Hydraulicity in ancient mortars: its origin and alteration phenomena under the microscope

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Abstract

Historical hydraulic mortars can comprise different reactive phases involved in the early- and mid-age development of binding properties such as pozzolana, brick powder or other reactive silica and alumina. However, the specific nature of the reactive phases in such binders is rarely clearly identified, particularly when different degradation or weathering patterns, frequently related to the carbonation of the binder, interact with dissolution and precipitation reactions. The question of which binder and aggregate components have contributed to the hydraulicity of a given historic mortar, a key to a better understanding of ancient technologies, is frequently not investigated in the case of mortars which underwent the above mentioned alteration processes. Microscopy provides a powerful analytical technique to determine the type of binders and differentiate between primary and alteration phenomena.

By the example of three groups of binders, namely Roman opus caementitium/cocciopesto mortars from Ephesus (Asia Minor) and Vindobona (Roman Vienna), a 16th C. Ottoman horasan masonry mortar from Budapest, and 19th C. highly hydraulic lime filling mortars from Switzerland, the present article discusses two phenomena frequently observed when dealing with ancient hydraulic mortars: firstly as to the source(s) of hydraulicity of the mortar and secondly, that after a long period of time exposed to moist environments, the binder tends to present an inhomogeneous composition of an impure silica gel separated from calcium carbonate, accompanied by leaching and precipitation of binder constituents.

These two phenomena are illustrated by polarized light microscopy (PLM) and scanning electron microscopy combined with energy-dispersive x-ray spectroscopy (SEM-EDX) and discussed in light of both conservation and understanding of ancient structures as well as how it can be applied to the current issues of alkali-aggregate reaction (AAR) and leaching in modern concretes.

Keywords: historical mortar, hydraulicity, carbonation, leaching, AAR

I. Introduction / Methodology

PLM and SEM-EDX are powerful tools when studying historical mortar samples, especially when used in conjunction on the same polished thin section. This is particularly true when observing the binder and binder-aggregate interaction. While PLM is a quick and convenient first step to visualizing reactive areas, characterizing the reactions and phases involved requires additional instrumental techniques such as SEM-EDX. This research presents two of these observations made from combining these techniques as applied to various types of mortar. One focuses on the potential of siliceous aggregates generally considered inert to contribute to the overall hydraulicity of a mortar; the other on the alteration of highly hydraulic binders, especially evident in applications where the mortar was used in highly humid conditions. Studying these two phenomena is not only useful in the historical or archeological context, but should further the understanding of such issues as alkali-aggregate reaction (AAR) in contemporary structures.

The issue of reactive aggregate was observed across a wide variety of sample types, all of which additionally show signs of binder alteration linked to carbonation and leaching. How these phenomena could be linked will be discussed in the conclusion. Presented here are a number of mortar samples from ancient Roman sites, an Ottoman-era bath from Budapest and a highly hydraulic mortar from the turn of the 20^{th} century. Cocciopesto mortars (such as those from the Roman era discussed here) have been well researched in terms of the interaction at the interface between ceramic fragments and the lime binder; what is presented here is the observation that the binder itself is highly hydraulic throughout, evidence that either the binder

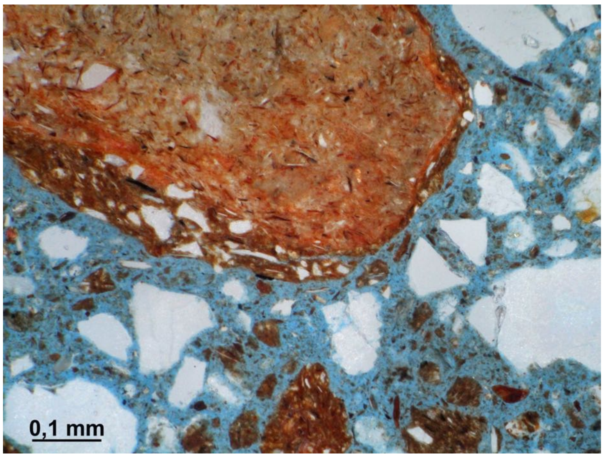

Figure 1: 90-day old experimental cocciopesto mortar; beside the larger ceramic fragments, a large amount of fines are visible as red particles. Incident light, white background.

has an additional source of hydraulic material, or that a much larger amount of the aggregate has reacted than previously observed. Similar high hydraulicity has been observed in mortars with little or no ceramic aggregate and no obvious primary silica source from the binder itself. The example of the early 20th century restoration mortar shows that these phenomena are observable in much younger mortar, potentially forming a bridge between observations on ancient mortar and issues seen in construction today.

Most of the micrographs presented and discussed in this study were obtained from polished thin sections produced after vacuum impregnating mortar samples with blue-dyed epoxy resin. Once a structure was observed by polarizing light microscopy (PLM) in the transmitted and incident modes, care was taken to study the same structure in the scanning electron microscope (SEM) at an acceleration voltage of 20 kV. In order to avoid irreversible impairment of the section by coating, most of the samples were analyzed uncoated under low-vacuum conditions of the SEM. Since the EDX results were supposed to be less accurate at low vacuum, quantitative data of analysis are to be handled with care. This does not apply to the data plotted in the graph of Figure 17, which were measured on carbon-coated samples at high vacuum at 15 kV.

II. Historical samples discussed

Late Republican/ Early Imperial Roman mortar from Ephesus, Turkey and Sisak, Croatia

One of the largest cities in the Eastern Mediterranean in ancient times, Ephesus was the capital of the province of Asia during the Roman Empire. Designed for approx. 25,000 spectators, the Roman theater was constructed and enlarged in several steps between the 1st and the 4th century A.D. The samples presented in this study come from various construction phases and parts of the building and comprise both opus caementitium and masonry mortars. The composition of these mortars did not show any significant difference in dependence to phase or mode of application. Additionally analyzed is a masonry mortar from Sisak (Siscia), Croatia, an important center of Southern Pannonia in Roman times. All mortars faced similar conditions of exposure in the interior of ancient walls which were later on buried until their excavation.

Early Imperial Roman mortar from Vienna, Austria

The Vienna Basin was controlled by the Roman Empire from roughly the turn of the first century until the early 5th century A.D. as part of the province of

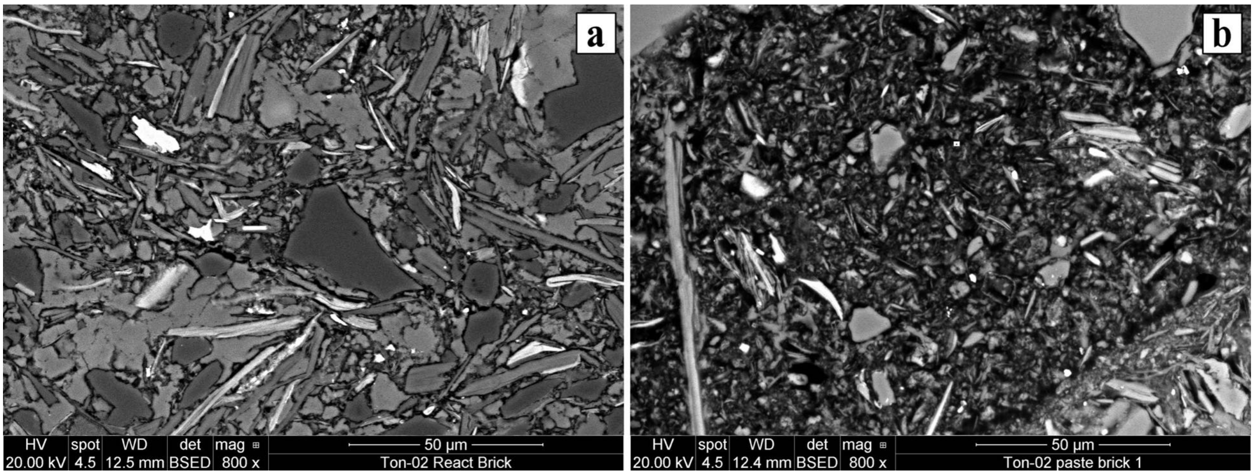

Figure 2: Sample as Figure 1; (a) Interior of brick fragment rich in mica and fine quartz. (b) Binder paste near brick fragment containing the same mica and quartz as fines embedded in a hydrated binder rich in silica.

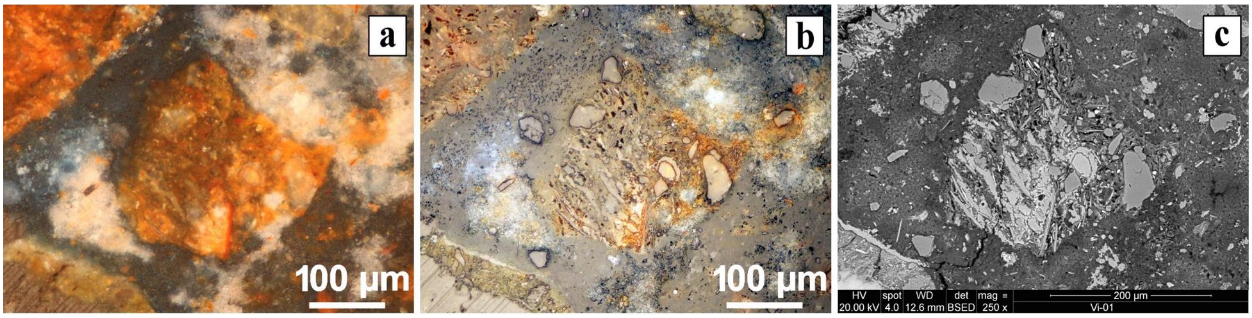

Figure 3: Ancient cocciopesto mortar from Vindobona. (a) Observed by PLM at incident light in the dark field mode, the brick fragment seems unreacted.(b) The bright field appearance of the same fragment evidences its high degree of dissolution.(c) The same fragment by SEM-BSE confirms that a significant amount of the ceramic fragment has undergone reaction; while quartz and mica have remained in the otherwise hydrated core part of the fragment, only quartz is present in the surrounding hydrate matrix where mica has apparently reacted away. The binder is altered to a silica-rich gel with popcorn like tiny crystals of calcium carbonate. Patchy compaction, very evident in the PLM micrographs by bright colors, is due to precipitation of a Mg-rich carbonate phase.

Pannonia. A legionary fortress called Vindobona, surrounded by a civilian settlement, was built at the current site of the innermost district of Vienna. To supply this city with fresh water, an aqueduct was built leading from the nearby hills. The sample discussed is of the cocciopesto lining of this aqueduct and includes a thick layer of accreted calcium carbonate from centuries of use. In the course of studying this mortar, experimental mortar of similar composition was made for comparison. Mortar was prepared in the proportion of 1 part lime to 3 parts aggregate (based on Vitruvius), with a portion of the aggregate being ceramic, and the other portion being siliceous (based on observed historical mortar compositions).

16th C. Ottoman mortar from Budapest, Hungary

Between 1526 and 1686, part of the Hungarian Kingdom was occupied by the Ottoman Empire. During this time, many buildings were constructed, including thermal baths. One of the largest Ottoman baths in Budapest, the Császár (Emperor) Bath, was built in 1574 by Sokollu Mustafa and has been rebuilt several times in the following centuries. During renovation-restoration activities of the bath, several samples have been taken in order to support art historical and scientific research (Pintér et al, 2011). The sample presented in this study is a lime-brick horasan bedding mortar of a water pipeline originating from the western part of the central bath building.

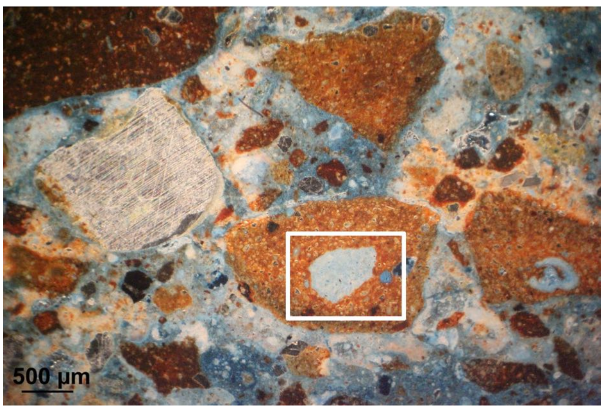

Figure 4: Apparently calcium-rich area within brick (framed); Vindobona Aqueduct. Transmitted light, dark field.

19th C. Restoration mortar of a Swiss Roman site

Aventicum, the capital of the Helvetians, was built in the early first century A.D. It grew considerably during the reign of Emperor Vespasian, who in 72 AD gave it the rank of colony. It was during this period that the imposing city wall (5.5 km) was built. The East Gate of this wall dominated the city and indicated the general direction of a transit route through several roads delimitated by adjacent walls. Almost completely razed to the ground, the gate and the walls were partly rebuilt during the restoration campaigns of the East Gate and the Fortification Wall (1910-1940), under the direction of the archaeologist Louis Bosset. The original Roman wall core was conserved and protected by a new wall over two meters high. The present sample has been collected from the filling joints of internal limestone rubbles of the wall n°8, the external masonry being composed of limestone joined ashlar.

Cocciopesto/horasan mortars

The ability of ceramic fragments or powder to improve the strength of a mortar, generically known as cocciopesto (called horasan in the case of Ot-

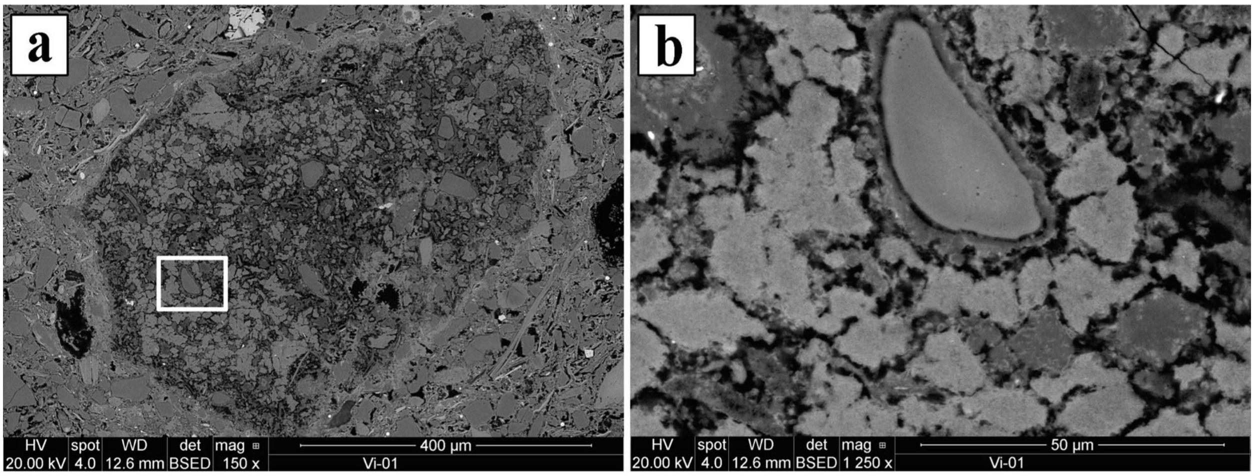

Figure 5: (a) SEM-BSE of the framed area of Figure 4: All dark grey areas are supposed to be hydrated. (b) Framed area from Figure 5a: C_2S with hydration rim.

toman mortars), is well known as a result of being recommended by Vitruvius. A number of recent papers have contributed to the understanding of the mechanisms involved, confirming the good mechanical performance and durability of these mortars [e.g. (Baronia & Binda, 1996); (Baronio et al, 1996); (Binda et al, 1999); (Böke et al, 2006); (Moropoulou et al, 2002); (Silva et al, 2007); (Nezerka et al, 2015)]. The strength enhancing reaction at the ceramic-lime interface is easily observable through microscopy.

It is the contention of this paper that it can be assumed that the same reaction is taking place on the ceramic fines within the binder matrix, indeed to greater extent due to their greater surface area in contact with lime. Over time, these smaller particles would mainly become invisible, leaving only vestiges such as iron oxide, quartz or mica as the clay minerals have reacted (Figures 1,2), interspersed within a highly altered binder of silica gel and compacted calcium carbonate (discussed below). As is well known and stated by numerous authors, the main reactive portion of a brick consists of dehydroxilated clay (Cultrone at al., 2001). When these residuals are found within the matrix, there is a tendency to oversee them or assume that they are part of the additional aggregate or the original binder, perhaps leading to an inaccurate assessment of the binder-aggregate ratio. These unreacted trace minerals leave a fingerprint of former ceramic aggregates, such as reddish areas visible in PLM (Figures 3 and 4).

However, there exist other potentially reactive constituents including calcium silicates formed during the firing of lime-rich bricks as well as other reactive silicate minerals included in the temper that may contribute to the overall hydraulicity of a mortar (Figures 4-6). The presence of partially hydrated silicates completely enclosed within a brick fragment lends credence to the idea that such phenomena would likely occur as well in the matrix. These cases exhibit the potential for additional observable hydraulicity in cocciopesto mortar beyond

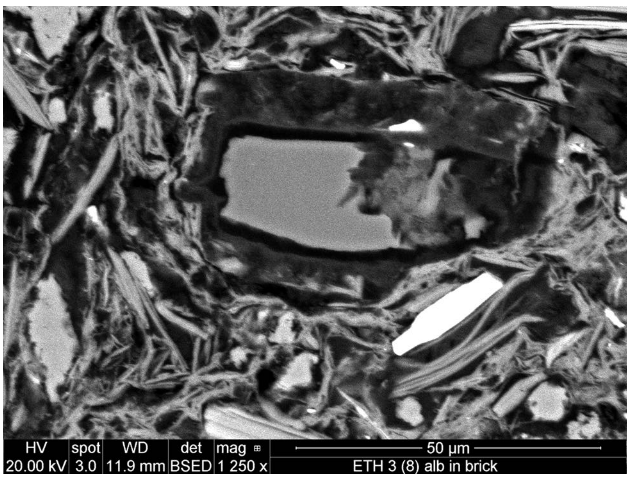

Figure 6: SEM-BSE of the interior of a brick fragment showing reactive albite with silica-rich hydration rim, Ephesus Theater.

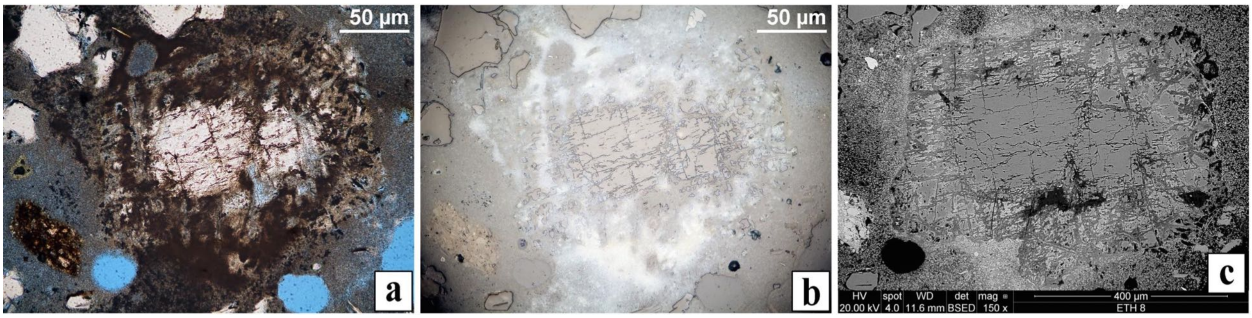

Figure 7: Ancient highly hydraulic masonry mortar with almost no ceramic aggregate from Ephesus Theater. Most of the aggregate is metamorphic, with frequent fragments of albite gneiss.(a) Highly altered plagioclase crystal, PLM, transmitted plane polarized light.(b) Incident light, bright field mode.The brown (a)/bright (b) areas in a and b are binder compacted by calcium carbonate precipitated in the course of carbonation.(c) SEM-BSE shows a thick rim of alteration with hydration to a silica-rich gel, preferentially along cleavage planes. EDX shows albite content of about 75 % in the remaining plagioclase.

that which can be explained by the pozzolanic reaction between lime and ceramic fragments.

Other highly hydraulic ancient mortars

There exist instances of ancient mortars in which neither brick powder nor volcanic pozzolans are present in sufficient quantity to explain the observable high hydraulicity, nor infer that they were intentionally added for this purpose. One possibility is that a hydraulic lime was used, however in this case generally remnants of the lime source can be found, for example marly lime lumps or unhydrated calcium silicates. The other possibility rarely discussed is that of reactive aggregates. Under certain conditions, plagioclase, feldspar, chert and potentially even quartz can react, releasing silicate into the binder and contributing to the overall hydraulicity (Chou & Wollast, 1985; Hodgkinson & Hughes, 1999; Broekmans, 2004). These are identifiable by a similar reaction ring that can be found around a pozzolan (Figures 7-11). As is the case with ceramic aggregate, over time only the larger aggregates would be visible, while the finer portion could be easily overseen or would be completely reacted away. While not commonly discussed in literature on historical mortars, a similar phenomenon is discussed in works on alkali-silicate reaction (ASR), a type of alkali-aggregate reaction in OPC based concrete. The conditions known to favor ASR are lattice defects and/or low crystallinity in SiO_2, high humidity over prolonged periods of time, sufficiently high pH and alkali content. At least some of these conditions can be present in historical mortars, especially when used in applications that expose them to high humidity such as masonry filling mortars - e.g. opus caementitium, hypocaust floors etc. Other observations supporting the idea that the conditions were in favor of the hydration of otherwise stable silicate minerals

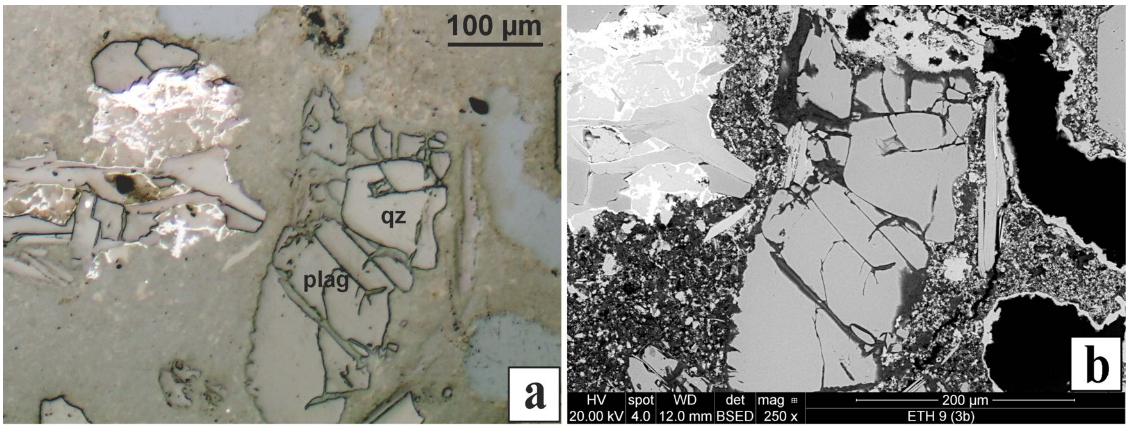

Figure 8: A similarly ancient highly hydraulic masonry mortar with almost no ceramic aggregate from Ephesus Theater. Again, the aggregate is of metamorphic origin, with frequent fragments of albite gneiss.(a) Aggregate fragment of plagioclase (plag) and quartz (qz); plagioclase appears slightly corroded at margins and along cleavage; incident light, bright field mode.(b) SEM-BSE of the same fragment. While plagioclase shows a thin layer of a silica-rich gel, quartz appears largely unreacted.

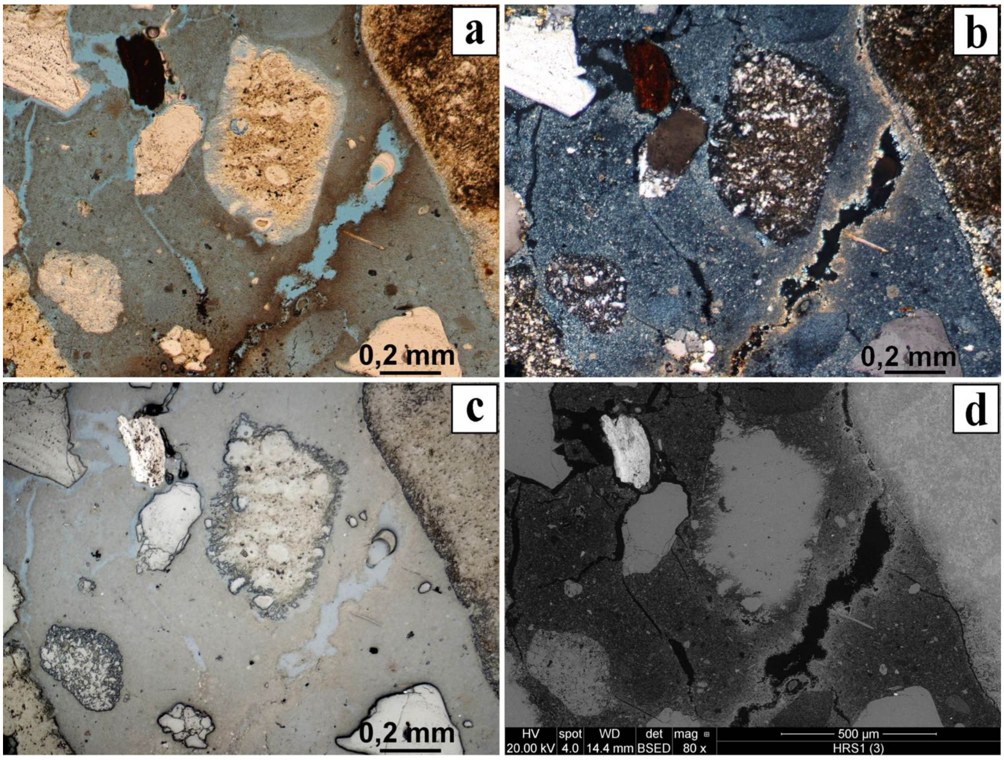

Figure 9: Ancient highly hydraulic masonry mortar from Siscia. Much of the aggregate in this mortar is chert and siltstone with microcrystalline quartz. Aggregate fragment of chert (center) with rim hydrated to silica gel. Also the margin of the big siltstone partly visible on the right appears hydrated. The surrounding binder matrix is very rich in silica, with Ca:Si = 1:2. Calcium carbonate is enriched along the cracks. (a) PLM, plane polarized light. (b) Crossed polarized light. (c) Incident light, bright field. (d) SEM-BSE.

are the eventual presence of dolomitic aggregates undergoing alteration to brucite and calcium carbonate due to dedolomitization (Figures 12 and 13), a process described e.g. by Katayama (2010) and Mittermayr et al. (2011), indicating elevated pH. An explanation for alkaline conditions that would favor dissolution of feldspar over a long period of time are a slow rate of carbonation due to limited exposure to the atmosphere in the case of the mentioned types of application. The condition of high humidity over prolonged periods of time is also evidenced by strong alteration of the binder matrix. It is likely that under such conditions even quartz, especially the metamorphic quartzes generally observed in all of the mortars presented here, may be subject to dissolution at low rates. (Broekmans, 2004).

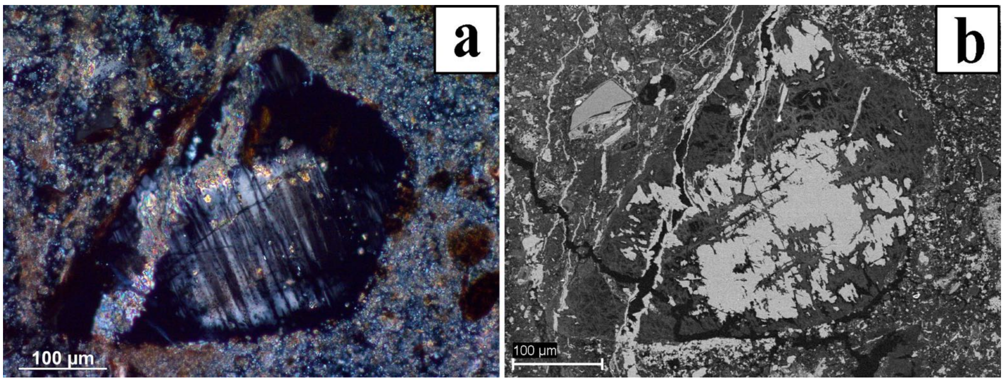

Figure 10: Altered alkali feldspar grain with residues of the original mineral exhibiting birefringence and surrounded by porous reaction products. The original shape of the mineral has entirely preserved. The altered matrix is composed up of an impure silica gel and finely dispersed $CaCO_3$. Ottoman mortar, thin section. (a) PLM, crossed polars. (b) SEM-BSE.

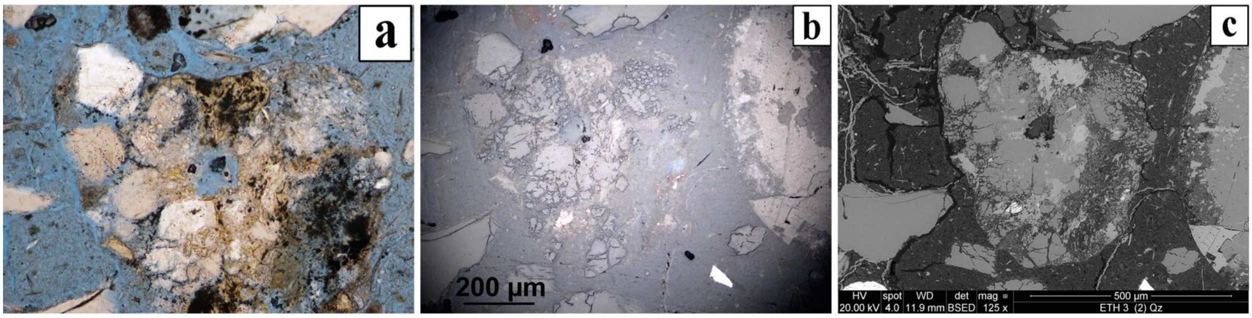

Figure 11: Ancient highly hydraulic opus caementitium mortar with just occasional ceramic additions from Ephesus Theater. Partly corroded polycrystalline quartz aggregate (center) next to a marginally altered dolomite aggregate (right margin).(a) PLM, plane polarized light.(b) Crossed polars.(c) SEM-BSE.

Alteration of highly hydraulic binder

The carbonation of hydrates constituting the matrix of hydraulic binders is a well-known fact attested to by a large amount of studies such as Goto et al. (1995). Much knowledge comes from research on concrete and modern cementitious materials; however, it is naturally applicable to hydraulic binders in historical mortar. Binder alteration linked to carbonation is reflected by a number of interesting phenomena observable in the microstructure, in particular when using appropriate modes of illumination under an optical microscope, in particular dark-field mode. The areas thus discovered can then be chemically analyzed with EDX, but it is important to remember that because of inhomogeneity, it is not possible to access the quantitative composition of the binder in this way. The process of carbonation is system-wide: not only is calcium hydroxide converted to calcium carbonate, but calcium silicate hydrates are likewise converted to calcium carbonate and a silica-rich gel. In cement mortars, the depletion in calcium, which forms compact rims of carbonate around the clinker, drastically alters the composition of calcium silicates in unhydrated clinker residues [e.g. Shtepenko et al. (2006), Gosselin et al. (2012)]. When carbonation is accompanied or followed by the circulation of water through the pore system of the binder, calcium carbonate can get dissolved and re-precipitated in specific places. When these conditions are met, this may lead either to "popcorn" like crystals of calcium carbonate growing within a silica-rich matrix (Figures 14a and b), often combined with re-crystallization along the margin of pores and cracks, or to the development of diffuse binder areas compacted by submicroscopic carbonate crystals. This effect is a clear evidence for degraded C-S-H due to strong leaching caused by percolating water. Additionally this can also be observed in more modern materials such as an early 20th Century highly hydraulic lime mortar (Figure 15). In this example a belite clinker nodule has separated into silicate and carbonate rich areas. The described phenomena are well-known for modern concretes. It is important to reiterate that as in the question of additional reactive aggregates, this phenomenon is particularly evident in building applications that featured a large amount of moisture or humidity.

From published XRD data we know that this secondary calcium carbonate, intermixed with decalcified C-S-H, frequently occurs as aragonite or vaterite (Elsen et al, 2012). In either case is the remaining binder, a chemically impure silica gel, strongly depleted of calcium. Though the described inhomogeneity makes it impossible to assess the original binder composition by EDX or other meth-

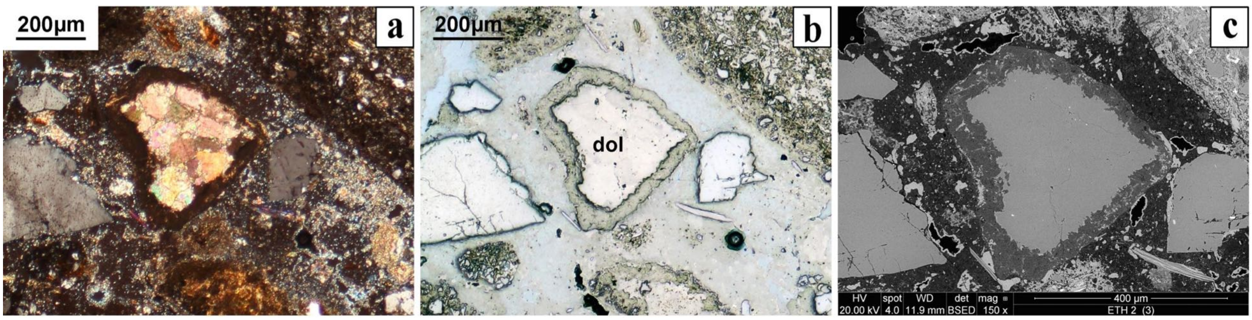

Figure 12: Ancient highly hydraulic opus caementitium mortar from Ephesus Theater. Dolomite aggregate with rim of conversion to a Mg-phase, presumably brucite. The surrounding binder is highly altered by carbonation.(a) PLM, transmitted light, crossed polars.(b) Incident light, bright field.(c) SEM-BSE.

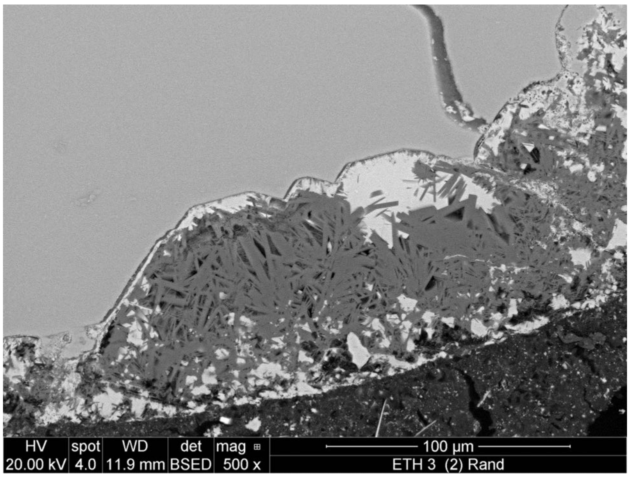

Figure 13: Ancient highly hydraulic opus caementitium mortar from Ephesus Theater. Rim of a dolomite aggregate converted to brucite and calcium carbonate (bright areas). The surrounding binder is an impure silica gel; SEM-BSE.

ods related to microscopy (Elsen et al, 2012), it is nevertheless possible to recognize its hydraulic nature and then search for potential sources of hydraulicity (Figures 16 and 17). It is worth mentioning in this context that the described process of alteration is usually resulting in increased strength and durability of the historical mortars affected.

Observations of the microstructure by microscopy and SEM generally support this fact: in contrast to the destructive effect of gel formation by AAR in modern concrete, silica gel formed in the course of carbonation of ancient hydraulic binders seems to form a fairly porous structure, chemically stable and not subject to volume expansion. The precipitation of carbonate on the other hand, though creating inhomogeneous patterns of compaction as described above, is yielding additional strength since it is likely to crystallize in weak and porous zones of the mortar, thus contributing to the so-called self-healing effect, a term frequently cited as advantageous of lime mortars (e.g. Borges et al., 2014), even if their inhomogeneity is enhanced which can cause the formation of weaker binder depleted areas In this way, the adhesion between binder and aggregates is usually strengthened due to preferential carbonate crystallization in fissures and voids between these two systems. In the case of porous aggregates such as brick fragments, the precipitation of calcium carbonate affects also the marginal zones of the aggregate, binding it tightly to the matrix (Nežerka et al, 2015). The latter effect yields a zoning of the brick often visible even by the naked eye, and can be easily misinterpreted as a reaction rim of hydrates. Both phenomena, however, are likely to improve the mortar strength in a similar way.

III. Conclusion

The wide variety of mortar samples discussed here share two common traits: that they have additional, unexpected observable hydraulicity not attributable to silicate phase in the raw feed (e.g. hydraulic lime) and that this hydraulic binder has drastically altered over time, as manifest by a silica-rich gel with clustered carbonate areas. These observations

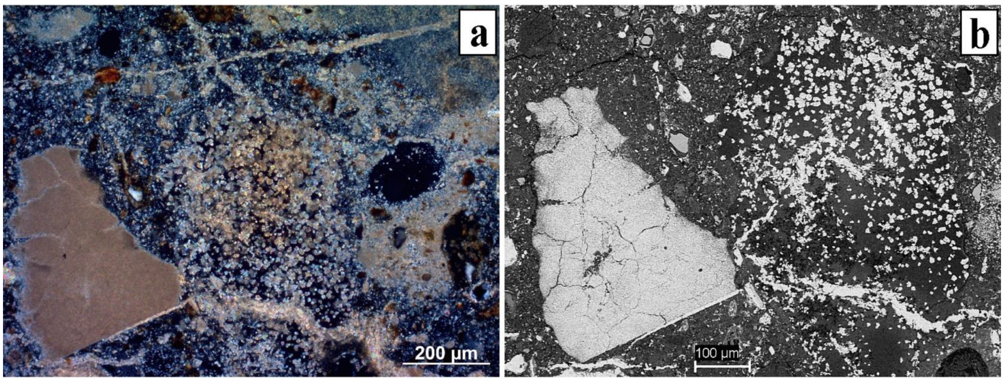

Figure 14: Horasan mortar from the Emperor's Bath, Budapest. Both PLM (a) and SEM-BSE (b) clearly show $CaCO_3$ "popcorn". EDX confirms that the binder is composed of this and impure and amorphous silica gel. White cracks are filled with re-crystallized $CaCO_3$. Small red fragments are remnants of reacted ceramic particles added as a pozzolan.

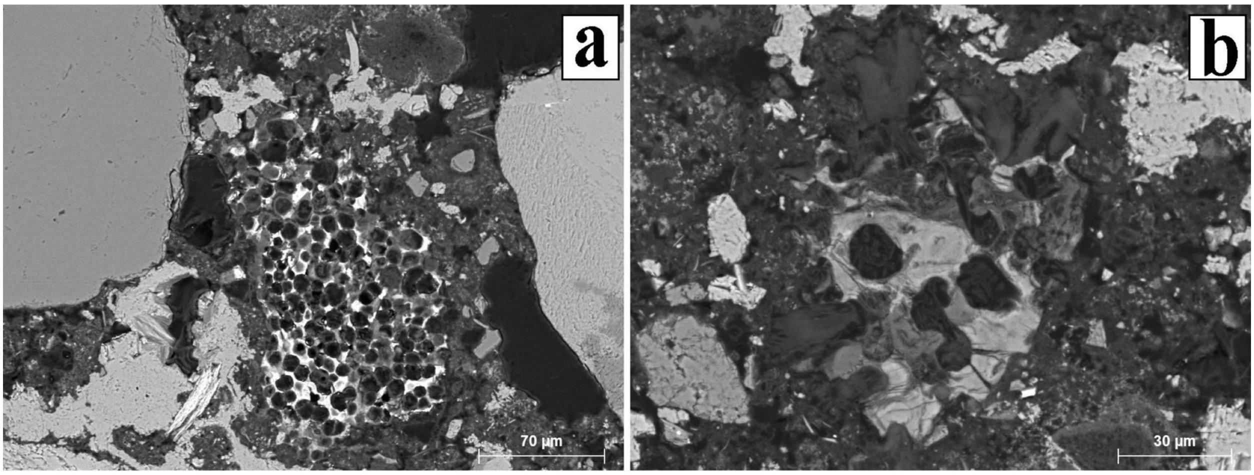

Figure 15: (a) Alteration of belite clinker remnant used to repair the Swiss Roman site of Aventicum(b) Image showing silica gel interspersed within matrix near clinker. SEM-BSE.

were not the initial goal of analysis of any of the samples; rather the similarities were discovered independently. Hydraulicity in each of the historical samples was enhanced by reactive aggregates, tempered and untempered, ceramic or natural. Despite these similarities, and the similarities of the silica gel and carbonate binder separation phenomenon, one must keep in mind that the rate of these reactions are not necessarily the same across all samples. One thing that all ancient mortars had in common was high exposure to humidity and probably a high pH over prolonged periods of time.

As a matter of fact, both phenomena were observed in the same mortar samples, because the extensive binder alteration of the described type can only occur in hydraulic mortar. Frequently found in ancient renders and plasters, the effect of binder dissolution and precipitation in air lime mortars is known to result in the re-distribution of the carbonate binder where, however, no dissolution of silicate aggregate is observed. This points to the necessity of a prolonged alkalinity in the service life of a mortar, a condition enhanced by high humidity as is the case for filling mortar and water pipes, water buildings, etc.

It is evident that feldspars would form alkalis upon their dissolution, thus adding a source of high pH at least in their immediate surroundings. In this way, a self-sustaining cycle of feldspar dissolution could be assumed. It would continue to operate until the alkalis get washed out and leave the system, which would allow carbonation. Whether or not this proposed mechanism can have played a role for the whole bulk of the mortar binder is under question at this stage of research.

This work represents a preliminary set of observations regarding important chemical processes and how they apply to the durability of ancient

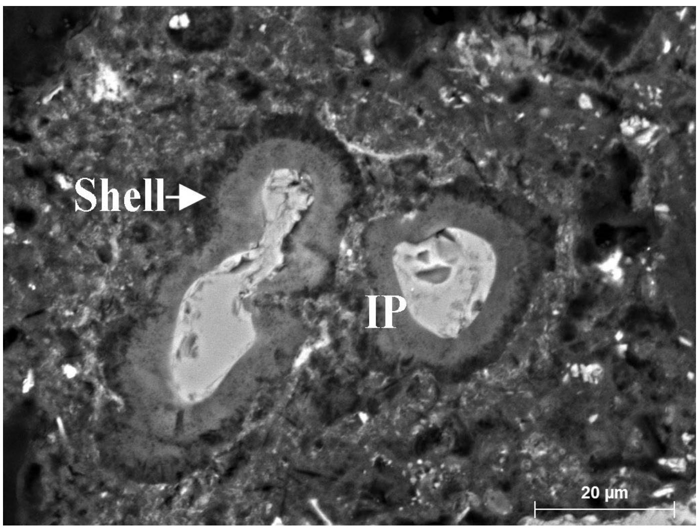

Figure 16: Aventicum mortar, morphology of the cement grains (original quartz core and C_2S rim) showing inner and outer hydration products discriminated by a hollow shell.

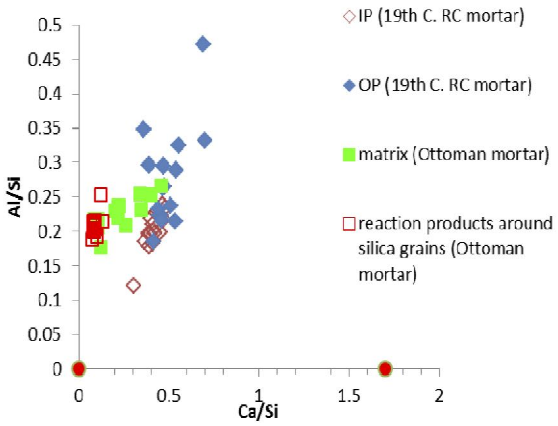

Figure 17: Composition of the inner and outer hydration products in the Ottoman and Aventicum mortars (cf. Figures 10a, b and 16).

mortar. The lessons that can be learned from this study and how they can be applied to the issues of conservation as well as to contemporary buildings require further clarification. Microscopy is an important starting point that should be followed by the use of other analytical techniques such as Raman microscopy. Additional studies on experimental mortars to establish e.g. the potential of feldspar dissolution to create sufficient alkaline conditions would include analyses of pore solutions as well as of alkali and feldspar contents, respectively.

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