represent the aqueous fluid responsible for material diagenesis in vadose zone burial environments. Using The Geochemist's Workbench (React),[37] theoretical simulation of the reaction paths between this fluid and a range of archaeological materials is then possible, to quantitatively predict end products of diagenetic alter-

Table 2. Preliminary Data from Laboratory Soil Solution Displacements[a]

sample	Na$^+$ (ppm)	NH$_4^+$ (ppm)	K$^+$ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	PO$_4^{3-}$ (ppm)	SO$_4^{2-}$ (ppm)	NO$_2^-$ (ppm)	Cl$^-$ (ppm)	NO$_3^-$ (ppm)	pH	Eh (mV)	conductivity (μS)
control (sand)	25	0.0	2.3	6.7	11	n.d.	45	n.d.	39	n.d.	6.3	20	199
control (duplicate)	19	0.0	1.7	4.2	7.1	n.d.	57	0.1	3.0	n.d.	6.3	19	139
test sample (soil)	19	0.0	51	7.9	90	n.d.	45	n.d.	30	460	6.5	48	738
test sample (duplicate)	16	0.0	46	7.3	82	n.d.	43	n.d.	23	400	6.5	48	707

[a] Sand was used as a control sample, and an urban soil as a test sample. Each was analyzed in duplicate. Ions were measured on a Dionex DX120 ion chromatograph. Ph, Eh, and conductivity were measured on solutions obtained. Data indicate ion concentrations and soil solution parameters can readily be derived by following simple displacement procedures (n.d. = not detected).

ation. Subsequent XRD analysis of real archaeological materials from real archaeological contexts allows theoretical predictions to be compared and validated by comparison with actual diagenetic change.

Implications for Archaeological Heritage Management and the Fate of the Archaeological Record

The implications of developing a geochemical model that can predict the occurrence and quantifiable extent of diagenesis are substantial. For cultural heritage management strategies, knowledge of the likely condition of archaeological materials prior to their excavation would assist in decision-making and planning. In terms of in-situ preservation of all archaeological materials, features, and sites, the clock continues to tick, and as yet we have no reliable model for burial conditions and activities. Competent diagenetic predictions are necessary to determine the appropriate course of action and (if necessary) recovery for a particular material at a particular site.

The potential also exists for the development of *reverse reaction-path models*. Construction of a geochemical model incorporating the mineralogical composition of a degraded artifact, and the chemistry of its aqueous burial environment, should theoretically allow the tracing of the reverse reaction, resulting in quantitative prediction of the *original* artifact composition. If possible, then its value in the study of diet, health, and migration from human bone, for example, needs no further elaboration.

Concluding Points

The following concluding points can be made: (1) Geochemical modeling is a powerful tool and suitable for studies of archaeological diagenesis in terrestrial (and marine) burial environments. (2) The soil burial environment is inherently complex, but simulation of its aqueous chemistry will further our understanding of diagenetic processes. (3) "The combined use of modeling and experimental data is an effective method of achieving a conceptual and quantitative understanding of individual reaction pathways."[42] "Without models we cannot predict what is likely to happen on a new site, or as the consequence of changes to a known site; without experimental measurements we will not have the data to build and test models."[4] (4) The combined experimental and modeling approach advocated here is feasible and necessary for a quantitative analysis of diagenesis. This research is, however, still at a very early stage, and there are many steps (both laboratory and theoretical) necessary to enable the construction of valid and useful models.

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