Noah Wiener
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<u>The Plaster and Mortar of Greene Farm</u>

Introduction

The excavations at Greene Farm, first owned by Surgeon John Greene in the early seventeenth century, reveal information about both general architectural materials used in Colonial New England, and improvised materials used to build on new land. The Old House on the property is the first residence in Warwick, and as such can be used as a study of improvisational colonial resource use as well as contemporary New England architecture.

The time period of the house's construction is a turning point in the creation of mortar and plaster, because around this time limestone was first used in Rhode Island to make lime putty, the binder in mortar and plaster[1], though judging by the quantity of shell fragments in the samples, it would appear that the colonists did not have access to the new quarried material[2]. Also, as most houses had an almost entirely wooden structure, mortar, plaster, and brick were often used only for the chimney. Judging by the sheer mass excavated, the Old House is unique in construction, as the quantities of mortar and plaster are far greater than needed for just a chimney, and would have been used in cellar construction, or perhaps throughout the building's structure.

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[1] Garvin, James L. "While glacial clay provided ample raw material for brickmaking, the lime necessary to lay weatherproof brick walls was at first hard to obtain in the Northeast. Accounts suggest that until the early 1700s, when stone lime began to be generally accessible along the New England coast, lime was frequently obtained by calcining (heating) oyster shells. Crushed shells also were added to stone lime to extend this valuable product. Lime was discovered in Rhode Island in 1660, and in northern Massachusetts in 1697, and in Thomaston, Maine, about 1730. Following each discovery, lime kilns were immediately constructed to meet the needs of the region. Despite its availability, however, lime was largely used in making plaster and in building the exposed portions of chimneys, not in constructing brick dwellings. These remained rare until after 1800." Page 54.
[2] See the methods section, which suggests using radiocarbon dating to truly decide whether limestone was used in the creation.

This study examines characteristics of the mortar and plaster samples found by contrasting them with each other and comparing samples of different colors (implying different sand types) through an examination of the binder to aggregate ratio, a comparison of the material inclusions, cataloguing of elemental composition, and studies of the differing compositions of the flatter edges of plaster.

Material Descriptions

Our samples of mortar and plaster are a combination of lime putty and aggregate.[3] The samples are divided into four groups: White plaster, darker plaster, lighter mortar, and darker plaster.[4] The flat edge of the white plaster is the most uniform substance, and is generally the least given to crumble. The darker plaster is still less crumbly than the mortar samples (especially the flat side) and has more inclusions, cracks, and varied coloring than the white plaster. The mortar samples as a whole are very rough, and tend to crumble quite easily, as their exterior is more quartz based than aggregate. The whitish mortar samples (darker than the white plaster—the mortar tends to be a bit
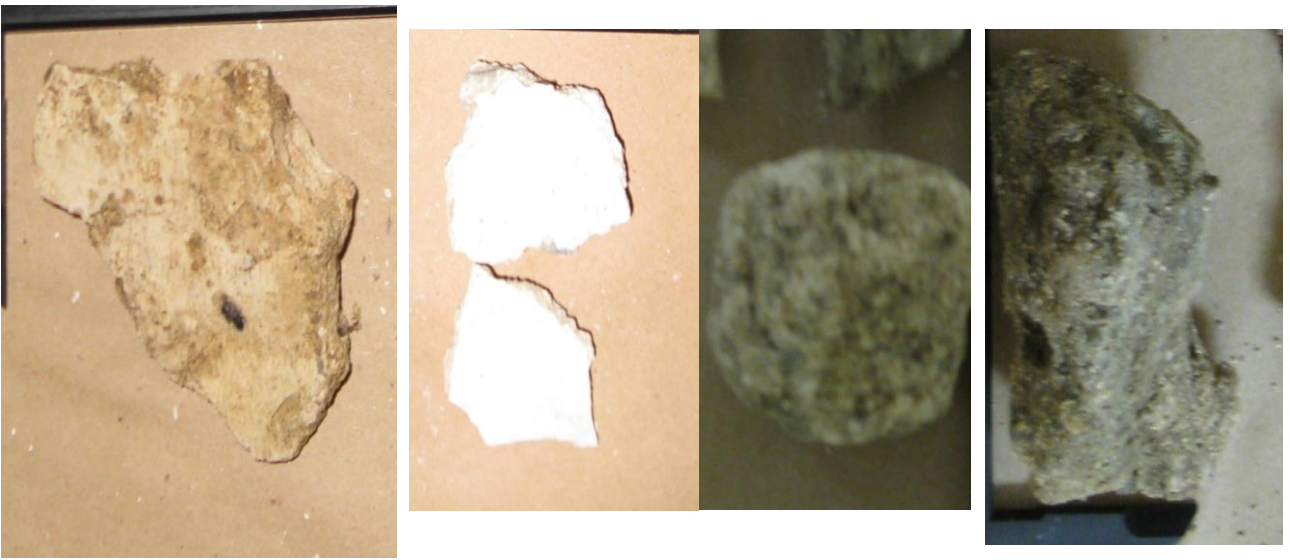
darker) vary greatly in numbers of inclusions, but the dark mortar samples have the most consistently large mineral inclusions within. The whiter samples appear to have the most shell inclusions. There are samples still attached to brick, shell, and slate, and these vary between shades of mortar, but we have very few plaster pieces that are attached to any foreign materials.
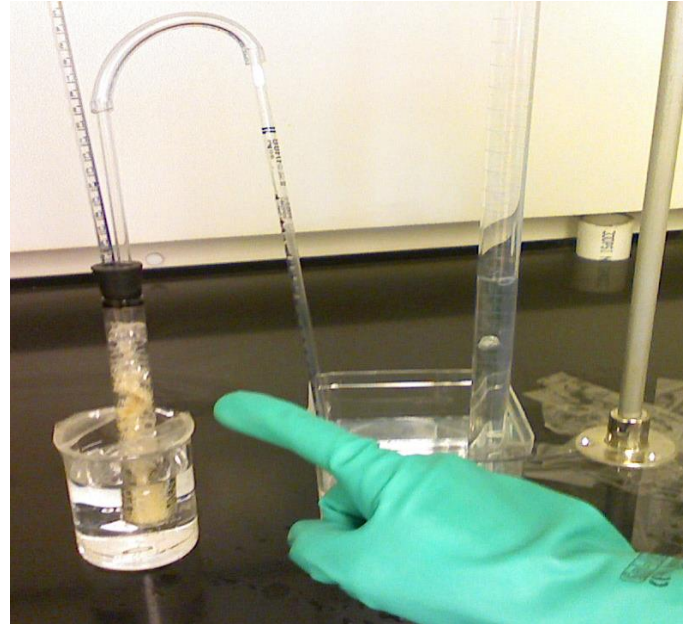
Methods

There are several means by which mortar and plaster can be examined.   The first method is simple petrographic analysis using a high-powered optical microscope, in order to examine closely how homogenous the surfaces of the samples are, as well as to view the individual components of the aggregates.

The next method of analysis involves the usage of hydrochloric acid to dissolve the binders in the mortar, in order to separate out the sand for individual analysis, as well as get volumetric values for aggregate versus binder. Average historical mortar samples are usually feature a ratio of around two-thirds aggregate and one third binder material, to make up for the fact that one third of the volume of average-sized sand is air space that can be filled with putty. This analysis can be improved on by collecting the CO_2 gas from the reaction, in order to see how much evaporates into CO_2 (the binder), how much sand is left behind (the aggregate), and how much material simply is left behind in an aqueous solution. If at least ten percent of the volume is becomes aqueous, this probably means that the sample in question is hydraulic, based in the quantity of complex silicates.[5] The process that I am using to dissolve the carbonates is a modified combination of the techniques of Donald L. Pile, Alana S. Benjamin, Klaus S. Lackner,

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[5] Stewart, John and James Moore

Christopher H. Wendt, and Darryl P. Butt[6], and Hanna Jedrzejewska.[7] This process will be useful for determining the volumetric quantities, and as a result, is telling about the size and structure of the sand used, as well as the composition and making of the aggregate.

Before the chemical test could be completed, the larger chunks of shell were removed from the aggregate, and their masses recorded. As the shells were part of the aggregate, but contain high amounts of carbonates, they would interfere with precise results in these tests. The chemical tests done on the Greene Farm mortar and plaster involved a modified version of the Jedrzejewska apparatus. The test tube is filled with a .1-.15 gram sample, and the initial height of the water level in the buret is recorded. The pipette then releases 1 mL of 6M HCl into the test tube, and a resulting CO2 gas is sent through the tubing to the buret. As the binder is mostly calcium carbonate, the acid in the following reaction dissolves it: $CaCO_3(s) + 2HCl(l) \rightarrow Ca_{2+}(aq) + 2Cl^-(aq) + H_2O(l) + CO_2(g)$[8]. The quantity of gas can be used to determine the mass of calcium carbonate/binder. The remains in the test tubes are put in an ultrasonic bath, and are then decanted with water and alcohol, dried, and then weighed to determine mass of the aggregate.

[6] Donald L. Pile, Alana S. Benjamin, Klaus S. Lackner, Christopher H. Wendt, and Darryl P. Butt
[7] Jedrzejewska, Hanna
[8] Donald L. Pile, Alana S. Benjamin, Klaus S. Lackner, Christopher H. Wendt, and Darryl P. Butt

The next comparative study of mortars and plasters was conducted with a handheld X Ray Fluorescence unit, which allows for an examination of some of the elemental composition of the substances. While it is not as detailed as a fuller XRF test, it allowed for a basic compositional comparison. Lacking in silicates and many other major element groups makes this test useful only for qualitative comparisons. For a fuller examination of mortar and plaster samples, I suggest conducting full XRF tests to get better results for composition.

Thin-section analysis was conducted on a piece of white plaster. Ideally thin samples would have been prepared for all sample types, but in the given time, only one sample received this treatment. There are particular difficulties with making thin sections of mortars and plasters, due to the fact that water cannot touch the sample. The sample is prepared with layered C:D epoxy, and polished on increasingly fine surfaces using mineral oil and acetone. The thin section allows for sample viewing under SEM/EDS[9], and, more importantly, allows for compositional analysis using polarized lenses on optical microscopes. Individual substances appear as different colors when a "polarizer" is put below the slide above the light, and an "analyzer" is put perpendicular to the polarizer, but above the specimen below the upper light source.[10] Based in the ability for light to penetrate the thin section we can identify particular inclusions as isotropic (including substances like glass) or anisotropic (such as quartz), depending on whether or not light travels through the substance at a single velocity. Isotropic substances appear as clear or black when examined with interference colored lenses, whereas anisotropic

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[9] The vacuum created by the SEM can pull mineral oil out of the thin section, leading to extremely charged and not especially high quality SEM pictures. If possible, make the section as thin as possible, and wash it with acetone and dry it many, many times to remove as much oil as possible for several days prior to using the SEM.

[10] Delly, John Gustav.

appear colored based on the differences between their refractive indices. Since the retardation of the colors appears uniquely different for each mineral type at particular thickness, using a birefringence chart, one can identify the components of a thin section. Not only does thin section allow for closer examinations of the individual components, it allows us to see structurally the non-sand aggregate substances, and their relative quantities, in good detail.

There are several other useful ways to test historical mortar and plaster samples that this experiment could not include for time or cost reasons. Beyond more in-depth XRF and thin section preparation, ICP-MS (Inductively coupled plasma mass spectrometry) could give a more accurate compositional analysis, and radiocarbon dating could tell us about the makeup of the binder,[11] specifically whether it was made entirely from the shells excavated, or if quarried limestone was used in putty production. The final important qualitative tests that could be completed for a comparison of the mortar and plaster samples to each other, and to other contemporary, ancient, or modern samples, would be hardness tests, which have a standardized scale and can therefore be used to compare the samples accurately with samples from other periods, or sites.

Results

Initial observations of the materials, using a non-polarized optical microscope, revealed several differences in the nature of the samples. The fact that the darker samples had larger quantities of mineral inclusions, but the whiter samples had more shell inclusions suggests compensation for the strengths and weaknesses of differing sand

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[11] If the samples dated to 800 years old, that would suggest that the binder was made from shell, as ocean samples tend to come up 400 years older than the shells, which were probably removed from the ocean about 400 years ago. If the binder was constructed from limestone, the binder would come out quite a bit older than 800 years in radiocarbon dating. From conversation with Yongsong Huang, Brown University GeoChem professor.

types, creation by different masons, or varying composition based in function. Despite the large amount of movement over time from wall-fall and erosion, the last idea seems least likely, as the samples were generally found mixed together without contextual or stratigraphic differences between locations of varying sample types.

The XRF displayed some interesting comparative studies on the samples. The general trend of materials seemed more uniform within mortar and plaster, and the color of sample seemed secondary. For example, the plasters had more sulfur than the mortars, with the highest amount of sulphur in the white plaster, followed by the dark plaster, followed by the white mortar. The dark plaster had the least.   Calcium and Iodine had the same order of frequencies as sulphur. This confirms the ideas that sample types share more characteristics with themselves than the like-colored pieces made with similar sands. The exception in XRF was iron, but with the varying amounts of iron in the surrounding soils, it can be assumed that the iron quantities have more to do with the location of the finds than mortar/plaster building materials. Potassium and Titanium were found mostly in the darker mortars. While silicates and many other important elements are not caught by the XRF, ones like calcium, (a component in calcium carbonate) a major constituent of the binders, gives ideas about binder to aggregate ratios in the various samples, and the high readings on the flat sides of the plasters, along with their less crystally surfaces, suggests that there may be more binders flattened out to create the surface of the plaster, with less aggregate put on one side. The white mortar samples were generally more similar to the plasters than the dark mortar.

Preparation for the acid digestion of the samples involved crushing the samples, and separating out as much shell from the samples as possible, to avoid misinterpretation

of the quantities calcium carbonate. Preparations of ten gram samples were made of each, and shells were removed as best as possible.[12] The samples that were used displayed certain unique characteristics. The dark mortar had the most orange inclusions, suggesting iron deposits in the sample. The white mortar had the most shell inclusions, making up over twenty percent of the mass of the sample. The white plaster had approximately four percent of its volume in shell, and the darker samples had negligible shell quantities. The amount of shell in the white mortar may have led to surprisingly large amounts of CO_2 released, as not all of it may have been digested by the HCl. The materials were sifted into several screens, and the darker samples had a higher concentration of extremely fine sand, though this may have come from the fact that a smaller percentage of the 10 grams of darker samples were composed of large inclusions.

The initial tests, designed to test the apparatus and get a sense of the quantities of gas released, were done with inaccurately weighed samples, but they gave an idea of the quantities of CO_2 that would be released. The white mortars and plasters released over three times as much gas as the dark mortar, and the dark plaster released about twice as much as the dark mortar.

Next, using properly weighed samples, five tests were done on each of the materials. The quantity of gas released was added up and divided by the total initial mass of the 5 samples, to get an overall picture of the results. 0.632 grams of dark plaster produced 91.8 mL of gas, .660 grams of white plaster produced 104.0 mL of gas, .672 grams of white mortar produced 116.8 mL of gas, and .705 grams of dark mortar

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[12] As the samples varied greatly in inclusions, the data presented for quantity of sand refers only to the samples used in the acid digestion, and is not meant to be representative for overall information on shell quantities. Still, it is important to note in the context of evaluating the results of the chemical tests done on these samples.

produced 58.3 mL of gas. The ratios of milliliters of gas per gram are shown in the following chart:

mL/g
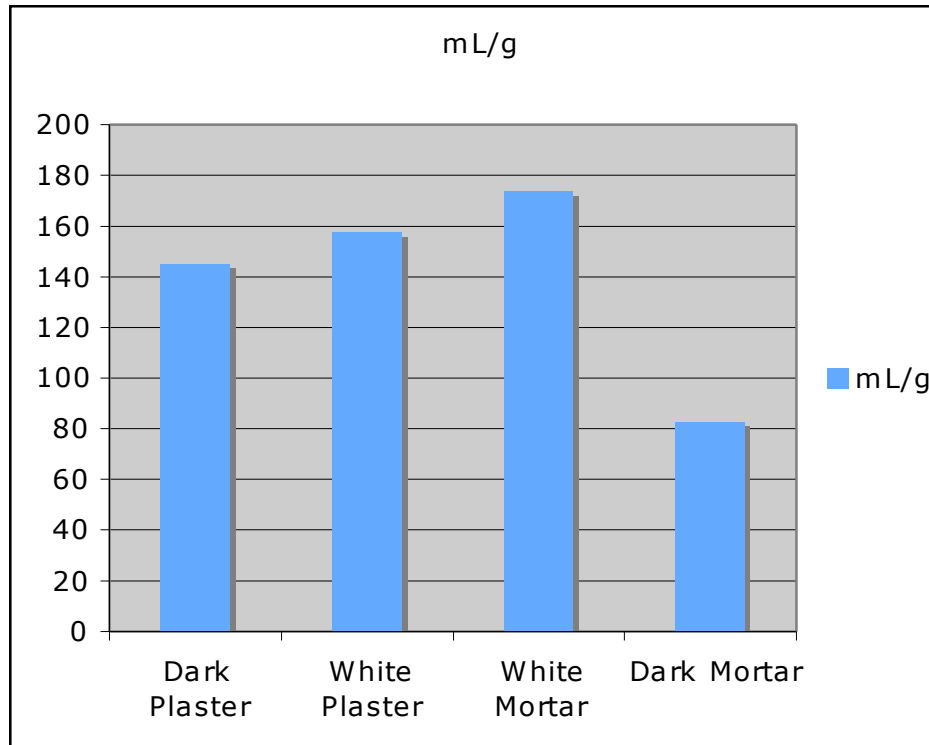
This data could be unrepresentative of the overall amounts of calcium carbonate for a few reasons. The first is that some of the samples (especially white mortar) may have had a bit of shell remaining from the aggregate, and as a result may have an inflated amount of binder according to the chemical tests. Also, the particular sample of dark mortar had more iron than most, and as a result (since iron is a heavy substance) there were less than ten grams of aggregate/binder, deflating the quantity of dark mortar binder. Still, these results make sense with the petrographic evaluations, in which quartz was seen extending most from the dark mortar, with less binder visible than in the other substances.

Donald L. Pile, Alana S. Benjamin, Klaus S. Lackner, Christopher H. Wendt, and Darryl P. Butt outline a means for converting collected gas volumes into a mass of

calcium carbonate digested.[13] For this experiment, there are a great number of variables

that would potentially make this inaccurate, due to the fact that the device created for this

experiment was a modified version of theirs, and as a result the gas collected was done

for a qualitative comparison rather than a quantitative mass. Not only was the device

modified (there was only one gas collecting area, the secondary tube was so thin that the

quantities of gas in it were negligible), there were also some other uncertainties. One can

estimate that the pressure in the lab (outside the buret) would be approximately 100025

Pa,[14] but this is not exact enough to get specific data, as the changing pressure in the

buret is calculated from this pressure. Lastly, the temperature of the water baths was not

checked after each measurement, and as a result may have had a slight effect on the gas

pressure. While all of these are very small issues when considering the volume of gas

collected, they are just large enough to throw off certain calculations necessary for the

mass of the CO_2.

The test tubes were decanted using alcohol and water into weighed tin-foil

containers, and were set in an oven overnight dry. This yielded surprising results. Some

of the remains on the foil weigh over .05 grams less than their original sample, and some

actually weigh more than the original, due to aqueous byproducts of the reaction

remaining as the liquid evaporated. Strangely, as much as there are great differences in

byproduct quantities, there were unexpected trends. The mortars generally gained mass,

whereas the plasters generally ended up with less mass on the tinfoil than in the original

sample. This is a seemingly counterintuitive trend, as the dark mortar produced the least

gas, and the white mortar produced the most, so it seems odd that they are grouped

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[13] Donald L. Pile, Alana S. Benjamin, Klaus S. Lackner, Christopher H. Wendt, and Darryl P. Butt

[14] The lab's altitude is approximately 130 feet above sea level.

together. The mortars could have a larger quantity of aggregate than the plasters (which would seem to be the case from optical microscopy), and the reason that the white mortar produced so much gas is due to the quantity of shell/concentrated calcium carbonate in the aggregate, with a smaller amount of putty absorbed by the acid. This would leave a high amount of aggregate behind, though not quite as much as the dark mortars, which left the largest quantity of sand behind. Regardless of the cause, it is enough of an unknown that we must consider these conclusions to be merely inferences, and look to the conclusions that can be drawn from these tests—that the dark mortars have the highest aggregate to binder ratio, and that the white mortar has the largest quantity of shell in the aggregate. As a whole, it is clear that the plasters have a high quantity of binder that was turned into CO_2, leaving the smallest amount of non-carbonate aggregate behind.

A thin section analysis was conducted only on one piece of white plaster, though for a fuller examination of historical mortars and plasters, one must do this study on both materials. The plaster was selected because of its high inclusion content, a firmer consistency, [15] and the ability to examine the creation of the flat edge of plaster. After much polishing, SEM microscopy was attempted, with some problems. The vacuum caused the tiny amounts of mineral oil in the sample to charge the entire area, making photography and compositional analysis/EDS difficult. Still, some useful photographs were taken of inclusions, including a few highly zoomed shots of non-calcinated shell fragments and quartz grains. See the attached SEM photography for a view of the plaster sample.

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[15] Thin section creation for mortar and plaster is extremely slow and difficult, compared to other thin section analyses, as the samples cannot be exposed to water in the polishing or cutting process. As a result, firmer samples are easier to section.

The thin section's primary purpose was to be viewed through polarized light sources in order to determine the minerals using birefringence. Please see the images on the wiki while reading this paper. The first two images (black and white) taken show a good deal of mineral inclusions. The surfaces are mostly quartz, and the 'striped' surfaces are feldspar. The sand used in the sample, while appearing relatively uniform with several types of inclusions, features only a few types of mineral inclusions, and has multiple sand types. The patch on the bottom right of the first four images is actually a more clay-based sand, rather than a separate mineral inclusion. Shell fragments can be seen in several parts of the slide. One interesting note about the sand grains is that they are relatively large (and contain feldspar), indicating that the sand was probably brought from a faster flowing water source to somewhere near Greene Farm, as the settlers presumably would not have transported the sand great distances. One possible source would be the large quantities of sand at the "Rhode Island desert" in West Greenwich.

The fifth and sixth images are details of feldspar inclusions in the sample, which appear as lined black and white (and blue with polarizing lenses) mineral inclusions. In the next few pictures, the larger white spots are larger quartz inclusions. Images 15-19 show the flat edge of the plaster, along the top half of the images. A white line can be seen near the edge, and this is where the change in material type can be seen. It appears as if the masons took the original samples, wore them down with something, perhaps a cloth or piece of wood, in order to flatten them, and then added a thin layer of extra plaster to smoothly coat the surface, perhaps with a slightly larger quantity of binder.[16] The white line by the edge shows signs of the quartz crystals decoupling and

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[16] Which would explain the larger binder constituents seen in X Ray Fluorescence on the edges of the plaster samples. This theory is backed up by the thin section images featuring finer grain materials in this area.

expanding/recrystalizing near the edge, as water penetrated into the calcium carbonate in the area. As the crystals expand, more water could seep in, and the crystals would continue expanding, in an ongoing process, pushing away the edge of the surface to create the white divide seen in the images.

The study of the mortar and plaster at Greene Farm could benefit from more time and resources put into the test, specifically through making thin sections of several sample types, non-handheld XRF studies of the composition, hardness tests performed on the materials, and radiocarbon/ICP-MS testing on the material types to see accurate composition and lime material. Even without these tests, we have witnessed and catalogued the varying types of sand used in the samples, the types of inclusions in the aggregate—from quartz to shell to feldspar, and relative differences in quantities of aggregate versus binder in several of the substances. It appears that the plasters have a higher quantity of binder, followed by the white mortar, which features disproportionately large quantities of carbonates because of the large amount of shell fragments in the aggregate. The construction at Greene Farm is a unique view of early colonial masonry, and this study of mortar and plaster samples is well supported both by archaeological comparative interpretations and material science evaluative techniques for determining base materials in the aggregate and binder, relative quantities of sample types, and varying inclusion types between the samples.[17]

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