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ANTHROPOLOGY

CALCIUM CARBONATE INCLUSIONS IN POTTERY: SOME CAUTIONS FOR THE ARCHAEOLOGIST

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Studies of original firing temperature of pottery based on thermal properties of calcium carbonate and cultural inferences about potters' capabilities derived from such studies must be examined in the context of other intervening variables. These variables include original firing atmosphere, length of firing, size and concentration of the carbonate inclusions.

† † †

The presence of calcium carbonate inclusions in pottery chiefly in the form of limestone, calcite, and shell, has for some time: 1) afforded a convenient gauge for estimating the original firing temperature of a ceramic piece (Tite, 1969:14; Kidder and Shepard, 1936:425-427); and 2) provided a basis for statements about limitations on firing temperature of primitive pottery which contains carbonate inclusions (Shepard, 1956:30, 1952:265, 1940:271; Colton, 1953:26). While such studies are meritorious in their own right and while they may have a scientific basis, they seldom consider some important variables and can, therefore, be dangerously oversimplifying. In view of the increasing attention being given to studies of ancient ceramic technology and in view of the widespread use of carbonate tempers and calcereous clays in primitive pottery, it is my intent to present some of the commonly glossed-over variables and to detail some of the fallacies associated with carbonate-inclusion analysis.

The estimation of original firing temperature from calcium carbonate is related to the distinctive properties which this mineral displays upon heating. Calcium carbonate (CaCO_3) decomposes rapidly to Calcium Oxide (CaO) with the emission of carbon dioxide in the 750°C - 850°C temperature range (Tite, 1972:229). The calcined calcium oxide is very porous and will absorb moisture from the air to form calcium hydroxide (Ca(OH)_2), which can combine with atmospheric carbon dioxide to reform calcium carbonate. Unaltered calcium carbonate differs in appearance from recarbonated calcium carbonate, the latter taking on a cryptocrystalline structure as opposed to a coarsely crystalline structure for the former. The presence of calcium carbonate which has not altered to CaO or Ca(OH)_2 is generally taken to indicate that the temperature of calcination was not reached and that the ceramic piece was probably originally fired below 800°C , while large calcined fragments indicate a firing temperature above 800°C - 850°C .

The formation of calcium hydroxide (Ca(OH)_2) from calcium oxide (CaO) is accompanied by a large expansion, and sufficient pressure can be developed to disrupt the fired product (Lawrence, 1972:35-36). This "lime-popping" is most evident on the vessel surface and can be structurally damaging to the vessel to the point that it crumbles. Because lime-popping occurs around 800°C in an *oxidizing* atmosphere, it is understandable that investigators might acknowledge the use of calcium carbonate inclusions in ancient pottery as setting stringent limitations on firing temperature (for example, Hammond, 1971:16; Colton, 1953:26; Shepard, 1940:276). In other words, the ceramic vessel would have to have been fired below the temperature at which calcium oxide and calcium hydroxide form.

Several factors which prevent precise statements of original firing temperature and potters' limitations (in regard to carbonate inclusions) are: initial firing atmosphere; duration of firing; size and concentration of the carbonate particles. These variables to a large extent influence at what temperature the conversion of calcium carbonate will occur, if the conversion will indeed occur, and if it does occur, the extent of structural weakness to the vessel.

It is well-known among brick manufacturers that "lime-popping" tendencies are significantly influenced by kiln atmosphere in that an environment of abundant oxygen produces more "lime-popping" than an environment deficient in oxygen (Houseman and Koenig, 1971:79-80). Hence, in a smoky fire with an excess of carbon monoxide or carbon from fuel combustion, the rate of calcination with strongly reducing gases would be retarded or calcination might not occur at all.

Laboratory experiments at the University of Utah Archaeometry Laboratory bear this out. Two groups of wafers made from the same raw clay (Kaolinite with some palygorskite and sepiolite), containing the same amounts of limestone temper, were fired separately under conditions of oxidation (group A) and reduction (group B). The wafers were fired in an electric-resistance furnace at 50°C increments, beginning at 700°C and continuing up to 1050°C (above

which the clay vitrifies). Reducing conditions were created by pulverizing block graphite and totally immersing the wafer in the powder, preventing oxygen from reaching the wafer. Group A oxidized wafers began disintegrating at 800°C and continued doing so when fired to 850°C and 900°C. Beyond 900°C these wafers did not evidence any calcination or "lime-popping." Evidently, these higher temperatures were sufficiently high to cause the calcium oxide to fuse with the clay, forming calcium aluminosilicates. These silicates, which form above 850°C, render the calcium oxide completely unreactive and insoluble (Lawrence, 1972:35-36; Matson, 1943:85-86), while, at the same time, they increase the strength of the ceramic body (Grim, 1962:268). All the reduced group B wafers failed to show any calcination and "lime-popping." Between 800°-900° these wafers failed to crumble because an excess of carbon dioxide prevented the reaction of calcium carbonate to calcium oxide. Beyond 900°C aluminosilicates were formed. In the above experiment, had the calcite inclusions been of greater size or concentration, the reduced wafers would have calcined, but at temperatures 50°-100°C above those wafers fired under oxidizing conditions (studies in the Archaeometry Laboratory also bear this out).

Clearly, any estimations of original firing temperature based on whether calcium carbonate had converted to calcium oxide and calcium hydroxide would have to consider the primitive firing atmosphere of the ceramics being studied. A calcite-tempered sherd originally fired to 900°C in a smoky, reducing atmosphere might still contain unaltered calcium carbonate, while the same piece receiving sufficient oxygen might have calcined at 800°C. At best, statements of original firing temperature using the calcium carbonate/calcium oxide/calcium hydroxide indicator must be limited to broad temperature ranges and can perhaps be most effectively used to supplement firing temperature studies employing other means (see Leicht, 1975:126).

Also, in light of the high-temperature phases which calcium oxides can display in the form of aluminosilicates, it is meaningless to talk about pottery-bearing calcium carbonate inclusions as being restricted to firing temperatures below those which cause calcination. Under sufficient oxygen deprivation, a shell, limestone, or calcite-tempered vessel can be fired to vitrification without incurring any structural damage or evidence of "lime-popping." Undoubtedly, many primitive firings were neutral and reducing, so the firing of carbonate-inclusion pottery above a critical temperature would have been less of a problem to the potter than is usually supposed. It is conceivable that limited oxidation would have been sought by the ancient ceramist, not necessarily for reasons of fuel economy, but for reasons relating to the bearing power (strength) of a vessel and/or its final color when fired under the right atmospheric conditions.

The length of firing time influences the rate of reactions which occur in the carbonates. At any particular temperature

high enough to cause calcination, a relatively longer duration of firing will result in more crystal dissociation than will a relatively shorter rate of firing. In fact, it is not uncommon to observe sherd cross-sections in which the central core has unaltered calcium carbonate, while the area near the surface contains calcium carbonate which has dissociated. The difference is due to a time/temperature/atmosphere differential in the interior and near the surface. Because original firing time is an imponderable in ceramic technology, one cannot be certain whether milky-white calcined calcite crystals were fired to, for example, 750°C for one hour or 850°C for five minutes. The investigator can at best only approximate a possible temperature range in which the pieces could have been fired.

The size of the carbonate grains in the clay body exerts a strong influence on the extent of structural disturbance a vessel displays when heated to the temperature where calcium carbonate breaks down to calcium oxide. Finely divided calcite, limestone, or shell fractions (for example, less than 0.05mm) when calcined will react with water vapor to form calcium hydroxide and, subsequently, a cryptocrystalline form of calcium carbonate. No "lime-popping" will accompany the hydration of these smaller particles; whereas, larger grains will exhibit popping to the extent that the vessel surface might disintegrate from expansion pressure of the larger grains. Because of the fineness of various types of carbonate crystals which occur naturally as accessory constituents in many clays, it is possible to fire these clays above temperatures of carbonate dissociation without harmful effects to the vessel (even under conditions of strict oxidation). Very often, however, the carbonate tempers added by potters are larger than the natural carbonate inclusions and may physically harm the fired product if they are calcined and hydrated. The structural damage caused by calcination will also be a function of the density of the carbonate particles, especially if the particles are relatively large. Experiments in our laboratory show that a shell or limestone concentration in the order of 10% of total clay volume will (if the grains are over 1.0mm in length) do less structural damage than if the same particles are in the order of 30% or more density.

Because of the various factors which govern the temperature of calcium carbonate dissociation and the extent of the dissociation, it is not possible to arrive at precise statements of original firing temperature solely on the basis of carbonate thermal properties. If the factors of atmosphere, grain size, and inclusion concentration can be controlled, an approximation of gross firing temperature range can be achieved for a given ceramic piece. However, such approximations must necessarily be only suggestive in view of the difficulty of obtaining an accurate determination of the duration of firing. After a consideration of appropriate variables, an investigator might be justified in making a statement that his originally oxidized sherds that show no evidence of calcination were originally fired below 800°C, or that his strong-

ly reduced ceramics that show evidence of calcium aluminosilicates were originally fired above 850°C. At no time, however, would he be justified in advancing as fact that all the sherds in his lot with unaltered calcium carbonate were fired below 800°C; nor would he be justified in supposing that sherds exhibiting dissociated calcium carbonate were a potter's mistake and were structurally unsound, especially if the calcium carbonate particles were initially small and sparsely scattered.

In areas where easy access made some form of calcium carbonate a desired tempering material, it is very probable that primitive ceramists, at even the most rudimentary level of pottery making, would quickly learn about the pyrochemical properties of the material. While the potter would doubtless be unaware of the actual reactions taking place in his heated wares, he would know from experience that by firing in a smoky, reducing, or oxygen-starved atmosphere, he could reduce vessel breakage or weakness caused by "lime-popping" and he could pay less attention to actual firing-temperature limits. He would also know that if he ground his shell, calcite, or limestone finely enough, the damaging effects of "lime-popping" could be minimized or avoided completely.

Archaeologically, we may never know how many vessels were destroyed by thermal changes in calcium carbonate because these vessels would have disintegrated within a few weeks of their manufacture (Shepard, 1956:30). However, we can observe, in an archaeological context, carbonate-tempered sherds in which the carbonate has dissociated or even popped, but which remain structurally sound—a phenomenon which seems enigmatic if one supposes that carbonate inclusions impose strict limits on firing temperature (see Shepard, 1940: 271). It is not puzzling if the investigator realizes the various circumstances under which the detrimental effects of "lime-popping" can be attenuated. If these conditions are recognized by the investigator, then misleading conclusions relating to the potter's technology can be avoided. Indeed, altered calcium carbonate and "lime-popping," rather than being attributed to lack of control and skill on the part of the potter, might more realistically be attributed to a potter's ingenuity and expertise which permitted his carbonate-tempered pottery to be fired to any temperature without structural damage.

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