

Igneous Rock Associations 12 **A Geologist's Look at Archaeological Ceramics and Glass**

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Résumé de l'article

La céramique et le verre représentent respectivement des roches métamorphiques et l'obsidien synthétiques. En conséquence, il n'est pas étonnant que beaucoup d'archéologues aient collaboré avec des géologues sur des projets traitant non seulement des objets façonnés lithiques, mais également des objets en céramique et en verre. Ce document présente un aperçu de ces derniers deux matériaux d'une perspective géologique, considérant comment ils sont caractérisés et classifiés, leurs âges, provenances et emplois parfois déterminés, et comment elles ont été faites.

SERIES



Igneous Rock Associations 12. A Geologist's Look at Archaeological Ceramics and Glass

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SUMMARY

Ceramics and glass represent synthetic metamorphic rocks and obsidian, respectively. Consequently, it is not surprising that many archaeologists have collaborated with geologists on projects dealing not only with lithic artifacts, but with ceramic and glass objects as well. This paper presents an overview of these latter two materials from a geological perspective, consid-

ering in turn how they are characterized and classified, their ages constrained, provenance and in some instances use determined, and how they were made.

SOMMAIRE

La céramique et le verre représentent respectivement des roches métamorphiques et l'obsidien synthétiques. En conséquence, il n'est pas étonnant que beaucoup d'archéologues aient collaboré avec des géologues sur des projets traitant non seulement des objets façonnés lithiques, mais également des objets en céramique et en verre. Ce document présente un aperçu de ces derniers deux matériaux d'une perspective géologique, considérant comment ils sont caractérisés et classifiés, leurs âges, provenances et emplois parfois déterminés, et comment elles ont été faites.

INTRODUCTION

In the course of their education, geologists become well versed in the traditional mainstays of their discipline – mineralogy, stratigraphy, petrology, geochemistry, paleontology, geochronology, structural geology, tectonics – along with a smattering of supporting sciences. Among other things, we learn to place time and space in a broader context than most other scientists aside from astronomers. Archaeologists are not much different, although their appreciation of time is on a much more restricted scale – typically centuries and millennia rather than mega- and giga-annum. Moreover, they usually map on a much more detailed scale than field geologists, and the third dimension of

their maps is correspondingly shallow. Like geologists, however, archaeologists have an acute appreciation of stratigraphy, again on a minute scale, and, given the importance of lithic artifacts in their discipline, archaeologists must be familiar with the types of rocks exploited by ancient civilizations.

Dacite, the most commonly used rock for stone tool manufacture in British Columbia and in some other parts of western North America, is a good example, although it is commonly referred to by archaeologists as 'glassy basalt'. Studies of this material reveal the utility of geochemical analyses for fingerprinting lithic artifacts but also illustrate some of the challenges. Mallory-Greenough et al. (2002; whole-rock study) and Greenough et al. (2004; mineral chemistry fingerprinting) showed that dacite used in tool manufacture tends to be of local derivation, perhaps because the benefits of using non-optimal but readily-available materials outweigh the cost of transporting high-quality dacite because of its weight (Beck et al. 2002; Greenough et al. 2004). Still, the scope of the Arrowstone Hills (Cache Creek) quarry site in central British Columbia, where artifacts occur over ≥ 4 km² and are locally buried over 2 m deep (Ball 1997; Mallory-Greenough et al. 2002; Greenough et al. 2004), implies long-term utilization and potential use in trade. Curiously, widespread identification of Cache Creek-derived artifacts has yet to be established, but this may largely reflect the limited application of fingerprinting to studies of habitation site artifacts.

As important as lithic artifacts are to many archaeologists, ceramics

Stoneware (integrated body-glaze layer)	Examples Salt glazed stoneware Red stoneware True porcelain	Typical characteristics Na-silicate glaze Red, vitrified body; usually unglazed Si-Al-rich white body; low-lead glaze ¹
Earthenware (no integrated body- glaze layer; relatively porous)	Examples Red-coloured earthenware Fine earthenware Faience Artificial porcelain	Typical characteristics Red body; lead-rich glaze White body ² ; lead-rich glaze Tan body; tin-rich glaze White body ³ ; lead-rich glaze

1— some early British true porcelains have a lead-rich glaze, so were fired in the biscuit kiln before being glazed and fired in the glost kiln.

2— the composition of some fine earthenwares (e.g. creamware, pearlware) can resemble some true porcelains.

3— early artificial porcelains have diverse paste compositions (e.g. phosphatic, magnesian, and/or lead-rich).

Figure 1. Schematic subdivision of ceramics based on firing schedule (one [stoneware] *versus* two [earthenware] firings, excluding over-glaze decoration), paste and glaze colour (e.g. different types of earthenware), and compositions (e.g. fine earthenware *versus* faience). This chart is broadly based on information appearing in Hamer and Hamer (1997); not all archaeologists or ceramists necessarily endorse it, and there are many exceptions to these categories.

are of equal significance, at least with respect to Neolithic (and possibly Paleolithic; Watzmann 2009) and younger civilizations, and artifacts made from synthetic glass (as opposed to naturally-occurring glass, e.g. obsidian) can date back thousands of years as well. Given the overlap in some of the materials that interest us both (e.g. rocks) and in the techniques we use to better understand them in terms of relative age (stratigraphy), absolute age (geochronology) and composition (geochemistry and petrology), it is not surprising that some geologists include archaeological artifacts among the media that they investigate. This contribution is a geologist's look at archaeological ceramics and glass.

WHAT ARE CERAMICS?

Ceramics are non-metallic solid materials prepared by heating and cooling of (generally) clay-bearing mixtures. Excluding some modern types of specialized wares, some of which border on glass, ceramics can be broadly subdivided into low-temperature earthenware (pottery) that is porous (typically ≥ 5 vol.% pores) unless glazed, and high-temperature (kiln T generally $\geq 1200^\circ\text{C}$) stoneware that commonly but not invariably has a relatively low porosity (Hamer and Hamer 1997; Fig. 1).

Few ceramics are made entirely of clay. They usually require the addition of aplastic material (e.g. sand particles, crushed rock and/or dried plant material [temper]) to improve workability if the ceramic paste is to be thrown on a potter's wheel. Some types of pottery, notably aboriginal wares, can include distinctive ingredients such as shells. Temper grains can be useful in sourcing the raw materials used in the manufacture of archaeological ceramics, as can mineralogical impurities in the clay itself.

There are, not surprisingly, different types of earthenware, including red-coloured earthenware ('redware'), yellow-coloured earthenware ('yellowware'), fine earthenware (such as creamware and pearlware), and faience. They can be subdivided according to glaze colour (e.g. pearlware *versus* creamware), or body colour (e.g. redware, yellowware), or grain size (e.g. fine *versus* coarse earthenware). Some types of porcelain ('soft-paste' or 'artificial' porcelain) are also considered to be earthenware even though they are partly vitrified, because they tend to be relatively porous, so are glazed after an initial, relatively high-temperature firing. So-called 'true' porcelains are a refined type of stoneware. They traditionally were made from pastes containing kaolin and hydrothermally-

altered peraluminous granite ('china stone' ['petunse']). In some instances, a source of lime was also included. Consequently, these wares can be modelled in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ systems, respectively. Unless decorated with over-glaze enamel colours, they are usually fired only once, in a high-temperature biscuit kiln, so that the glaze bonds with the vitrified and translucent body of the ware, creating an integrated body-glaze layer. It is this latter feature (rather than porosity) that most clearly distinguishes stoneware from earthenware, which is usually fired twice, first in a biscuit kiln, and then, after glazing, at lower temperature in a glost kiln. The glazes on earthenware, including artificial porcelain, were traditionally lead-rich, unlike those on true porcelains. These low-temperature glazes fail to fuse with the substrate, sitting on it as a separate layer.

Porcelains are translucent owing in large part to the partial filling of pore spaces by a glassy melt phase. Unlike true porcelain, most other stonewares are opaque, in part because they tend to be thickly potted. They are made with lower-quality but relatively plastic refractory clays (stoneware clays) that can contain relatively high concentrations of mineralogical impurities (e.g. heavy minerals). In contrast,

true porcelain is made with relatively high-quality clays that generally contain fewer impurities. Some of these clays (notably kaolin) have low plasticity, so porcelain objects are commonly slip cast in plaster of Paris moulds rather than thrown on a potter's wheel.

Artificial porcelains were invented in the mid-18th century by Europeans seeking to reproduce the true porcelain that originated in Asia roughly 1000 years ago (and reinvented in Germany in the early 18th century (Roentgen 1996), and in the UK later in the 18th century). Unlike the chemically less-complex true porcelains, artificial porcelain spans a wide range of compositions that reflects the variety of starting materials used in their manufacture. In addition to clay and quartz or flint, these can include crushed glass ('frit'), calcined bone ash, soapstone, barite, and/or gypsum. Bone china is a hybrid ware formed by blending ingredients used in true and artificial porcelains (more specifically, those containing bone ash). Regardless of which ancillary ingredients are used in artificial porcelain pastes, the amount of clay used in the manufacture of these wares can be surprisingly small (often as little as ~10% clay by weight). In Mg-rich British porcelains, steatite from ophiolites on the Lizard Peninsula replaced most of the clay used in the porcelain paste (cf. Sandon 1989). The mineralogy of these wares reflects their bulk compositions and the conditions at which they were fired. Owing to the purity of many of their ingredients, solid solution minerals tend to approach end-member compositions. They can include, in different types of artificial porcelains, various combinations of enstatite, (pseudo)wollastonite, diopside and/or anorthite.

WHAT IS GLASS?

Glass is an amorphous solid that undergoes a transition between a hard and molten state. The glass transition is characterized by a dramatic change in viscosity, and by changes in heat capacity and thermal expansivity (Ojovan and Lee 2006). Glass in the transition has a rubbery character; below the transition, it is hard and solid, above the transition, it is relatively fluid. Although the widely held view (based on the observation that some ancient

window panes are thicker at their base than top) that glass is a highly viscous fluid has been refuted (e.g. Zanotto 1998), the character and structure of glass remain controversial topics in materials science.

Just when and where glass was first made are open questions. Pliny the Elder claimed that glass was accidentally discovered by Phoenician merchants while preparing a meal on the shore of the Belus River in Palestine. Unable to find rocks to support their cooking pots, they reputedly used blocks of natron (principally $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; a flux) instead. The heat from the fire caused the beach sand and natron to melt together. The melt cooled quickly, forming glass. This anecdote has long been discredited by scholars on the basis that the temperatures produced by campfires are insufficient to cause beach sand to melt, even in the presence of a flux such as natron. Instead, it has been proposed that the discovery of glass originated with the manufacture of early glazed objects such as Badarian steatite beads (Shortland et al. 2006) and faience (Bowman 1991). Glazes, after all, consist of glass.

The successful manufacture of glass requires the addition of fluxes (usually alkalis, lead and/or borates) and stabilizers (e.g. lime, to render the glass strong and relatively insoluble) to glass-grade (silica-rich) sand. Colourants (to tint the glass) and decolourants (to reduce the green colour caused by the presence of iron) can also be used. This mixture of ingredients constitutes a glass batch, the material intended to be melted to form glass. Broken scrap glass (cullet) is often added to these batches to promote melting. Glass batches are melted in large, ceramic firing pots (refractory clay crucibles) that must be free of any flaws to minimize the risk of catastrophic breakage in the furnace. Like the temper grains used in the manufacture of some pottery, impurities (e.g. heavy minerals) in the sand used by glass manufacturers can be used to source this raw material, even though it was completely melted during firing of the glass batch in which it was used. This is possible because the trace element signatures of these impurities are inherited by the glass.

INVESTIGATION OF ARCHAEOLOGICAL CERAMICS AND GLASS

Archaeologists who investigate historical and ancient ceramics and glass usually focus their attention on one or more of five aspects of particular artifacts: (1) what is it?, (2) how old is it?, (3) where was it made?, (4) how was it made?, and (5) for what was it used? These points will be considered separately.

What Is It?

This question is somewhat ambiguous: does it address the item as a formed object or as a material? Small sherds excavated from archaeological sites can sometimes be pieced back together, so the form of the original object can be identified. More specifically, however, this question also refers to the type of material, be it ceramic or glass, of which the artifact is made. Ceramics are routinely subdivided into broad categories based on aesthetic criteria such as colour, grain size and degree of translucency (e.g. Hamer and Hamer 1997). This allows the distinction between, for example, coarse redware and porcelain. In the case of visually-similar wares (e.g. the fine earthenwares), chemical and petrographic analysis (e.g. 'fabric analysis' *sensu* Peacock 1967 and Moody et al. 2003, among many others) may be required to make this distinction. For example, it was only after chemical analysis of samples originally described as either pearlware or protoporcelain (South 2007) that the porcelaneous character of sherds from the Cain Hoy, South Carolina site of John Bartlam's potworks was recognized (Owen 2007a). Bartlam is now recognized as having produced the first porcelain in what is now the United States. The decorative features of these porcelain sherds were subsequently recognized on some teabowls that hitherto had been attributed to London manufacturers (e.g. Isleworth). Strong evidence for their American provenance raised their commercial value in the antiques market a hundredfold (one such teabowl sold at auction for US\$146,500 in January 2013). Their historical significance is inestimable.

Although some experts can distinguish different types of glass (e.g. soda-lime *versus* potash-lead glass) sim-

ply on the basis of its character (e.g. clarity, density, relative refractive index, and 'ring' when struck) or using a UV lamp, this distinction can require some type of chemical test, if not a complete chemical analysis. The advent of inexpensive analytical tools (e.g. portable XRF) that can analyse a variety of media quickly and non-destructively has the potential to make the compositional classification of glass (and some types of high-fired ceramics; e.g. Owen 2007b) routine. Not all ceramics are so readily distinguished. For example, creamware and true porcelain can have overlapping compositions (Owen 2011), although their mineralogy, microstructure and porosity are quite different.

How Old Is It?

Archaeologists have recognized temporal changes in the form, design, style of decoration and means of production of ceramic and glass artifacts since the early days of the discipline. This required careful documentation of artifacts with good archaeological (as opposed to mixed or disturbed) context, and the comparison of these objects with those from older and younger sites related to the same culture. From this, a relative chronology of artifact forms and decorations emerged for particular regions and cultures over broad and sometimes overlapping periods of time (e.g. Eastern Woodland aboriginal pottery, ca. 2500 BCE – 1000CE; see Peterson and Sanger 1991, and Lattanzi 2009 and references therein). Absolute ages for some ceramic wares can be established by dating the objects themselves or related material from the same archaeological context. Examples include dosimetry dating (thermoluminescence and optically-stimulated luminescence; e.g. Godfrey-Smith and Casey 2003), paleomagnetic and archaeomagnetic dating (e.g. Hagstrum et al. 2005), and ^{14}C dating of charcoal associated with potsherds. Direct dating of carbon residing in or on potsherds, however, has proven problematic (e.g. Hedges et al. 1992; Stott et al. 2001). In the case of historical fine ceramics produced by particular factories, compositional criteria can be used to constrain the ages of wares made during particular periods of that factory's history (e.g. Owen

2003). If authentic, factory marks circumvent more recondite means of assigning wares to particular enterprises.

A major limitation to using aesthetic criteria to estimate the age of artifacts is the longevity of forms and designs. Likewise, widespread copying of commercially successful objects (and their marks) can hamper determining the provenance of these artifacts.

Where Was It Made?

Determining the provenance (i.e. 'sourcing') of objects is an important objective in many archaeological studies. Although this can sometimes be achieved by simply using aesthetic criteria, archaeologists increasingly rely on analytical data for the objects themselves (i.e. their bulk chemical compositions) and/or, in the case of ceramics, their mineralogical constituents, to source these artifacts. In this regard, provenance studies on ceramics mirror those for lithic artifacts. There is a vast literature on sourcing both types of media. What these studies have in common is the requirement that data be available both for the artifacts themselves and material from suspected source areas. Even the composition of glass, which preserves none of the raw materials used in its manufacture, can be sourced in this way, since even glass-grade (high silica) sands invariably contain heavy minerals that control the signatures of many trace elements. These trace element profiles can be passed down to the glass (and ceramic) artifacts manufactured from these raw materials. For example, glass-grade silica sand ($\geq 98\%$ SiO_2) occurring in southern New Jersey and western Massachusetts is known to have been used by the Boston and Sandwich Glass Co. (Sandwich, Massachusetts, ca. 1826–1888). The sand from these two localities have differing Nb concentrations, a feature that can be recognized in the Sandwich glass each was used to make (Owen et al. 2005).

Ancient glass presents an additional problem because some major glassmaking centers exported ingots of this material to be shaped into useful objects elsewhere (e.g. Walton et al. 2009); indeed, the wrecks of ships carrying raw glass cargo have been discov-

ered in the Mediterranean (Foy and Jezegou 2004). In this instance, the origins of the glass itself and of the finished objects differ, and require separate sourcing. Strontium isotopes have proved useful in determining the provenance of some of the glass (and the character and identity of its raw materials) from this area (Freestone et al. 2003), and both Sr and Pb isotopes have been used to identify the recycling of glass at ancient glassworks (Degryse et al. 2006). Recently, the isotopic compositions of Sb from various stibnite deposits have been determined to facilitate sourcing ancient Sb-bearing glass artifacts from the Middle East (Lobo et al. 2013).

Ceramic and glass provenance studies mirror sedimentological sourcing in terms of design and implementation. Some of the minerals commonly used to identify the terranes from which sedimentary detritus was shed are also used to constrain the provenance of historical and ancient ceramics and their raw materials. Among the titania polymorphs, rutile has found wide use in sedimentary provenance studies (e.g. Triebold et al. 2012). Care must be taken to correctly identify the particular titania polymorph(s) in ceramic artifacts, since these minerals partition trace elements differently. Moreover, distinction must be made between *bona fide* detrital rutile and that formed diagenetically (e.g. Pe-Piper et al. 2005). Notwithstanding these potential problems, heavy minerals have been used to constrain the origin of particular ceramic artifacts. For example, porcelain sauceboats excavated in Philadelphia contain heavy minerals (e.g. anatase) that compositionally resemble those found in kaolin from a tributary of the Delaware River that is known from historical documents to have been the source of at least some of the clay used by America's second porcelain manufacturer (Bonnin and Morris, Philadelphia, ca. 1770–73; Owen and Hunter 2009; Owen et al. 2011a).

In some instances, heavy minerals in ancient pottery can be traced to specific rock units. Eastern Woodland period Mi'kmaq pottery from the Annapolis Basin/Bear River area, Nova Scotia is a good example. These potsherds are loosely dated by their

incised/impressed decorative motifs (e.g. Peterson and Sanger 1991) to as far back as 2 ka. Some contain large (mm-scale), (sub)idiomorphic biotite clasts that analysis suggests were derived from granodiorite of the South Mountain batholith cropping out inland. This inference is substantiated by the composition of monazite inclusions in biotite both in the granodiorite and the pottery, and by the composition of the biotite itself (Fig. 2; J.V. Owen, D. Forfa, and J.D. Greenough pers. comm. 2013).

Not surprisingly, the source of heavy minerals found in ancient pottery cannot always be traced to a specific locality or rock unit, but at least some specific sources of this material can usually be excluded. For example, the ancient Egyptians quarried basalt for use in open vessels and paving stones. Comparison of the trace element composition of pyroxenes and plagioclase (determined by laser probe) have helped link specific artifacts to quarry sites, but not the basalt temper found in some ancient Egyptian pottery (Mallory-Greenough et al. 1999, 2000). Bulk compositional data are also useful in characterizing archaeological earthenwares, and are widely used in provenance studies (e.g. Weaver et al. 2013 and references therein). They can even hint at climate change-induced variations in the sediment used in their manufacture (e.g. Mallory-Greenough and Greenough 1998). Statistical analysis (e.g. principal component analysis; multi-dimensional scaling [MDS]) is commonly applied to analytical

datasets to help identify compositional groupings of wares and relate them to other archaeological artifacts and/or suspected sediment sources. An example showing regional variations in the composition of late Neolithic Ghanaian pottery and its sediment sources is shown in Figure 3. This MDS diagram plot shows that ancient Ghanaian potters gathered the raw materials for their trade from a wide area (Owen et al. 2013).

How Was It Made?

The investigation of excavated objects and of the sites where they were made has revealed much about the production of ancient and historical ceramics and glass, and it is beyond the scope of

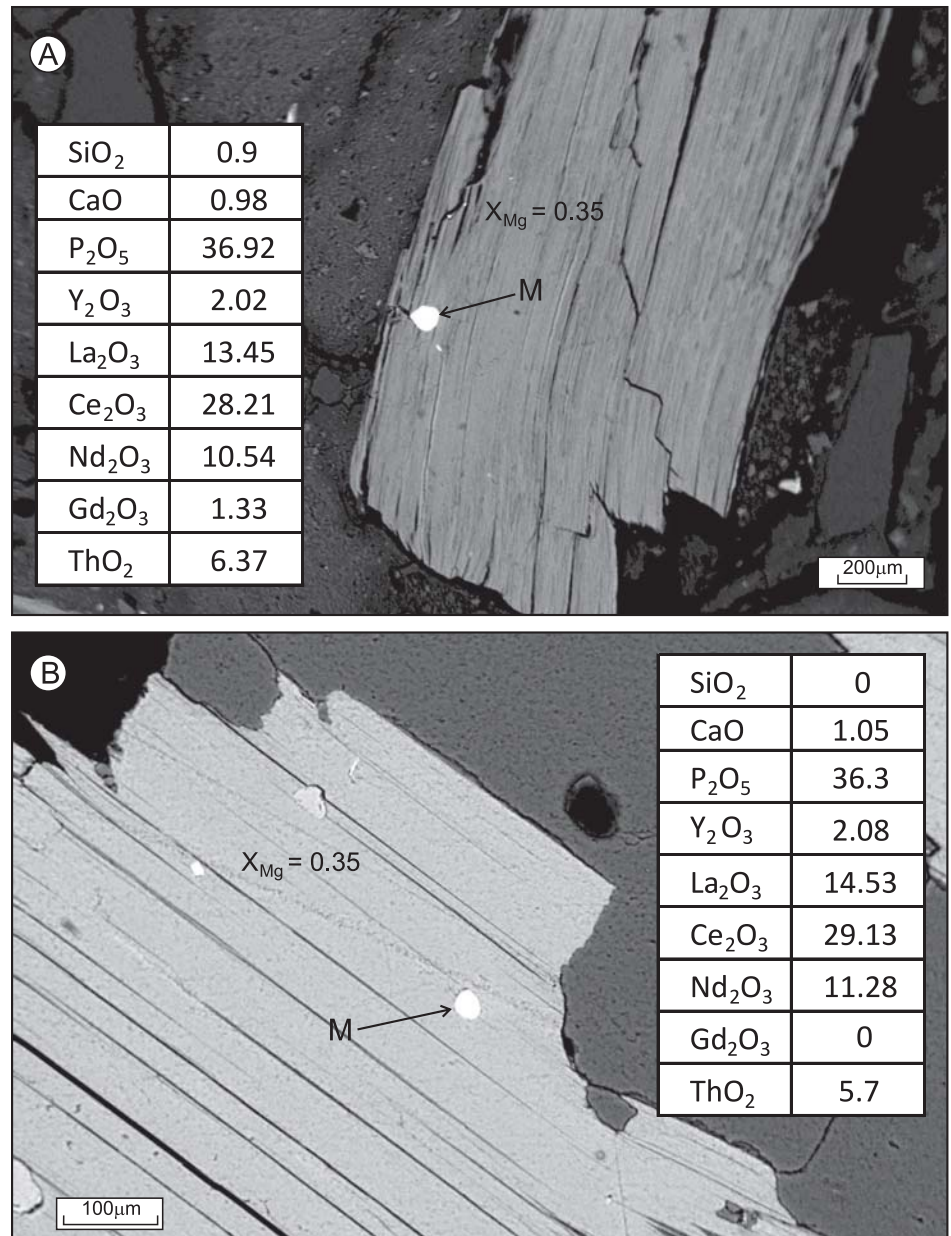


Figure 2. Backscattered electron images of compositionally-similar monazite inclusions ('M') in biotite in (A) ancient Mi'kmaq pottery from the Annapolis Basin (Nova Scotia) and in (B) their suspected source rock, biotite granodiorite of the South Mountain batholith that crops out inland of the archaeological site where the pottery was found (J.V. Owen, D. Forfa, and J.D. Greenough pers. comm. 2013). Monazite analyses and the Mg/(Mg+Fe) ratio (X_{Mg}) of biotite in both samples are shown.

this short review article to delve into these topics. Geologists, however, can contribute to a better understanding of the conditions (T, fO_2) in the furnaces in which some of these objects were made, provided that the minerals in these samples formed and/or equilibrated during firing. For example, Philpotts and Wilson (1994) used iron oxide mineralogy to reconstruct the peak temperature and oxygen fugacity

conditions at which aboriginal pottery was made. Aboriginal pottery aside, kiln-fired pottery was sometimes over-fired, and so suffered body distortion (sagging). Red-coloured earthenware from the Eby pottery (Conestogo, Ontario, late 19th century) can show this effect. These distorted sherds contain a melt phase that reacted with diopside temper grains to form low-Ca pyroxene (enstatite) coronas, and from

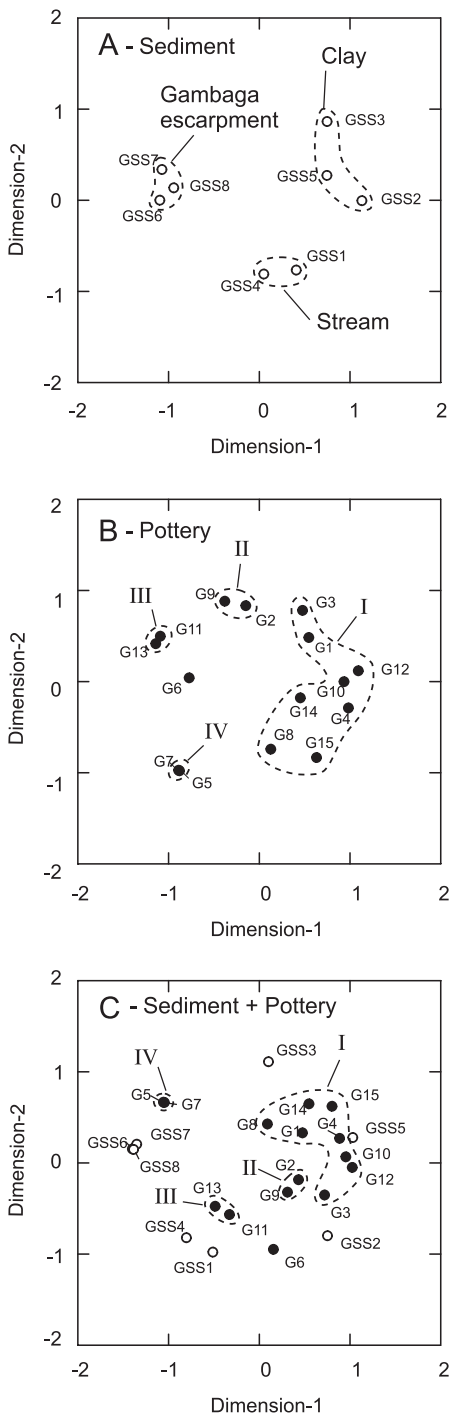


Figure 3. Multi-dimensional scaling plots showing the compositional clustering of (A) sediments (lateritic clay from Bulunga and Dabila, stream sediment, and sediment from atop the Gambaga Escarpment) used in making (B) late Neolithic Ghanaian pottery, subdivided into four groupings (I to IV) with one outlier (sample G6). (C) Overlapping compositions of potsherds and different types of sediment from northern Ghana. Modified after Owen et al. (2013).

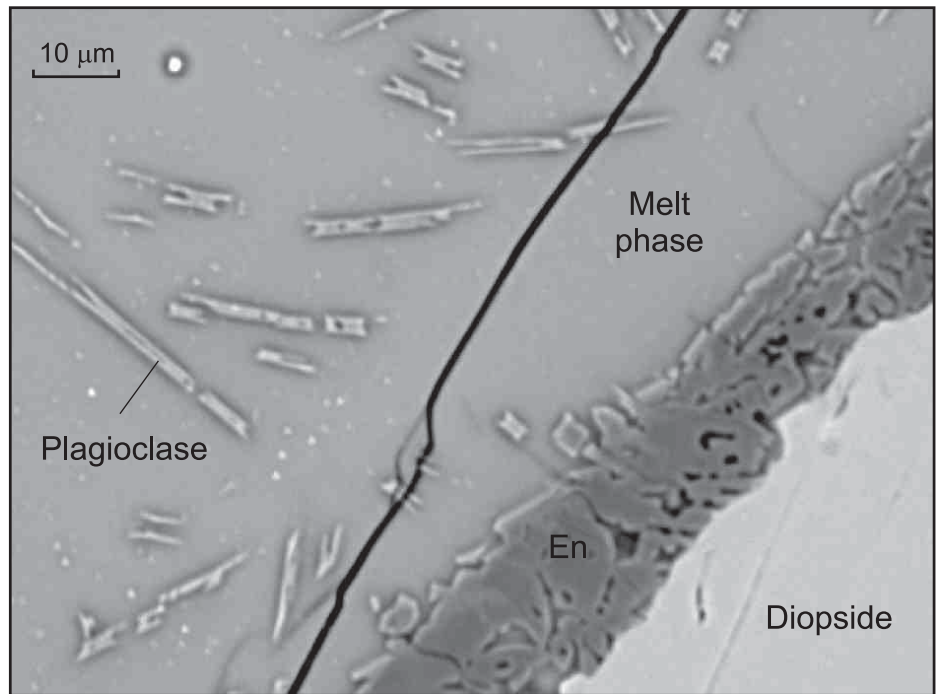


Figure 4. Backscattered electron image of a diopside temper grain embayed and enclosed by a low-Ca pyroxene (enstatite; En) corona in the melt phase (glass) of an overfired sherd of Eby pottery (Conestogo, Ontario, late 19th century). Note the dark symplectic intergrowths (a silica polymorph?) in the inner part of the corona, and quenched morphology of plagioclase microlites in the adjacent melt phase. Modified after Owen and Dostal (2006).

which plagioclase crystallized (Fig. 4). Peak firing temperatures exceeded 1100°C (Owen and Dostal 2006).

Although the brief firing schedule (typically ~24–48 h) of high-*T*, vitrified wares (stoneware, porcelain) generally precludes the attainment of equilibrium among crystalline and melt phases, phase diagrams nevertheless can be used to constrain their firing temperatures. Melts, however, rarely plot on or near eutectics and cotectics on these diagrams, probably because of the influence of contiguous phases on their compositions (i.e. equilibrium is approached only on a domainial scale; Iqbar et al. 2000; Owen et al. 2011b). It is, however, the simplicity of the chemical systems on which these diagrams are based more than evidence for lack of equilibrium that can limit the usefulness of phase diagrams in determining firing temperatures. Commonly, one or more fluxes (e.g. Na, K, Pb) present in the ware is lacking on pertinent phase diagrams, so estimated kiln temperatures for vitrified ceramics will be maxima. In principle, analogue experiments for these wares can be

undertaken to better constrain the firing conditions of early ceramic pastes, but it is rarely the case that the results of this work faithfully replicate the artifacts themselves in terms of mineralogy and microstructure.

In rare instances, porcelain samples can contain microstructural features reminiscent of high-grade metamorphic rocks, and these can help constrain aspects of the firing history of these wares. For example, a mid-18th century teapot lid excavated in London contains double coronas that separate relict glass frit particles from metakaolin in the matrix. The inner coronas correspond to a quenched melt phase. They are enclosed by feldspathic (labradorite; An₆₂) coronas that extend into the clayey matrix (Fig. 5). The glass frit, now devitrified to a silica polymorph – diopside – pseudowollastonite symplectite, served as a source of alkalis that fluxed the kaolin, promoting anatexis (Owen 2012). Extraction of Ca from the inner coronas by the developing labradorite rinds displaced the composition of the melt phase away from the 1345°C eutectic

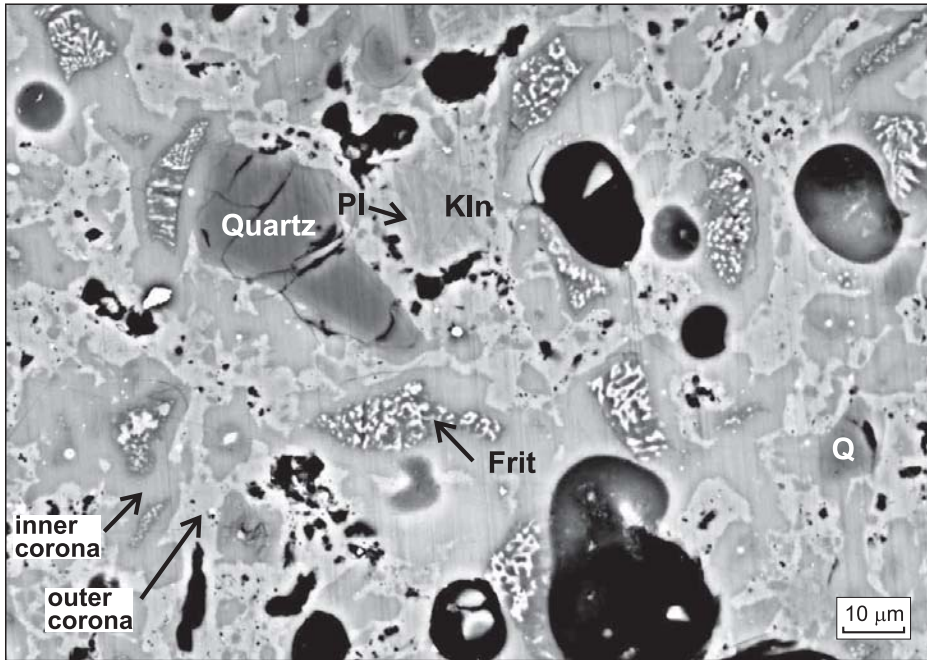


Figure 5. Backscattered electron image of double corona structures separating devitrified glass frit (now symplectites) from metakaolin (Kln) in mid-18th century British porcelain (1st patent Bow teapot lid). The coronas consist of an inner, glass layer and an outer, feldspathic layer from which plagioclase microlites (PI) extend into matrix metakaolin. Note the concentration of pores (black spots) in the outer coronas, and presence of partly resorbed silica polymorphs (probably alpha quartz, Q) in the matrix. Modified after Owen (2012).

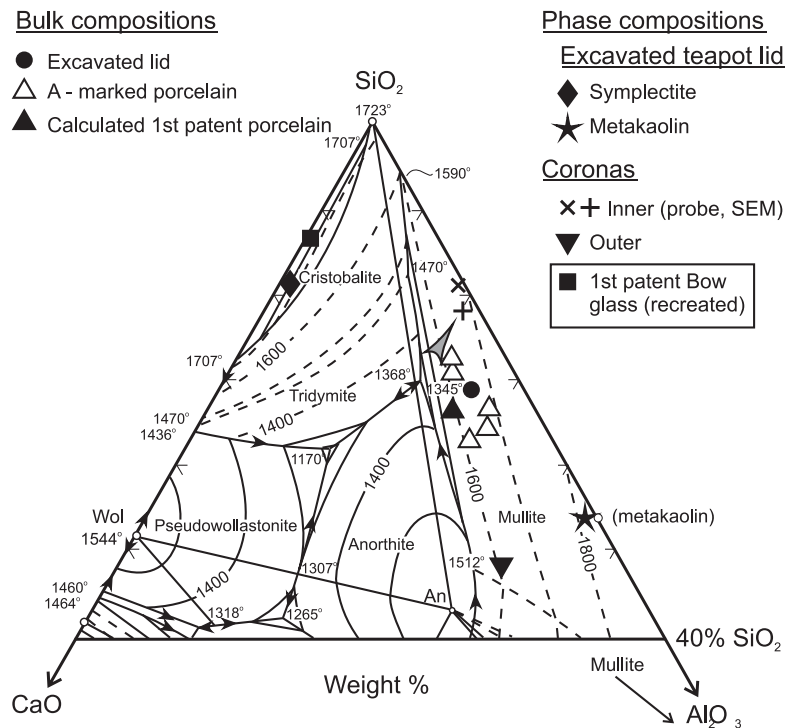


Figure 6. Displacement of melt compositions (see grey arrow) away from the 1345°C eutectic on the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ phase diagram (Osborn and Muan 1960). The melt phase, represented by inner (glass) coronas in this 1st patent ('A-marked') Bow porcelain teapot lid, changed to more Ca-poor compositions as labradorite in the surrounding (outer) corona (Fig. 5) formed. Modified after Owen (2012).

on the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ phase diagram (Fig. 6). The composition of the inner coronas is co-linear with the 1345°C eutectic and the CaO apex of the diagram, confirming that melting occurred at the thermal minimum. The extent to which the presence of alkalis suppressed this eutectic, however, is not known. The feldspathic coronas are porous, so must be a subsolidus feature (i.e. formed during cooling).

Archaeological glass rarely if ever preserves unmelted batch ingredients. Soda-lime waste glass from glassworks sites commonly contains (pseudo?)wollastonite, but this evidently formed as the molten glass cooled. Distinguishing glass produced at these glassworks from cullet added to glass batches can be problematic. Since cullet commonly included exotic broken glass as well as waste glass produced at the factory itself, this material can mislead as easily as inform archaeologists seeking to characterize the wares produced at particular glassworks. So too can melted pieces of the furnaces in which glass batches were fired. For example, black glass rinds (Fig. 7A) on what are inferred to be parts of the rock base of a furnace at Caledonia Springs, Ontario, the location of one of Canada's first known glassworks and one that advertised for workers familiar with blowing black glass, proved to have compositions coinciding with the rock itself. The rock shown in Figure 7B is fused to a brick, and contains silicate and oxide minerals (calcic plagioclase, (pseudo)wollastonite, diopside, Fe-olivine and pleonaste; Fig. 8); it compositionally corresponds to a calcareous mudstone with subordinate, disrupted, dark metapelite layers (Fig. 7B). Unlike any metamorphic rock formed naturally, it is vesicular (Fig. 7A, B). It is essentially a man-made migmatite, a product of pyrometamorphism related to kiln-firing. Based on plagioclase-melt and Ol-Cpx thermometry, it evidently formed at $T > 1000^\circ\text{C}$ at 1 bar pressure (Owen and Culhane 2005). As usual, caution should be exercised when applying mineral- and mineral-melt thermometers to ceramics and related materials (in this case, a rock from the kiln), given evidence for disequilibrium (e.g. quench crystals; Fig. 8) in these wares. A minimum temperature of

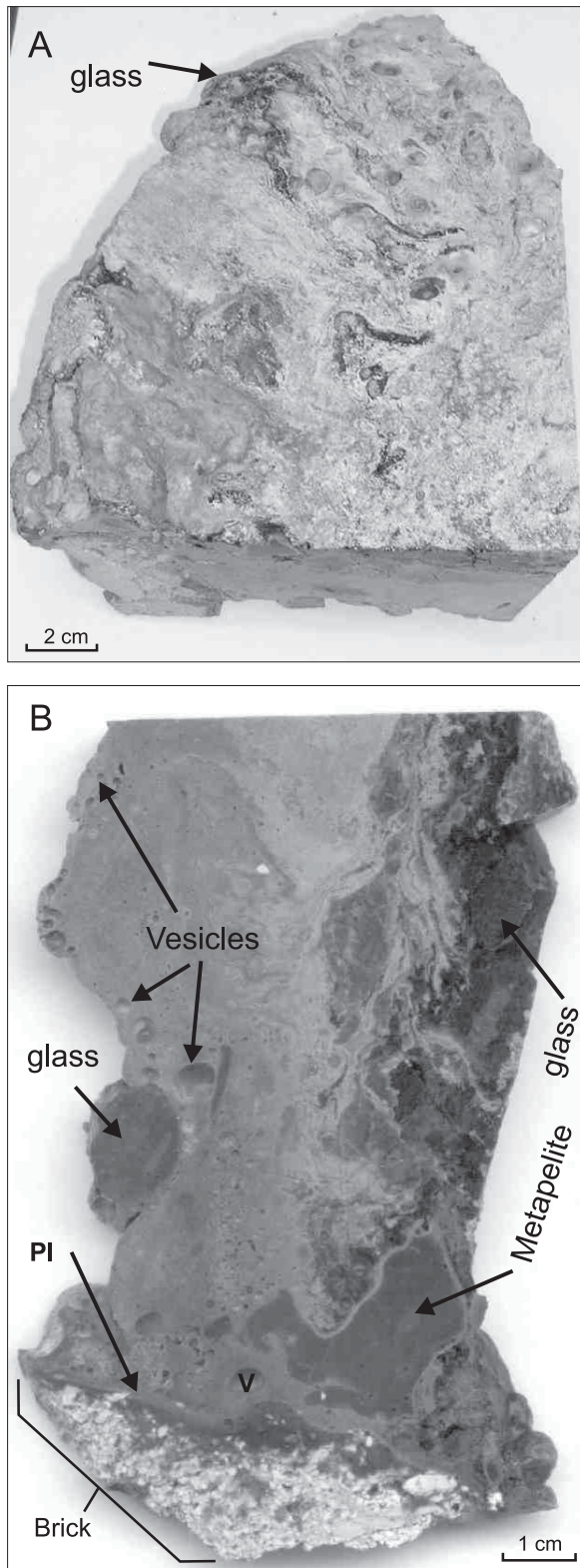


Figure 7. Photographs of a partly melted, vesicular, calcareous metamudstone from a 19th century glass furnace at Caledonia Springs, Ontario, showing (A) the partial glass rind coating (especially conspicuous at arrow) the surface of grey calcareous metamudstone from Caledonia Springs, and (B) the same sample in cross section, revealing a broken brick fused to the grey rock by a narrow layer of plagioclase (Pl)-bearing glass, the thicker black glass rind on the rock, disrupted black rock (metapelite) layer, and vesicles (V) in the rock. Modified after Owen and Culhane (2005).

~1000°C is nonetheless consistent both with the extensive melting of this specimen, and with what is known about the firing conditions that were routinely achieved in historical kilns. Until they were analysed, the black glass rinds on these rocks and bricks were considered to be *bona fide* Caledonia Springs glass, intact examples of which still elude identification.

For What Was It Used?

The purpose for which particular ceramic and glass artifacts were originally used can often be surmised simply based on the form of (reconstructed) objects. It may not be obvious, however, what specific materials individual vessels once held. However, residues of these materials are sometimes preserved on sherds of these vessels, and their compositions can help identify them. Various types of organic residue have been recovered from ancient ceramic vessels, including amino acids, waxes, cholesterol and fatty acids. Attention has focused on the latter because of their stability (although they are still subject to decomposition), ease of extraction from the artifact, and the widespread availability of instruments required for their analysis (Eerkins 2007). Analysis of fatty acids has led to the identification of the original contents of vessels, and this in turn places constraints on the diet of ancient peoples, and helps to identify the character of some of the other materials they used in their daily lives (e.g. glue; Mitkidou et al. 2008). These specialized analyses have revolutionized the investigation of ancient ceramics, and by shedding light on aspects of the day-to-day activities of our early ancestors, address one of the main objectives of archaeologists.

CONCLUSIONS

Geologists have long contributed to archaeological studies of lithic artifacts, particularly with respect to the source of raw materials used in their production. Increasingly, archaeologists are consulting geologists (and other scientists) about ceramics and glass, which can be likened to synthetic rocks (metamorphic rocks in the case of ceramics; obsidian in the case of glass). High-fired wares can be objectively classified based on their chemical com-

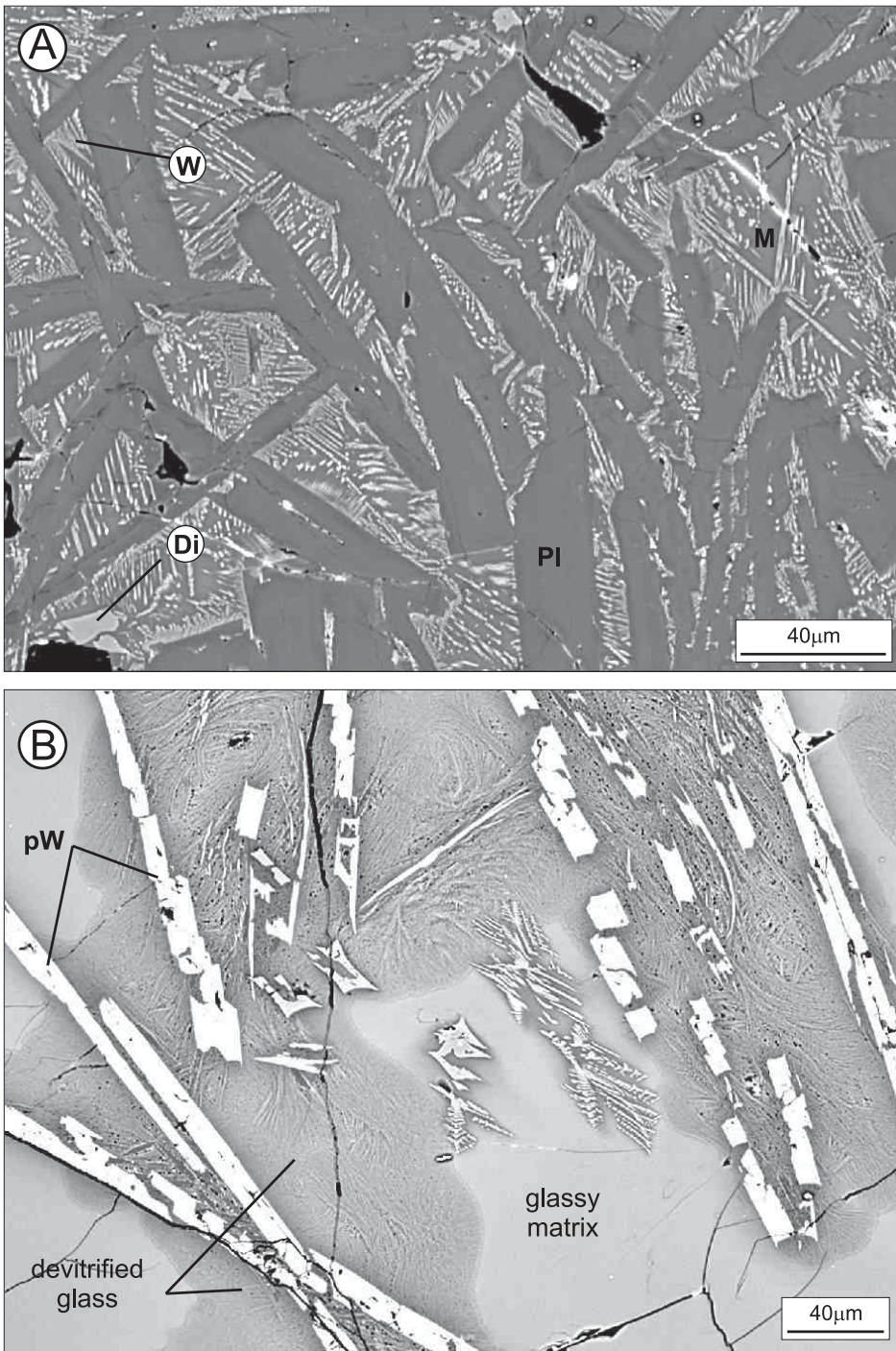


Figure 8. Backscattered electron images of mineral assemblages in calcareous metamudstone from Caledonia Springs showing (A) dendritic, quenched (pseudo)wollastonite (W) nucleated on plagioclase (labradorite, Pl) microphe-nocrysts set in a glassy matrix (M). Note the diopside microphenocryst (Di); and (B) quenched (pseudo)wollastonite microphenocrysts enclosed by partly devitrified glass. Modified after Owen and Culhane (2005).

position in much the same way as volcanic rocks, which, like vitrified ceramics, can contain both crystalline and glass phases.

The expertise that we, as geologists, acquire during the course of our

careers provides us with a unique perspective on these media, as well as the knowledge and means to analyse them. We are not trained to properly excavate archaeological artifacts, and shouldn't, but we can work on them once they

arrive at our lab. The burgeoning collaboration between archaeologists and geologists is but one example of the increasingly cross-disciplinary aspect of scientific research. For academics facing diminishing research funding, one of the appealing aspects of investigating archaeological artifacts is that it can be done in a cost-effective manner. Archaeologists do the field work; we can do some of the analyses, and in many instances, the analysis of a single, informative artifact can produce significant, publishable results. Perhaps more importantly, collaboration with archaeologists not only broadens our horizons, it provides an opportunity to expand the application of the skills we have honed while working on more traditional geological projects, and provides additional information on artifacts that otherwise would not have been discovered.

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