

Mineralogical investigations on pozzolanic dolomitic lime mortars to assess the phase development at different climatic storage conditions

Abstract

For a long time, historical mortars were primarily associated with mortars based on calcium carbonate as the main binder phase. Recent publications show that considerable amounts of magnesium are often present in the binder of historical mortars, which is attributed to the use of dolomite rock (dolostone) as raw material. A special feature are antique and medieval dolomitic lime mortars with the addition of brick fragments as a pozzolanic component.

In order to characterize the phase formation in pozzolanic dolomitic lime mortars, mortar prisms based on dolostone, limestone and magnesite were produced with three different additives (antique and modern brick dust and blast furnace slag). The samples were stored under different humidity conditions, examined by X-ray diffraction (XRD) and simultaneous thermal analysis (STA) after periods of 28, 90 and 180 days and compared to historical mortars.

The results show that the binder phases in the dolostone-based samples clearly depend on the storage conditions. The samples stored at low humidity contain large amounts of calcite, as well as portlandite, brucite and partly aragonite. The samples stored at high humidity and without CO₂ supply include higher portlandite contents, in addition calcite, brucite, monocarboaluminate and partly aragonite. There are indications on C-(A)-S-H and M-(A)-S-H phases.

The different mineral contents in the binder can be attributed to the interacting processes of carbonation, hydration and pozzolanic reaction. Depending on the storage conditions, one of these processes predominates. In addition to temperature and humidity, there are a number of other factors that influence the hardening process and the alteration of hydraulic mortars over time.

Overall, the mineralogical composition of the binders produced appears to be similar to that of the antique mortars examined. The present study is believed to be beneficial for a better understanding of the phase formations in dolomitic lime based mortars at different climatic storage conditions.

1. Introduction

The use of calcined lime has its origins in antiquity and can be traced back around 10,000 years. In combination with water and aggregates such as sand and gravel, a kind of mortar was made from calcined lime, which was typically used as screed and masonry mortar. In later phases of antiquity, such mortars were used in the construction of the pyramids at Giza (around 2500 BC) and in palaces in Pergamon and Crete (around 1700 BC). Chemically speaking, these were mainly pure lime mortars that harden due to the carbonation of calcium hydroxide (Stark & Wicht, 2000).

Around 1000 BC Phoenician builders discovered the pozzolanic effect of brick dust, which they added to the calcined lime (Scheidegger, 1994). The binders produced in this way develop a hydraulic character due to the presence of reactive Si and Al phases in the brick dust. This means that the calcium hydroxide reacts in aqueous solution with the silica and the aluminum oxide to form calcium silicate hydrates (C-S-H phases) and calcium aluminate hydrates (C-A-H phases), later referred to as C-(A)-S-H phases. The mortars produced in this way are, so to speak, waterproof and can also be used in moist environments and in building in contact with water. In addition to the hydraulic reaction, carbonation also contributes to strength gain. Knowledge of this technique was later perfected by the Greeks and Romans and spread across large parts of Europe (Stark & Wicht, 2000). Even today, designations for this building material can be found in numerous countries: in Turkey it is known as Horasan, in India as Surkhi, in Arab countries as Homra and in Italy as Cocciopesto (Shi & Day, 1993; Böke et al., 2006). The collapse of the Roman Empire meant that this technique was

largely forgotten for several centuries. Only for a few areas, e.g. the Byzantine Empire, there is evidence that pozzolans continued to be used there (Bakolas et al., 1998; Moropoulou et al., 2002). Extensive studies on medieval binders in the Alpine region have shown that these are often hydraulic in nature. The hydraulic character is less due to the deliberate use of pozzolans than to the unconscious use of marly limestone (Diekamp, 2014). This rock contains variable amounts of clay minerals and is thus hydraulically effective. In addition, many of these medieval binders contain considerable amounts of magnesium, which is due to the use of dolostone or marly dolostone as a raw material. Over time, magnesite and hydromagnesite can form in these mortars (Diekamp, 2009). Antique and medieval mortars, which contain both pozzolanic brick fragments and significant amounts of magnesium in the binder, are known from few buildings in the Alpine region. The mineralogical composition of some of these mortars is examined in detail in a recently published study. The main component of all binders is calcite. In addition, aragonite is found in some samples. Magnesium-containing phases occur in the form of brucite and lizardite. There are indications of C-(A)-S-H and M-(A)-S-H phases in the binder in both medieval and antique samples. The character of all mortars examined in the study can be described as hydraulic (Schidlowski, 2019). There are a number of factors that influence the formation of mineral phases during the setting process and their alteration in these mortars over the centuries. In addition to the mineralogical composition of raw materials and additives, changes in air humidity and temperature as well as the presence of chemical compounds (e. g. sulfur compounds) in the surrounding air play an important role among others (Elsen et al., 2010; Weber et al., 2015; Paama et al., 1998). In order to investigate the effects of the mineralogical composition of the raw materials and the humidity in more detail, mortars with different formulations were produced, stored under controlled environmental conditions and analyzed after different periods. Another focus was on comparing these samples with historic pozzolanic mortars with regard to the mineralogical composition.

2. Materials

2.1 Raw materials

Limestone, dolostone and magnesite were chosen as raw materials that form the basis of the binder. These differ essentially in the different levels of CaO and MgO (Table 1). In a first step, these raw materials were calcined to produce oxides. While limestone mainly reacts to CaO and magnesite to MgO, the calcined dolostone contains a mixture of both oxides. The calcination was carried out at different temperatures in order to avoid a decrease in reactivity due to sintering processes. This was 900 °C for limestone (Moropoulou et al., 2001), 800 °C for dolostone (Gu et al., 2014) and 700 °C for magnesite (Mitina et al., 2015). After a residence time of 180 minutes at maximum temperature, the raw materials were completely decarbonated.

2.2 Additives

Three different additives were used, including two pozzolanic ones in the form of brick fragments and a latent hydraulic one in the form of blast furnace slag (Table 1). Pozzolanic materials contain reactive silica and harden in combination with Ca(OH)₂ and water in the course of the pozzolanic reaction. Latent hydraulic materials contain enough free CaO to be able to harden hydraulically in water without the addition of other substances. The reaction product of these reactions are the aforementioned C-(A)-S-H phases (Stark & Wicht, 2000).

Two different types of bricks were used as pozzolanic additives. Antique bricks (117-130 AD) from the area around Rome are rated as moderately reactive due to low calcination temperatures and amorphous proportions. The high calcite content of these bricks, which was determined using XRD, is

attributed to progressive alteration and contact with calcareous water. Modern bricks produced at the HTL Innsbruck are rated as not very reactive due to high calcination temperatures and high crystallinity. Furthermore, granulated blast furnace slag (later referred to as slag) from the Ukrainian Kaolin Company was used, which is known as a highly reactive latent hydraulic additive.

Table 1: Mean chemical composition of the raw materials and additives (in weight percent) determined by XRF (LOI: loss on ignition; Na₂O not detected).

	Limestone	Dolostone	Magnesite	Slag	Antique bricks	Modern bricks
SiO ₂	1.73	2.14	1.97	37.04	39.76	67.12
Al ₂ O ₃	0.27	0.19	0.00	10.19	11.81	13.34
Fe ₂ O ₃	0.28	0.12	0.68	1.22	6.75	8.11
CaO	51.40	28.73	1.00	36.26	18.14	1.85
MgO	1.50	21.41	45.83	9.24	3.40	2.12
MnO	0.00	0.01	0.06	1.49	0.16	0.31
TiO ₂	0.00	0.00	0.01	0.95	1.04	1.56
K ₂ O	0.18	0.10	0.00	1.36	2.14	2.45
P ₂ O ₅	0.03	0.01	0.00	0.00	0.15	0.13
SO ₃	0.00	0.04	0.00	1.14	0.00	0.00
LOI	44.63	47.26	50.46	1.11	16.64	3.01
Total	100.00	100.00	100.00	100.00	100.00	100.00

3. Methods

3.1 Analytical methods

The chemical composition of the raw materials was determined on pressed pellets (using boric acid powder) with the help of the energy dispersive **X-ray fluorescence (XRF)** spectrometer Oxford XR 400 (rhodium tube). Mean values of several analyses were calculated.

The **X-ray diffractometry (XRD)** for the qualitative analysis of the mineral phases was carried out with the EMPYREAN, a multi-purpose diffractometer from PANalytical. The measurements were carried out using CuK α radiation in an angular range from 5° to 70° 2 θ . The mineral phases were evaluated semi-quantitatively according to the system suggested by Middendorf, 2005.

With the help of **simultaneous thermal analysis (STA)**, a combination of differential thermal analysis (DTA) and thermogravimetry (TG), hydraulic and non-hydraulic binder phases were identified on the basis of dewatering and decomposition reactions and thus the character of the binder was determined. The measurements were carried out with a NETZSCH STA 449 F5 Jupiter in a temperature range from 25° C to 1000° C at a heating rate of 10 °C/min.

3.2 Experimental setup

The oxides were slaked with deionized water. In preliminary experiments it was determined how much water has to be used so that on the one hand they react completely to hydroxides, but on the other hand the resulting binder does not become too fluid. After storage for one week, the binders were mixed with the different additives. The ratio of binder to additive in weight percent was 1:1 (Zendri et al., 2004; Fortes-Revilla et al., 2006). Based on the workability, water was added if necessary. The water-solid ratio was kept as low as possible to prevent shrinkage cracks during hardening (Nežerka et al., 2014).

The addition of aggregates in the form of sand or gravel was deliberately avoided because their influence on the phase formation should be excluded. There is also evidence in the literature that the properties of the pastes must be examined without the addition of other additives in order to

understand the behavior of the lime-based mortar and the influence of the pozzolans (Nežerka et al., 2014).

Since there was only a limited amount of antique bricks and the determination of flexural and compressive strengths was not the aim of this work, small prisms of dimensions $W \times H \times L = 10 \times 10 \times 40$ mm were produced instead of standard prisms (Figure 1). Initially, all test specimens were stored in accordance with ÖNORM EN 196-1 at a constant temperature of 20 ± 1 °C and a relative humidity of at least 95%. The prisms were removed from the mold after two days. Half of the test specimens of each mixture were still stored at 20 ± 1 °C and at least 95% relative humidity in sealed bags without the supply of CO₂ (20/95). The other half was stored in a climate chamber at 20 ± 1 °C and 65% relative humidity (20/65). After 28, 90 and 180 days, the test specimens were ground to a powder using isopropanol and dried at 40 °C to stop further reactions.



Figure 1: Prisms before and after demolding.

4. Results

4.1 XRD analysis

The results of the XRD analysis are shown in Table 2. As the results of the different analysis periods (28, 90 and 180 d) differ only slightly, they are summarized in this table.

Some general comments on the evaluation of the XRD analysis:

- Due to the high quartz content of the modern bricks and their good crystallinity, the diffractograms of prisms with modern bricks have significantly higher count numbers than other samples. As a result, the proportions of binder phases in the semi-quantitative evaluation appear to be lower despite comparable count numbers.
- Since the antique bricks have significant calcite contents, the calcite contents in the semi-quantitative evaluation of these samples have to be corrected downwards.
- Due to the higher amorphous content in the blast furnace slag, these diffractograms mostly have elevated backgrounds (Figure 2).

In the dolostone-based samples five different mineral phases that were assigned to the binder could be identified. These are calcite, brucite, portlandite, monocarboaluminate and aragonite. Depending on the storage conditions, there is a noticeable difference in the content of these mineral phases.

Calcite is present to dominantly present in the samples stored at 20/65, while it only occurs in traces in the samples stored at 20/95. Brucite and Portlandite occur only in traces regardless of the storage conditions. Monocarboaluminate is only found in traces at 20/95. Aragonite was only found in trace amounts in samples with blast furnace slag. The detection of C-(A)-S-H typically occurring in hydraulic binders and M-(A)-S-H, which can also form in hydraulic binders, is only possible with difficulty due to their poor crystallinity. However, elevated backgrounds at certain 2-theta values, especially in the samples with slag, give indications of quantities of these phases.

In the limestone-based samples there is no brucite, the other binder phases are identical. Depending on the storage conditions, the mineralogical composition fluctuates significantly more. This is particularly evident in the minerals calcite and portlandite. In contrast to the samples stored at 20/65, the samples stored at 20/95 have a significantly lower calcite and significantly higher portlandite content. The portlandite content decreases slightly over time, while the calcite content is rising. Monocarboaluminate is only contained in the samples stored at high humidity (20/95). In the magnesite-based samples, brucite is the dominant binder phase. Aragonite occurs again only in the samples with blast furnace slag. The small amounts of calcite may have formed from the low calcium levels in the magnesite or have their origin in the bricks. There are virtually no differences between the two storage conditions in the magnesite-based samples.

Table 2: Semi-quantitative XRD analysis data. Based on the peak intensities, the individual proportions were quantified according to the system used by Middendorf, 2005: +++ dominantly present; ++ present; + traces; ? possibly present; - not detected. MCA = monocarboaluminate.

Raw material	Additive	Storage	Mineral phases				
			Calcite	Aragonite	Portlandite	MCA	Brucite
Limestone	Modern bricks	20/65	+++	-	? to +	-	-
	Antique bricks		+++	-	- to ?	-	-
	Slag		+++	+	- to +	-	-
	Modern bricks	20/95	+	-	++	+ to ++	-
	Antique bricks		+ to ++	-	++	+ to ++	-
	Slag		+	?	++	? to +	-
Dolostone	Modern bricks	20/65	++	-	+	-	+
	Antique bricks		++ to +++	-	+	-	+
	Slag		++ to +++	+	+	-	+
	Modern bricks	20/95	+	-	+	+	+
	Antique bricks		+	-	+	+	+
	Slag		+	? to +	+	? to +	+
Magnesite	Modern bricks	20/65	?	-	-	-	++
	Antique bricks		?	-	-	-	++
	Slag		?	+	-	-	+++
	Modern bricks	20/95	?	-	-	-	++
	Antique bricks		?	-	-	-	++
	Slag		?	- to +	-	-	++ to +++

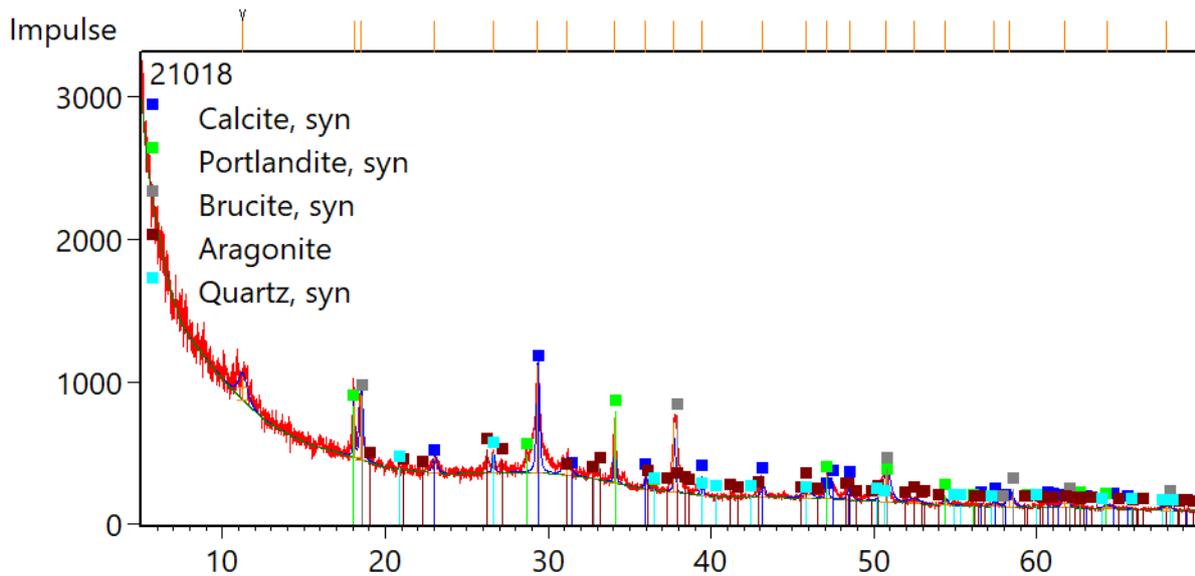
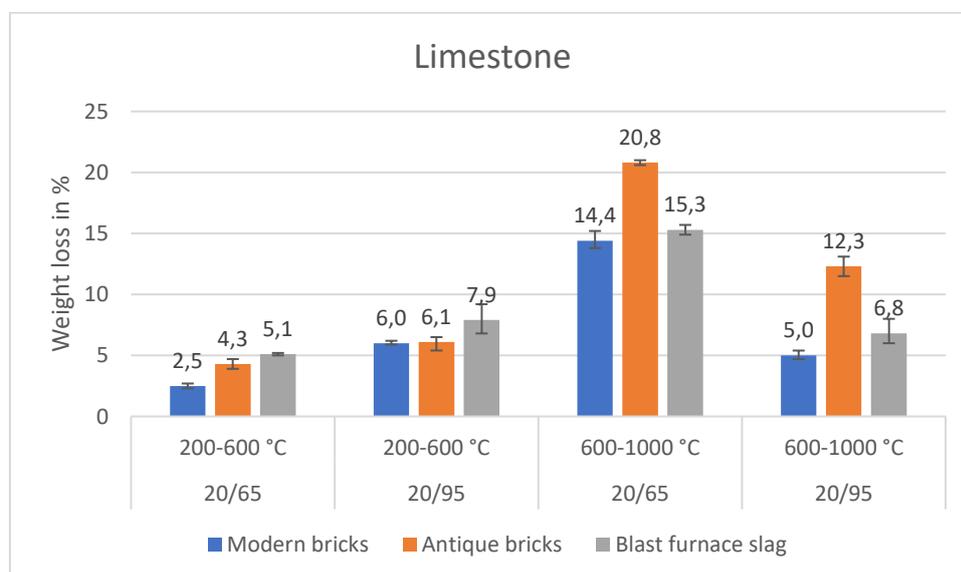


Figure 2: Diffractogram of a sample based on dolostone and metakaolin.

4.2 STA analysis

STA measurements were carried out for each sample to verify the trends identified in the XRD evaluation. The results are shown in Figure 3. The weight loss in the range between 200 and 600 °C is due to the loss of hydraulic (chemically bound) water from water-containing mineral phases (portlandite, brucite, monocarboaluminate, C-(A)-S-H phases). Between 600 and 1000 °C there is a loss of weight due to the decarbonation of carbonates (calcite and aragonite). The strikingly high values for the samples with antique bricks between 600 and 1000 °C are due to the fact that these bricks have high contents of calcite, which decarbonates in this temperature range and thus gives off weight.

In general, the differences in the weight loss between the two storage conditions are noticeable for the dolostone-based samples, strong for the limestone-based ones and almost nonexistent for the magnesite-based ones. The weight losses after 28, 90 and 180 show no significant differences. This coincides well with the findings of the XRD analysis with regard to the mineralogical composition under different storage conditions.



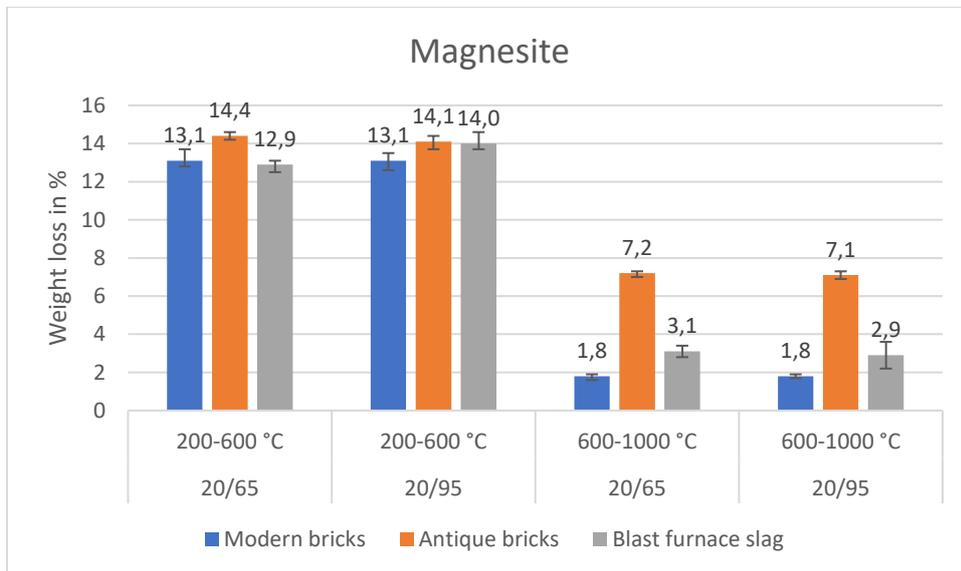
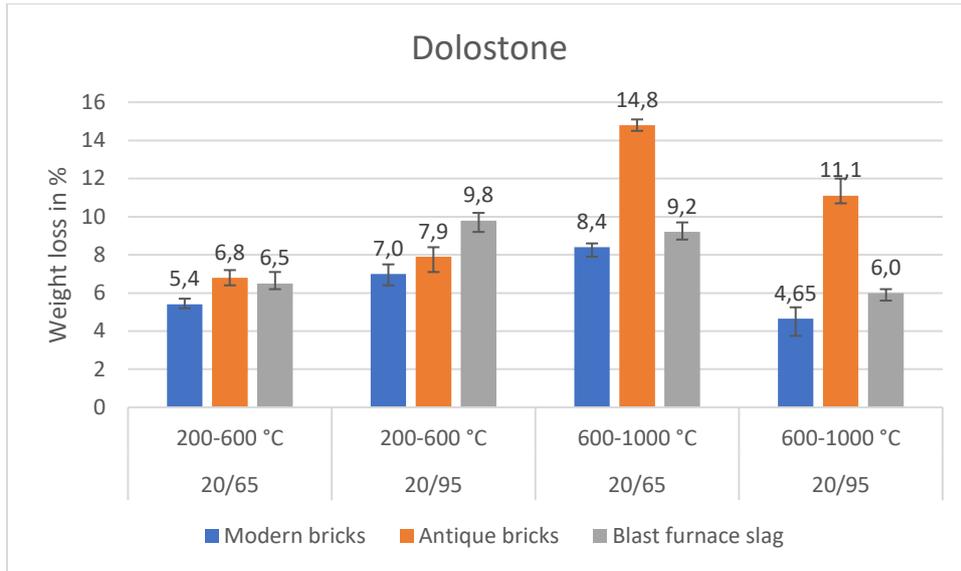


Figure 3: Graphic representation of the STA results. The values represent average values of the measurements after 28, 90 and 180 days.

5. Discussion

It can be said that the interacting processes of carbonation, hydration and pozzolanic reaction form the basis for the development of the different mineral phases in the analyzed binders. Depending on the storage conditions, one of these processes predominates. For this reason, there are clearly identifiable differences between the two storage conditions with regard to the mineral content. Due to the supply of CO₂ from the air, carbonation occurs increasingly in the samples that were stored at low humidity, resulting in higher carbonate contents. In the prisms stored at high humidity, hydration and pozzolanic reaction dominate. This leads to higher proportions of water-containing mineral phases. While hydration and pozzolanic reaction normally are fast-moving processes that contribute to the early strength of binders, the carbonation process lasts over significantly longer periods (Cizer et al., 2010).

The mineralogical differences in the examined prisms are only slight after 28, 90 and 180 days. It can be concluded that a large part of the hydraulic and pozzolanic reactions had already ended after 28

days, which is mainly attributed to the small size of the test specimens. The only noticeable change is the increase in the calcite content in the limestone-based samples due to the carbonation of the calcium hydroxide. In the samples based on dolomite rock, this phenomenon can be observed in a less pronounced form due to lower calcite contents. For this reason, the difference between the two storage conditions is smaller. The phenomenon does not exist in the magnesite-based samples due to the lacking calcite content. This explains why there is only a small or no difference in the amount of the observed binder phases between the two storage conditions.

Some hypotheses regarding the formation of certain mineral phases found in the mortars are explained below.

Possibilities for the formation of aragonite in hydraulic mortars are dealt with in the literature. Of all the options described, the formation of aragonite by carbonation of C-S-H phases is most likely (Cole & Kroon, 1959). The reason for this assumption is that aragonite is only found in samples with slag, in which the highest proportions of C-S-H phases are suspected. Traces of aragonite can also be found in the historical brick dust mortars containing C-S-H phases.

The presence of monocarboaluminate is described in the literature primarily in binders with hydraulic components. Stable phases are, especially in the presence of carbonate and in the absence of sulfate or chloride, hemicarboaluminate and monocarboaluminate. Hemicarboaluminate is being converted to monocarboaluminate (Kuzel & Pöllmann, 1991; Lothenbach et al., 2006). Furthermore, the occurrence of monocarboaluminate is described in the literature as a result of hydration processes in Portland cements (Ipavec et al., 2011).

The reaction of brucite and CO₂ to magnesite, which can occur in the binder of Mg-containing mortar, could not be observed. This reaction usually proceeds very slowly via metastable intermediate phases such as nesquehonite, hydromagnesite or X-ray amorphous intermediate phases and is dependent on general conditions such as moisture content in the mortar and CO₂ content in the environment (Diekamp, 2014). Due to the high background in most samples, the formation of these phases, especially the X-ray amorphous ones, cannot be excluded.

Overall, the mineralogical composition of the binders produced appears to be similar to that of the antique mortars examined. The missing or very low levels of portlandite and brucite in the historical mortars are attributed to the fact that they have been completely carbonated over the course of time or have changed to C-S-H and M-S-H phases.

6. References

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