Methods of Microscopy to Identify and Characterise Hydraulic Binders in Historic Mortars—A Methodological Approach

J. Weber, T. Köberle and F. Pintér

Abstract The contribution focuses on microscopic techniques for use in the identification and characterisation of historic mortars, with the assumption that the key information to understanding historic mortar is contained in the binder. While bulk chemical or gross phase analytical tools may provide preliminary information on the binder type used, imaging methods such as light and electron microscopy offer a more detailed assessment due to the possibility to study simultaneously mineral compounds, textures and microstructures of reacted and unreacted binder components, as well as their interaction with the other constituents of a mortar. This holds not only for traditional air lime based mortar systems, but most specifically also for all those containing cementitious compounds. The use of standard techniques of polarising light microscopy (PLM) and scanning electron microscopy (SEM) on thin sections to identify the binder constituents of hydraulic mortars is discussed. Residual cement grains indicative of high temperatures of formation (typical in Portland cement mortars) can be observed and classified by reflecting light PLM on polished sections eventually supported by staining techniques, even if present in only small amounts. On the contrary, natural or Roman cement mortars, in which the binder was calcined at low temperature, require the use of thin section PLM with transmitted light, possibly complemented by SEM-techniques. For hydraulic lime mortars, either of the above approaches can be optimal, depending on whether they were naturally or artificially mixed. The contribution presents a

J. Weber (✉)
Institute of Arts and Technology, Section of Conservation Sciences,
University of Applied Arts Vienna, Salzgries 14/1, 1013 Vienna, Austria
e-mail: johannes.weber@uni-ak.ac.at

T. Köberle
Geologie-Denkmalpflege-Bauforschung, Nordstrasse 39, 01099 Dresden, Germany
e-mail: TKoeberle@gmx.de

F. Pintér
Scientific Laboratory, Federal Monuments Authority Austria,
Arsenal 15/4, 1030 Vienna, Austria
e-mail: farkas.pinter@bda.at

few examples of mortars made from each of the above binders and addresses additional observations, e.g. the leaching of the matrix by weathering agents.

Keywords Historic mortar · Hydraulic binder · Unhydrated residuals Optical microscopy · SEM

1   Introduction

When dealing with mortars sampled from historic structures, there are many qualities that are of interest to the material analyst, such as physico-mechanical performance, microstructure, the petrographic or granulometric composition of the aggregate, and/or the types and causes of alteration of the mortar over time. In virtually all cases, however, one piece of information is considered key for any kind of mortar characterisation: namely the type of binder used to prepare the mortar. Understanding the binder greatly helps archeologists and conservation scientists to make sound decisions when searching for compatible materials to restore, repair and/or replace parts of a building. Additionally, it greatly enhances our understanding of the history of technology. It is usually the binder that lends its name to a mortar, be it lime, pozzolanic, hydraulic or cement based.

Identifying a mortar's binder can be simple to the experienced eye, particularly when examined in the context of a group of mortars whose properties are well understood, but even the most experienced researcher can have unexpected difficulties—a situation met by the authors on a nearly daily basis. As pointed out by several authors (St John et al. 1998; Elsen 2006; Krotzer and Walsh 2009; Ingham 2010), investigating binders petrographically, i.e. by employing imaging methods such as polarising light or scanning electron microscopy (Winter 2009), may yield much information about the binder's nature and mode of production.

Within this scope, the concept that "the key to binder identification lies in the unreacted residuals" (Walsh 2008) holds particularly for hydraulic binders.

Whether or not there is a sufficient unreacted portion of binder left in a mortar is not a matter of age, but rather of the fineness of to which it has been milled and the quality of reactions achieved during the manufacturing process—both factors are likely to be observable in historic mortars from before the First World War. The most widely used hydraulic binders of the 19th and early 20th centuries comprised cements calcined below sintering, usually called Roman cements (RC), natural hydraulic limes (NHL), and cements produced by sintering, called Portland cements (PC). The history of their production is generally known (e.g. Blezard 2003), though many details still need to be researched or have remained unpublished to date. These products were far less subject to quality regulation at this time than they are now that European norms define clear standards for composition and performance of commercial building limes and cements. Thus, the quality varied from one product to the other within certain limits, as did the process of production. Considering also the frequent practice of blending of various binders to prepare a

mortar on any particular project, the value of precise determination of the constituents of a historic mortar in terms of its binder becomes clear. The optimal method of this is careful and skilled assessment of the unhydrated binder residuals. Instrumental bulk analyses such as X-ray diffraction or chemical binder analysis are less capable of tracing all types of constituents relative to imaging analytical tools.

Microscopy is frequently used by three groups of professionals from the field of mortar research—conservation scientists on the one hand, and cement respectively concrete experts on the other. However because these groups are searching for different information, they utilise different approaches. Cement chemists usually are interested in the composition and microstructure of clinker sampled from the production process and use incident light microscopy in the bright field mode, eventually supported by etching and staining the polished section and using scanning electron microscopy (SEM) combined with X-ray diffraction (XRD). Concrete experts are mostly interested in the composition and causes of alteration of the sample over time. Such analyses are traditionally carried out on thin sections in transmitted polarised light and/or on polished sections by using SEM. Conservation scientists typically are trained in incident light microscopy employing the dark field mode, where stratigraphical features and paints can be better visualised. Eventually complementing this work with petrographic thin-section microscopy or SEM, many conservation microscopists are not well aware of the additional possibilities offered by the light microscope when switched from dark to bright field mode of observation. It is hence the aim of this contribution to demonstrate by a few examples the added value achieved by employing the full range of observation techniques offered by a petrographic microscope in combination with a scanning electron microscope.

2 Samples and Methods of Microscopy

2.1 Sample Preparation

In principle two types of microscopic sections can be produced from a mortar sample: either petrographic thin sections, usually covered by a glass slip, or polished cross sections. Neither type can be used for every mode of observation in a light or scanning electron microscope, so compromises have to be made taking account of the most appropriate technique to analyse the material.

The ideal case would be to produce both a thin and a cross section from adjacent parts of a sample, a rather expensive approach which moreover requires sufficiently large samples. A drawback to this approach is that a unique phenomenon seen in one section might not be visible in the other, depriving the operator the possibility to verify certain observations and their interpretation by another method. In this case, even the combination of all available techniques may not reveal a sample's true nature.

Probably the best choice is to produce polished thin sections, which allow for all light microscopy and SEM work to be done on the same section. PLM observations under incident light in the dark field mode yield images different from those from polished cross sections. This is caused by a part of the light passing through the material reflecting off its lower surface, thus creating images similar to the ones obtained by transmitted light under crossed polars. Another factor to consider is the necessity to sputter the section surface for SEM at high vacuum. The drawback to this is that this process is is not fully reversible thus the sample should have been carefully analysed and documented by PLM before sputtering. A possible solution would be to sputter just a part of the section

Whether polished or not, thin sections require great skill to prepare. A surprising number of bad thin sections are produced which greatly reduces the quality of information obtainable. The same holds for the method of impregnating the sample with a resin, which must penetrate the pore space to the highest possible extent. It is important to add a dye to the resin in order to get a good contrast between pore space and solid components. The yellowish UV-fluorescent dye mainly used for concrete petrography is less appropriate for conventional microscopy than the blue dye which gives better contrast.

2.2   Low Power Stereo Microscopy

Stereomicroscopes are usually designed for 3-dimensional images of uneven samples. They can also be used in a beneficial way to study plane microscopic sections utilizing a range of low magnifications, about 5 to 100x, which cannot be easily achieved with most polarising microscopes. Any mortar analysis on thin and/ or polished sections should start with low power observation of the binder and aggregates to establish the major microstructural features of a mortar.

Modern stereomicroscopes provide not only incident light but also transmitted light facilities. If equipped with polarizers, they may offer a wide range of observation modes for thin sections. Some of them are rarely used by microscopists, e.g. using incident light on thin sections impregnated with dyed resin. If laid on a sheet of white paper, residuals of cement are usually easily visible by their brownish colour. Without a reflective white background, they would have probably remained undetected. Using the usual method of observation with transmitted light (Fig. 1a, b), the aggregate can be identified and phenomena like the full carbonation of the cementitious binder can be assessed. The high amount of unhydrated cement particles is only visible in the incident light mode provided that the section is placed on a white background (Fig. 1c).

Roman cement mortars can be identified equally well at low magnifications as their binders contain residual compounds that are larger than the clinker of historic PCs. To clearly distinguish them from aggregate takes some experience; the frequent zoning of the binder related nodules can be helpful. Figure 2a, b illustrates this with an example of a RC mortar, where even the high degree of leaching by
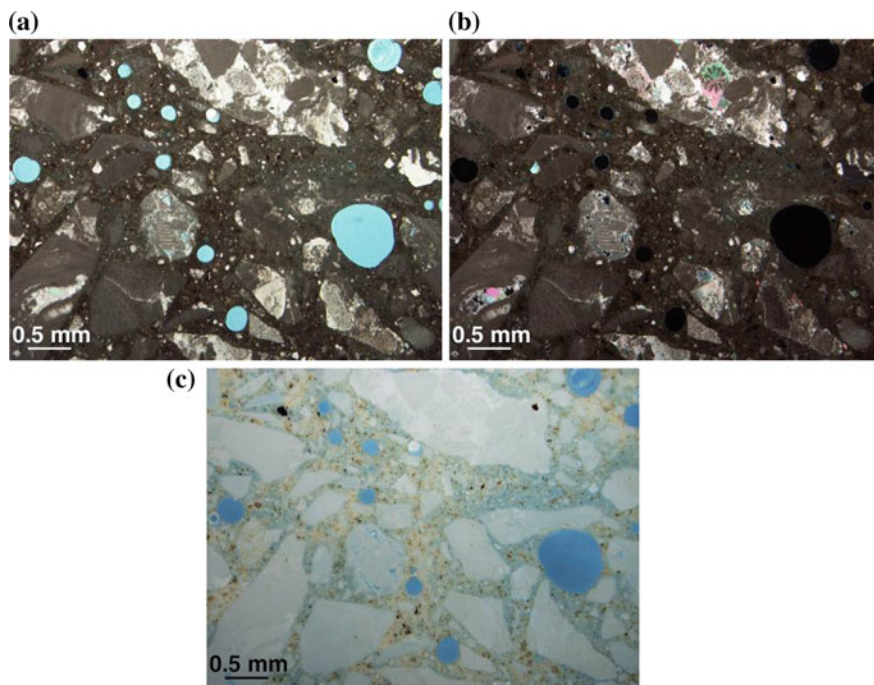
Fig. 1 Polished thin section of a 1910 White-PC mortar with limestone aggregate under the stereo-microscope; **a** transmitted light parallel polars, **b** crossed polars, **c** incident light. The PC clinker residuals are well visible in the incident light mode as brownish spots in the binder
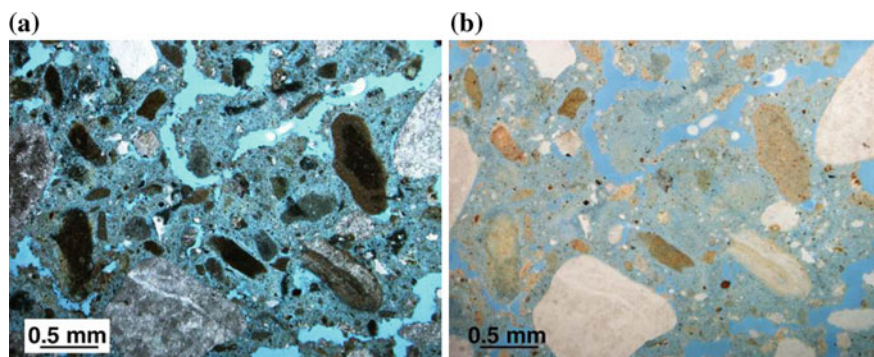

Fig. 2 Polished thin section of a 1870 RC bedding mortar under the stereomicroscope; **a** transmitted light parallel polars, **b** incident light. The RC residual nodules exhibit strong zoning which is best visible in transmitted light with parallel polars (**a**). The mortar is strongly leached and decayed by the action of percolating water

weathering has left the distinctive nodules unaltered. As shown below, however, an attempt to characterise these lumps more precisely by polarising microscopy may fail.

2.3   Polarising Microscopy

When equipped with facilities for light transmission and reflection, a polarising microscope is a versatile tool to study many details at magnifications up to about 1000 times. For our purposes this includes a more precise determination of the residual clinker in terms of crystal size and shape, phase identity and mutual relationships between the different phases. The usual mode of observation is under reflective light in the bright field, producing images of grey values according to the reflection coefficient of a phase. Traditionally used by cement chemists, this method provides quick access to several useful pieces of information about the type of cement used for a mortar, in particular when PC mortars are investigated. Figure 3a, b illustrates the advantage of reflective over transmitted light, especially when the clinker grains are small. However when studying coarse unhydrated clinker grains composed of large crystals, which are frequently found in historic PC mortars, it is worthwhile to have produced a polished thin section in order to observe the clinker also under transmitted light where additional optical parameters such as the interference colours become visible (Fig. 4a, b). Thus, by simply switching between transmitted light at parallel or crossed polars one can use the full range of facilities offered by the polarising microscope on one single preparation.
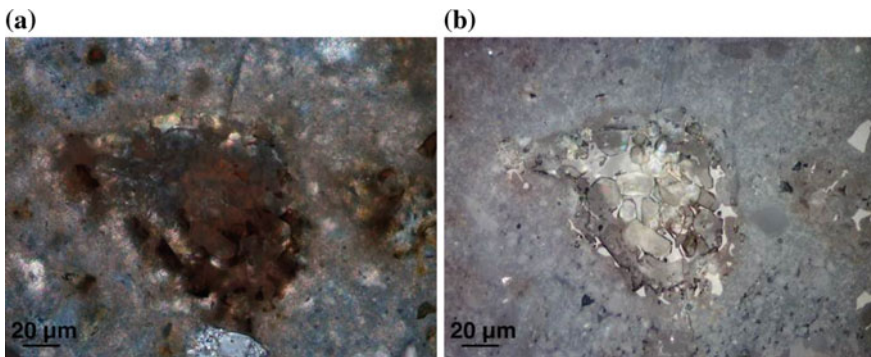

Fig. 3   Polished thin section of the White-PC mortar from Fig. 1; residual clinker grain under the polarising microscope, **a** transmitted light parallel polars, **b** reflective light, bright field. Angular alite, spherical belite and an interstitial phase mainly composed of aluminate while high reflecting ferrite occur only in small amounts; carbonation has led to the formation of a compact rim of carbonate, visible by its birefringence (**a**), while the calcium silicates are strongly depleted in calcium
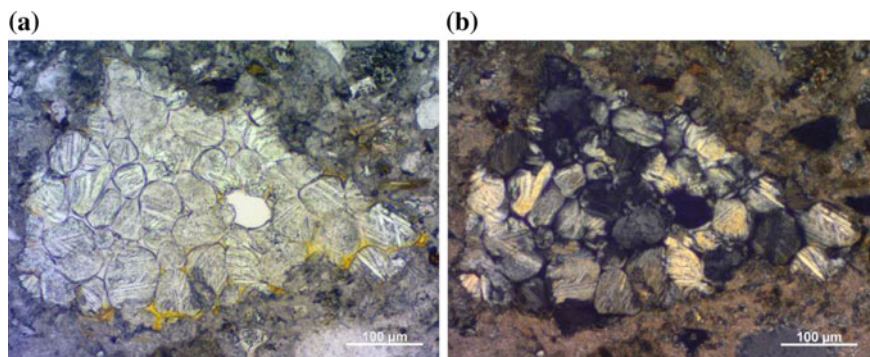
Fig. 4 Polished thin section of a 1879 PC pointing mortar; residual clinker grain under the polarising microscope, **a** transmitted light parallel polars, **b** crossed polars. Coarse belite crystals which can be clearly identified by their shape, interference colour and intersecting sets of twinning lamellae
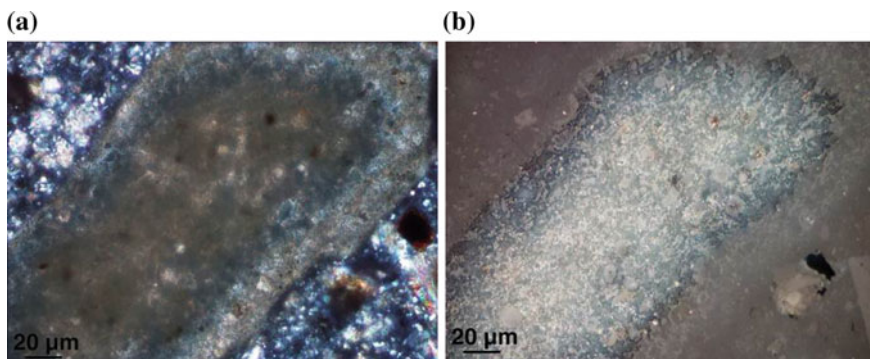

Fig. 5 Polished thin section of the RC mortar from Fig. 2; detail of a residual nodule under the polarising microscope, **a** transmitted light parallel polars, **b** reflective light, bright field. While the nodule as such is indicative for the RC nature of the sample, its fine grained texture makes it difficult to identify any of the phases by this method

In contrast to PC mortars, the polarising microscope is less convenient to study the precise phase composition of RC mortar residual structures, since these nodules are typically composed of very fine grained clinker phases of less well defined stoichiometry and hence less significant optical parameters (Fig. 5a, b). In this case the use of SEM is more promising.

A large range of methods to etch and/or stain polished thin sections by the use of different chemicals are used (see e.g. Gille et al. 1965; Campbell 1999) to allow for a clearer identification of clinker phases and to reveal microstructural details of individual crystals. Hydrofluoric acid, borax, salicylic acid, potassium hydroxide/sucrose, and nitric acid in ethanol (Nital) are just some of the most commonly employed etching agents, each of them having unique benefits for the identification
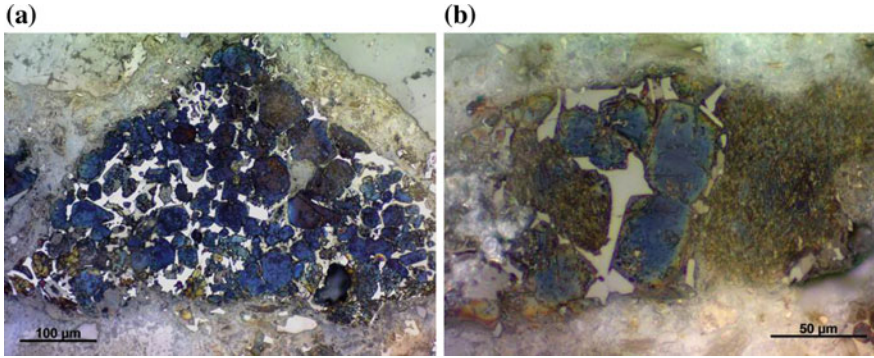
Fig. 6 Polished section of the PC mortar from Fig. 4; residual clinker grains under reflective light. Caused by etching with Nital, alite is easily detectable by its blue colour, while belite has turned brownish and the interstitial phases ferrite and aluminate have remained unaltered. The variety of alite sizes can be considered characteristic of historic PC, indicating an inhomogeneous raw feed and/or firing conditions
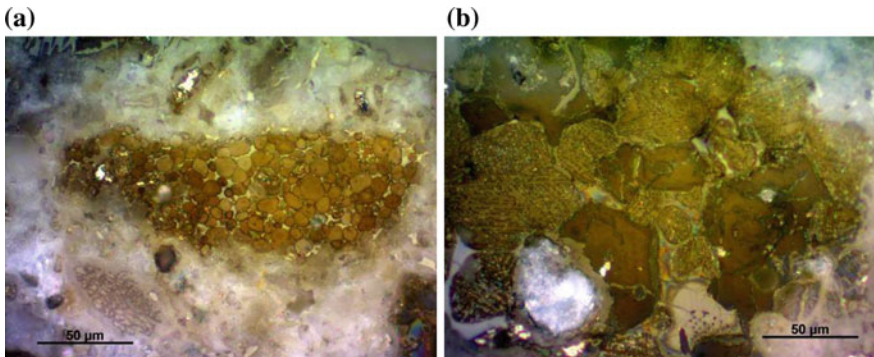

Fig. 7 Polished section of the PC mortar from Fig. 6; residual belite clinker grains under reflective light, etching with Nital. Similar to alite (Fig. 6), belite is of varying crystal size, the internal structure made visible by the etching allows conclusions to be drawn on the calcination process. Thus, the structurally uniform crystals have probably formed by conversion from the coarse belites with intersecting twinning lamellae, a process indicative of the use of a shaft kiln

of certain phases and visualisation of internal microstructures. The full range of possibilities has probably not yet been exploited for historic PC mortars; the use of Nital as illustrated in Fig. 6a, b and Fig. 7a, b serves just as an example.

2.4 Scanning Electron Microscopy

Despite all benefits offered by the techniques of light microscopy, the microscopist may have good reasons to decide to use SEM as additional tool to study the binders in a historic mortar sample (Winter 2012). It is clear that the instrument needs to be equipped with a good back-scattered electron detector and a X-ray analytical device (EDS) in order to make the desired observations. If it can be operated in the low vacuum mode, the operator should first try to study the section without coating it with a conductible layer of carbon This is especially true of a polished thin section since it would be altered by carbon-coating which is not fully reversible. Things to keep in mind when working under low vacuum are that the image resolution is lower and that the chemical spot analysis by EDS is less precise and confined than it would be in the high vacuum mode, due to the interaction between electrons and air molecules in the chamber.

SEM investigations are useful not only to study the unhydrated portion of the binder, but also can be employed to improve knowledge of the reacted part, which is usually of much finer grain size and hence less understandable by light microscopy than clinker residues. EDS-analysis of the hydrated binder may yield unpredicted results as to its nature: a mortar rich in residual cement may show very low amounts of silica in its hydrate binder, or on the contrary, it may lack calcium
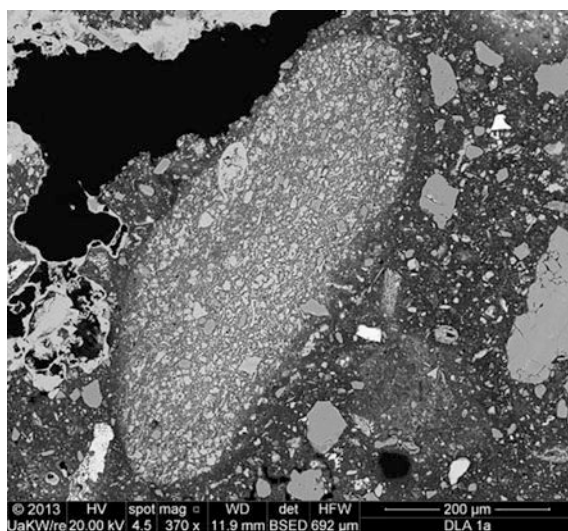

Fig. 8 Polished section of the RC mortar from Figs. 2 and 5; SEM/BSE image of an underfired residual nodule of the type shown in Fig. 5. The tiny mineral phases contained in the particle are quartz and calcite, unreacted minerals inherited from the raw feed marl. The surrounding binder is strongly depleted in calcium ions due to leaching effects which have caused calcite precipitates along the pore—visible on the top left. In fact, due to these alterations it cannot be excluded that we deal with a NHL instead of a RC mortar

Fig. 9 Polished section of a 1899 NHL mortar; SEM/BSE image of an underfired residual nodule of the type shown in Fig. 5. The residual particle contains non-stoichiometric calcium silicates in compositions between CS and C_2S and aluminate ferrites (bright). The surrounding binder matrix is mostly lime
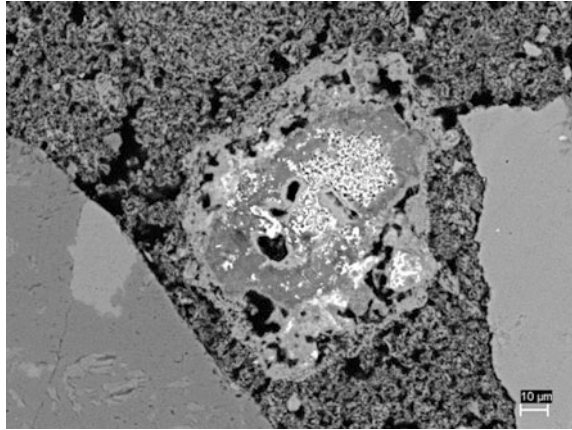
ions, as in the example shown in Fig. 8. While the first case would indicate a mixture of lime and cement with very low reactivity, possibly due to cement grains that are either overly coarse or of an inappropriate composition, the latter case is usually due to strong leaching effects caused by weathering.

With unhydrated residues, the advantage of high resolution imaging and elemental analysis offered by the SEM is of special benefit for small and/or non-ideally reacted phases as they occur in RC and NHL mortars. This is especially true of analysing RC mortars rich in "underfired" nodules, i.e. residual grains which did not calcine sufficiently to form reactive clinker phases (Gadermayr et al. 2013) (Fig. 8). Additionally the well fired portion of RC nodules frequently contains phases below the resolution of a polarising microscope or non-crystalline solid solution phases which can not be identified by their optical parameters (Fig. 9). In these cases using the SEM can be beneficial.

3   Conclusions

Historic cementitious or highly hydraulic mortar binders are chemically less well defined than modern ones. Their characterisation in mortar samples therefore requires a thorough analysis of the unhydrated residual particles in their structural context, a task which can be best accomplished by the use of microscopic means, possibly combined with chemical point analysis. Generally one can profit from the use of different modes of observation preferably performed on the same sample section. Within that frame, reflective light microscopy proves useful for mortars containing different amounts of PC, while PLM in transmitted light is advantageous for all types of hydraulic mortars. In all cases SEM techniques can provide significant additional insight.

In general the quality of sample preparation requires the highest possible standard. Polished thin sections are probably the best choice since they allow for the full range of microscopy on one sample.

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