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## **ANALYSIS AND RECOGNITION OF DOLOMITIC LIME MORTARS**

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### **ABSTRACT**

*Mortar analysis usually is performed by microscopy and wet chemical methods, at times completed by X-ray diffraction, infrared spectroscopy or other more complicated methods. For pure lime mortars with a river sand filler, mainly consisting of quartz and feldspar, the analysing methods and the interpretation of the results are straightforward, however analysis and interpretation become more complicated if there are other binders and/or aggregate types present.*

*Our paper focuses on dolomitic lime mortars. We lie out, that depending on the kind of raw material that was burned, on the burning temperature, on the way of slaking, on the manner of the actual mortar preparation and finally on the further history of the mortar, different mineral phases will actually grow in dolomitic lime mortars. The possible magnesium phases are listed and discussed in regard to their likelihood of being present, Further it is shown, what information is necessary to be able to interpret the analytical results and to distinguish dolomitic lime mortars from other mortar types.*

*It is also shown, that a very useful analytical method for mortars, is thin section microscopy. It allows to recognise the mineral phases and also to observe, whether these minerals are present as a part of the aggregate or of the binding media, a differentiation which is crucial for the interpretation. Other analytical methods like XRD or IR are shown to be very helpful to give additional information on constituents that are too small in grain size to be analysed by polarising microscopy, however some products of the setting reaction of dolomitic lime mortars cannot be detected by these methods.*

*Further we give some examples of dolomitic lime mortars and discuss the analytical limitations.*

### **INTRODUCTION**

There are several reasons why mortars from monuments and excavation sites are analyzed. Sometimes it is done to compare the different mortars occurring and to get evidence for them being of the same or a different construction period (e.g. Kühn 1987; Jedrzejewska 1981), on other sites the mortar repairs should be done with a similar material (e.g. Streicher 1991) or the analysis is done to gain more knowledge about the building techniques and/or where the materials have been supplied from.

The analysis usually is performed by microscopy and wet chemical methods, at times completed by X-ray diffraction, infrared spectroscopy or other more complicated methods. The steps in which an analysis is actually done and the interpretation of the results are depending on the individual aim. For pure lime mortars with a river sand filler, mainly consisting of quartz and/or feldspar, the analyzing methods and the interpretation of the results are straightforward, however analysis and interpretation become more complicated if there are other binders and/or aggregate types present, than the ones named before. The situation is usually aggravated by the fact, that in practise

there is only a very limited amount of sample available, which makes it necessary to select the analytical steps carefully.

When examining a historical mortar macroscopically, with a hand-lens or with a binocular microscope-normally the only analytical methods used on site before the sample taking-it is hardly ever possible to distinguish pure lime mortars from other types of mortars, therefore the subsequent analytical steps have to be selected, so that no information is accidentally lost.

For the following dolomitic lime mortars will be the main subject of interest. In some regions where dolomites are the predominant carbonaceous rocks, mainly dolomitic lime was used for construction. One such area is Trier where dolomitic lime was used ever since Roman times and where some of our samples, however of younger age, come from. We would like to lay out here our way of analyzing mortar samples, emphasize some theoretical notions on the interpretation of the results based on examples to show what the analytical limitations are.

## LIME MORTARS AND DOLOMITIC LIME MORTARS

For the following discussion of the analytical results, it is necessary to summarize the possible components of such mortars.

### Sand

The aggregate for both types of mortars is the same. It consists of sand with a certain grain size distribution, grain shape and mineralogy, depending on where it was supplied from (see sand, river sand). In most cases it contains quartz and feldspar grains which do behave inert during the setting of the mortar, i.e. they do not react with the binder. Bérubé et al. (1990) have shown, that hydraulic reactions between lime and quartz or feldspar can occur after very long reaction times. We were however not able to detect the resulting reaction products (calcium silicate hydrates) by means of secondary electron microprobe imaging in several lime mortar samples, so that we suppose, that these reactions only play a minor role in mortars. Apart from quartz and feldspar the sands can contain to a small extent micas, clay minerals, and a whole range of other minerals, which here also are considered to behave inert to the setting process. However some very fine grained minerals can probably be dissolved or leached to a certain extent by the hydrochloric acid used for the chemical analysis (25%, see 3.2) and therefore have to be considered when interpreting the results.

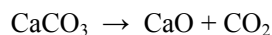
Depending on the source for the sand, it can also contain carbonates - mainly calcite:  $\text{CaCO}_3$  or dolomite:  $\text{CaMg}(\text{CO}_3)_2$  -, or ground or chipped limestone, marble of dolomite have been added to the sand (see e.g. Drack 1986, 82ff). These parts of the aggregate are particularly important to distinguish from the binding media by means of a microscope, as they cannot be distinguished from the binder by only performing chemical analysis.

Organic additives as wood or hair can also make part of the mortar, but they do hardly influence the result of the chemical analysis.

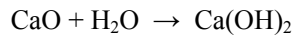
### Binder

*Pure lime* (see also Krenkler 1980)

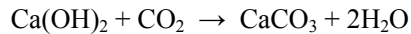
Limestone is burnt at 900 to 1000°C, the product of which is calcium oxide, according to the reaction:



The burnt lime is slaked with water. Depending on how this is done (see e.g. Pursche 1988), the resulting material is physically, but not chemically different. E.g. lime that was slaked for a longer period of time in a pit, forms a smooth very homogeneous putty, whereas lime that was prepared on the building site by inter layering sand and burnt lime and then slaked with water, usually contains little lumps of lime, which later can be observed in the mortar (Wisser 1989). The slaking reaction is very quick and exothermic, and it can be written by the equation:



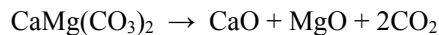
During the setting of the lime mortar, calcium hydroxide takes up  $\text{CO}_2$  from the surrounding air following the equation (simplified):



This reaction can only take place in a humid environment, where water acts as a catalyst, however it cannot take place under water. The reaction is rather slow because of the limited supply rate for  $\text{CO}_2$  from the surrounding atmosphere, and it takes place from the outer surface inwards. Usually the calcium carbonate calcite is formed. During slaking of pure lime high temperatures are reached, so that it is theoretically possible, that aragonite (an other modification of  $\text{CaCO}_3$ ) is formed.

*Dolomitic lime* (see also Niesel, Schimmelwitz 1971):

Dolomitic limestone of dolomite is usually burnt at the same temperature as pure lime stone, this process follows the reaction (simplified):



Kühn (1985) adds the information, that if dolomite is burnt at lower temperatures (700 to 800°C), the reaction result will be a mixture of calcite ( $\text{CaCO}_3$ ) and periclase ( $\text{MgO}$ ), which can set hydraulically. A dolomite which we burnt at 750°C for one hour was transformed by this to calcite and periclase and some dolomite was left over.

Burnt dolomite reacts slower during the slaking process than pure lime. The reaction can simplified be written as follows:

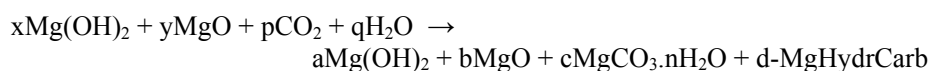


In this slaking process the transformation from calcium oxide to calcium hydroxide is a quick reaction, the magnesium oxide component however shows only a very slow water uptake, so that in many cases a mixture of calcium hydroxide, magnesium hydroxide and magnesium oxide is used to prepare the actual mortar.

When the burnt lime is slaked in a pit and rested there for several years, all the magnesium oxide will have time to take up water and the calcium hydroxide and the magnesium hydroxide will gravimetrically form separate layers, because the denser brucite  $\text{Mg(OH)}_2$  is sinking to the bottom of the pit. For any other ways of slaking, that only provide shorter times of contact between water and periclase, not all periclase will transform to brucite. An analysis of a burnt and slaked dolomitic lime given by Niesel and Schimmelwitz (1971) shows that magnesium oxide is clearly dominating magnesium hydroxide, and that some calcium hydroxide is already carbonated.

The setting of dolomitic lime can be described by two reactions, the first of which only considers the setting of the calcium hydroxide and is exactly the same reaction as stated above for pure lime, however magnesium phases accelerate the reaction speed of calcium carbonate production.

The second reaction considers the magnesia phases and can be described by the following equation (Mg-HydrCarb stands for magnesium hydroxide carbonates, see also table 1):



The coefficients a to d depend very much on the reaction time and on the amounts of water and CO<sub>2</sub> available (see below).

Table 1 *Calcium and magnesium phases possibly occurring in dolomitic lime mortars after setting, with an evaluation of their likelihood to be present as part of the binder or the aggregate.*

Mineral name	Chemical formula	Abundance in:		Detectable by:		Information from:
		binder	sand	XRD	IR	
Portlandite	Ca(OH) <sub>2</sub>	+	-	+	+	L,A
Calcite	CaCO <sub>3</sub>	++	+	+	+	L,A
Aragonite	CaCO <sub>3</sub>	+	+	+	+	A,T
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	-	+	+	+	A
Periclase	MgO	+	-	+	-	L,A?
Brucite	Mg(OH) <sub>2</sub>	+	-	+/-	+	L,A
Magnesite	MgCO <sub>3</sub>	+	-	+	+	L,A
Nesquehonite	MgCO <sub>3</sub> ·3H <sub>2</sub> O	+	-	+	+	T,A?
Lansfordite	MgCO <sub>3</sub> ·5H <sub>2</sub> O	+	-	+	+	T,A?
Artinite	MgCO <sub>3</sub> Mg(OH) <sub>2</sub> ·3H <sub>2</sub> O	+	-	+/-	+	T,A?
Hydromagnesite	3MgCO <sub>3</sub> Mg(OH) <sub>2</sub> ·3H <sub>2</sub> O	+		+/-	+	L,A?

(sand=aggregate; ++=certain; +=possible; -impossible) and with information on their detectability by means of XRD=X-ray diffraction or IR=infrared spectroscopy (+/- stands for "depending on the degree of crystallinity"). The last column gives the sources for the information listed in this table: A=mineral phases found by the authors in dolomitic lime mortars (see also table 3); L=phases listed in publications (see text for exact quotations); T=theoretically assumed mineral phases (see text for argumentation).

In ancient lime or dolomitic lime mortars portlandite is usually completely carbonated. However Mairinger and Schreiner (1986) found that the Gothic dolomitic lime mortars from the vaults of the convent church of Münstair (Switzerland) still contained portlandite. The carbonation of portlandite only takes place in a humid environment, so portlandite can only remain not carbonated at places which dried out rather quickly and did not get wet again, whereas at places where the mortar got wet frequently (e.g. rain exposed façades) or where the mortar was kept wet long enough to carbonate completely no portlandite can be expected. Portlandite was never found and is not likely to be part of the aggregate.

Calcite is probably the main calcium mineral present in the binder. It can also be present as part of the sand, but thin section analysis will help to distinguish the two types, which is important for the interpretation of the results. Calcium carbonate can also be present in the form of aragonite, either belonging to the aggregate in the form of shells or belonging to the binder, if the mortar has reached high temperatures during setting.

Calcium and magnesium seem exclusively to form separate phases (Niesel, Schimmelwitz 1971), therefore dolomite can only be present as part of the aggregate.

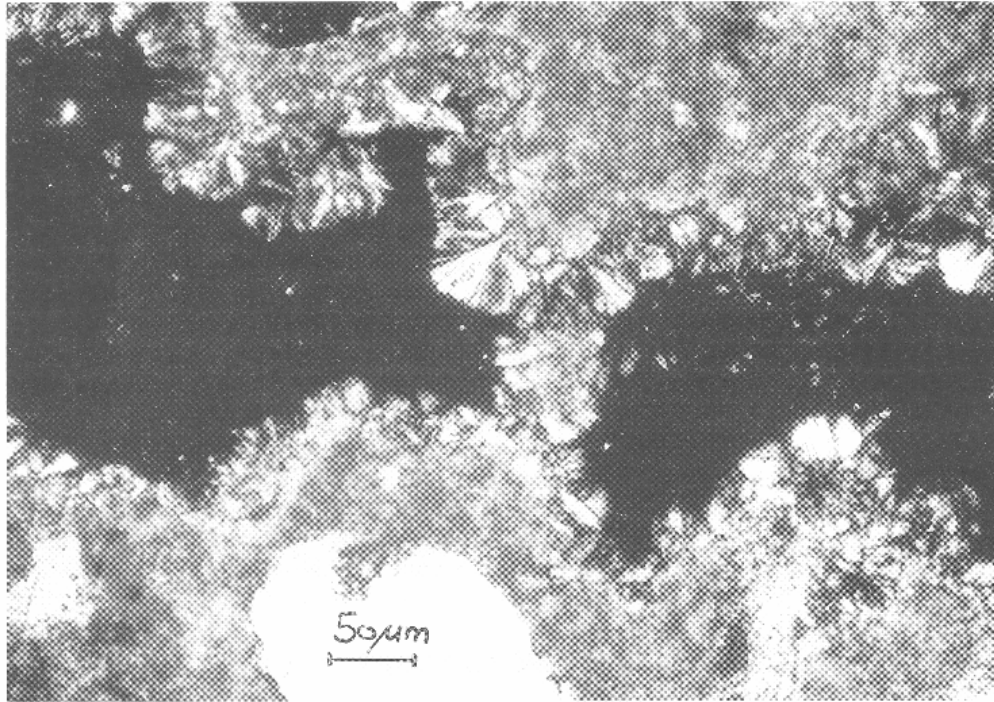


Figure 1 *Brucite needles growing in a dolomitic lime mortar closing a fissure. More, microscopically barely visible brucite is intergrowing with calcite in the ground mass (sample 30311, from St. Maximin, Trier, Germany, see also part 5)*

In mortars that were frequently of permanently wet (exposed to rain or buried under ground) periclase will most likely be hydrated, however as the transformation to brucite of an amorphous form of magnesium hydroxide takes place only very slowly, it is anyway possible that periclase is present as part of the binder of old mortars. Kühn (1985) found some periclase besides brucite and calcite in paint layers, which, how he supposed, have been painted by using slaked dolomitic lime. Periclase is very unlikely to form part of the aggregate.

The first product of the hydration of periclase is an X-ray amorphous magnesium hydroxide, which is only later transformed into brucite. The speed of reaction is dependent on how long and at what temperature the periclase was burned, with the reaction being slower for high temperatures and long burning periods (Gmelin 1939). Brucite crystallizes, under water or in wet or humid environments, forming long needles (Fig. 1) intergrowing each other, which can result in a certain stiffness of the mortar, hence dolomitic lime mortars can set hydraulically without containing calcium silicates. Neither brucite nor amorphous magnesium hydroxide do occur as part of the aggregate. Kühn (1985) found in mortars from Leonardo Da Vinci's "last supper" brucite and Mairinger and Schreiner (1986) analyzed X-ray amorphous magnesium hydroxide in mortars of Müstair.

According to Gmelin (1939), magnesite is only precipitated at high and lansfordite at low temperatures, and the carbonate which is most likely formed under the circumstances predominant during mortar setting is nesquehonite, which can be formed from humid magnesium hydroxide by taking up CO<sub>2</sub> from the air.

None of the three minerals is likely to be part of the sand admixture. Mairinger and Schreiner (1986) did analyze magnesite as being part of the Müstair mortars.

Basic magnesium carbonates (hydromagnesite or artinite) can be formed by reaction of magnesium salt solution with alkali salt solution or by air reacting with a suspension of nesquehonite in water (Gmelin 1939). The basic magnesium carbonates however seem not to be very stable and can be transformed into nesquehonite under certain conditions. Siedel (1992) reports to have found hydromagnesit besides X-ray amorphous magnesium phases in the mortars of the Tulpenkanzel of Freiberg. Basic magnesium carbonates are not likely to be part of the aggregate.

To summarize the setting reaction of dolomitic lime mortar, it is important to take into account, that some parts of this reaction (the formation of brucite) can take place under water and other parts need a supply of considerable amounts of CO<sub>2</sub> and therefore do not take place under water. Which implies, that depending on how long the setting mortar is kept wet or only humid, it will show a different mineralogical composition compared to a mortar with the same chemical composition but an other (setting) history. This indicates also, that the chemical analysis of a dolomitic lime mortar can only be recalculated into mineral phases, if the minerals it contains have actually be measured quantitatively, which is usually not possible with reasonable effort.

## ANALYTIC METHODS

### Sample preparation and optical microscopy

The whole problem of selecting, taking, storing and transporting the sample is discussed in Knöfel and Schubert (1993), and therefore will not be discussed here. Once the sample arrives in the laboratory it is weighed and afterwards dried in the oven at 40°C to constant mass as defined by RILEM-PEM (1980). We choose 40°C as our standard drying temperature to avoid loosing crystalline water in case of the presence of gypsum. The weight loss then reflects the water content of the sample.

Only after this treatment the sample is examined by means of a binocular microscope and it is described in terms of size, colour and type of aggregate, colour of binder, homogeneity, hardness, presence of other materials like wood, fibres, hair and little lime lumps etc.

Whenever the sample size allows it, a thin section is made from one part of the sample. This needs at least 2g (about 1cm<sup>3</sup>) of coherent material, possibly showing also the attached paint layers. It is advisable to impregnate the sample for thin section by a coloured epoxy resin, to solve analytical problems concerning the pore space, although in such sections it is more difficult to distinguish the often small minerals forming the binder. If possible the grinding should be done without using water, because some of the constituents of the binder are water soluble to a certain extent. The section is analyzed by polarising microscopy, with the diverse methods described by Müller and Raith (1987). This examination gives the mineralogical and petrographical composition of the sand and to a limited extent of the binder, the interconnection, shape and size of aggregate, grains and pores. With this method only individual grains of at least 2mm can be analyzed, accordingly particles of the binding media, which are usually smaller cannot be identified unambiguously by this method.

## **Wet chemistry**

For the following discussion of wet chemical analysis, we are only considering the cases of rather fine grained mortars, as they often occur as a ground for wall paintings or as finishing layers. For the basic wet chemical analysis at least 2g better about 5g of homogeneous and representative sample are needed (see also Wagner 1992).

Paint or white wash layers are removed mechanically. The carbonate content is then measured by means of a Scheibler apparatus (see e.g. Müller 1967), on at least two individual parts of the sample. In principle hydrochloric acid (water: concentrated HCl=1:2 by volume) is added to the sample to dissolve the carbonates, from the volume of the thereby released gas, the carbonate content is calculated. For the interpretation it is important to keep in mind, that hydrogen carbonate is also releasing CO<sub>2</sub>. The relative error of this method is approximately +/- 5% of CO<sub>3</sub>.

The remaining sand and the acid solution are heated to 90°C for an hour to dissolve possibly contained gypsum and then separated by filtration. The filter is washed until there is no chloride left, which can be tested by means of silver nitrate solution (see Hofmann, Jander 1972). Calcium and magnesium are measured titrimetrically (Jander, Blasius 1990), and sulphate is analyzed by means of Merck photometric tests in the filtrate. The detection limit is 0.1% for calcium and magnesium and 0.4% for sulphate, with an error of about 2%. The sand is dried to constant mass and is then used for the sieve analysis, which gives the grain size distribution.

## **X-ray diffraction and infrared spectroscopy**

For the following it is necessary to give a short discussion on the detectability of the setting reaction products of dolomitic lime mortars by means of X-ray diffraction and infrared spectroscopy, as these two methods are the ones most frequently used for that purpose.

With X-ray diffraction (XRD) lattice widths within crystals are recorded, which means that no non crystalline phases can be detected. Therefore Mairinger and Schreiner (1986) were only able to detect X-ray amorphous magnesium hydroxide by differential thermal analysis and thermogravimetry. Even some of the crystalline phases in the binder are very difficult to detect with XRD especially if several of them are present. The detection limit lies in ideal cases at 1% by weight, but for some minerals much higher. Further, for some of the minerals that are possibly present in the binder many of the characteristic peaks in the diffractogramme lie at the same 2-theta angles, which makes it often impossible to be sure which one of these minerals is present or to recognize mixtures of them.

By means of infrared spectroscopy (IR) chemical bonds are detected, therefore with the exception of materials containing a single element or pure oxides (e.g. periclase) all chemical groups can be detected. However similar to the problems arising with XRD, it is difficult to detect mineral phases in mixtures with other minerals containing the same chemical groups.

In spite of these problems it can be helpful to separate mechanically a little part of the binder with as little aggregate as possible and analyze it by means of XRD and/or IR to state the composition of the binder, if these equipments and enough sample are available. For an unambiguous interpretation it will however be necessary to compare these results with the thin section analysis, e.g. to distinguish carbonate of the binder from carbonate of the aggregate. Both IR and XRD usually are only performed qualitatively.



Table 2 *Theoretical chemical composition of calcium and magnesium phases possibly present in lime or dolomitic lime mortars after setting (all values in weight %), "analysis" gives the sum of the chemical constituents that are measured during a wet chemical analysis (Mg, Ca, CO<sub>3</sub>, SO<sub>4</sub>) and "Rest" give the part of each mineral which is not analyzed.*

Mineral	Mg <sup>+2</sup>	Ca <sup>+2</sup>	CO <sub>3</sub> <sup>-2</sup>	SO <sub>4</sub> <sup>-2</sup>	OH <sup>-</sup>	H <sub>2</sub> O	O <sup>-2</sup>	An.	Rest	Rest/ Mg
Portlandite		54.1			45.9			54.1	45.9	
Calcite		40.0	60.0					100	0	
Dolomite	13.2	21.7	65.1					100	0	0
Periclase	60.3						39.7	60.3	39.7	0.7
Brucite	41.7				58.3			41.7	58.3	1.4
Magnesite	28.8		71.2					100	0	0
Nesquehonite	17.6		43.4			39.0		61.0	39.0	2.2
Lansfordite	13.9		34.4			51.7		48.3	51.7	3.7
Artinite	24.7		30.5		17.3	27.5		55.2	44.8	1.8
Hydromagnesite	26.6		49.3		9.3	14.8		75.9	24.1	0.9
Gypsum		23.3		55.8		20.9		79.1	20.9	

## INTERPRETATION

For the interpretation of the data from the wet chemical analysis it is important to keep in mind, that, except for pure lime mortars, not all the chemical constituents actually present in the minerals of the set mortar are measured, this means, that hydroxide, oxide and crystal water are not detected directly. The following table 2 gives a listing of the relevant minerals with their composition in weight-%, the sum of constituents analyzed and the rest which is not detected directly.

For pure lime mortars that are completely carbonized the sum (Ca+Mg+CO<sub>3</sub>+Sand) should equal theoretically 100%, as they contain only inert sand and calcium carbonate as a binder. If there is no dolomite present Mg should be zero. Even if dolomite was present the sum would have to be 100% as all constituents are actually measured (see table 2). In reality lime mortars usually give sums of 95% or higher. There are several reasons why the theoretical sum is never matched exactly. Firstly there is the analytical error which e.g. can reach as high as +/- 10% for the CO<sub>3</sub> determination (see Müller 1967). Then, especially if there is calcite present in the aggregate, this is hardly ever pure stoichiometric calcium carbonate but it can contain certain amounts of e.g. iron (see Deer et al. 1962). Similar notions can go for dolomitic rock fragments present, which can also contain considerable amounts of other ions than calcium or magnesium. But also if calcite is only present in the binder, it is depending on the history of the binder making how pure the calcium carbonate in the final mortar will be. Further, very fine grained silicates, that are usually present, are not inert to the use of hydrochloric acid. Finally at lot of time mortars contain some not carbonized portlandite, which cannot always be detected easily if present in small amounts (detection limit for X-ray diffraction in samples with only a few mineral phases is about 1%; and 1% portlandite would result in nearly 0.5% reduction of the sum).

Out of twelve samples of pure lime mortars of different ages (14th to 19th century) from the church of Mussbach (see also example PH06 below), nine reached sums of more than 97% and the rest more than 95%. However mortars containing some other binding material, such as volcanic material, dolomitic lime or portland cement the sum of  $\text{Ca}+\text{Mg}+\text{CO}_3+\text{sand}$  always reaches less than 95% usually less than 90% and sometimes even below 80%. From the above it can be stated that if the sum of  $\text{Ca}+\text{Mg}+\text{CO}_3+\text{sand}$  lies below 95% the mortar is probably no pure lime mortar and if the sum is below 90% it is definitely no pure lime mortar.

If the mortar contains some gypsum besides lime the sulphate will have to be added to the sum of  $\text{Ca}+\text{Mg}+\text{CO}_3+\text{sand}$  and the result should be close to 100%. To calculate the amount of calcium and water that is contained in the gypsum,  $\text{SO}_4$  is multiplied by 0.42 and 0.37 respectively and gypsum is calculated by multiplying sulphate by 1.79.

A further hint that a mortar is not a pure lime mortar lies in the fact that the pH lies for pure lime mortars usually below 9, if however this mortar contains some not carbonated calcium hydroxide the pH will be higher than 9. For dolomitic lime mortars we usually measured pH values of around 10, probably because most of the reaction products of dolomitic lime setting are basic. It is very important to notice however, that mortars which contain portland cement or which are contaminated by alkaline salts (Arnold 1985) will also have elevated pH values.

A mortar made out of dolomitic lime would of course contain magnesium, there are however other mortars that can also show high contents in magnesium, like e.g. if they include magnesium rich volcanic rock fragments, that are partly soluble in hydrochloric acid, but also lime mortars containing dolomite as part of the aggregate. Already magnesium contents as low as one or two percent have to be considered 'elevated". This can be explained by the fact, that the products of the setting reactions of dolomitic lime mortars contain only a mean value of about 25% magnesium (see table 2), so that 2% magnesium represents 8% of these minerals.

Pure dolomitic lime mortar should have a ratio of Ca to Mg of about 1.64. This is still true if there is dolomite present in the aggregate. The ratio becomes much higher for lime mortars and it becomes lower if there are other magnesium phases present that are soluble in hydrochloric acid and do not release calcium when dissolved in it.

The ratio of the "Rest" to magnesium for the reaction products of dolomitic lime mortars lie between 0.66 and 3.72 with an average value of 1.34 (table 2). E.g. if the only reaction product would be brucite and all the "Rest" would be the hydroxide from this brucite, the ratio of the "Rest" to Mg would have to be exactly 1.4. However, as mentioned above, there is always a "Rest" of a few percents, even in pure fully carbonated lime mortars containing only sand which is insoluble to hydrochloric acid. Therefore this ratio should only be used for the interpretation of the results if the "Rest" is greater than about 5%. In these cases the ratio Rest/Mg gives a further indication, whether the mortar in concern is a dolomitic lime mortar. The average ratio of twelve dolomitic lime mortars we analyzed was 3.3, however the average ratio analyzed on five lime mortars containing volcanic fragments was 4.4 and thus not very different. Therefore a ratio of between 1 and 5 can be but it must not be an indication that the mortar contains a dolomitic lime.

In a lime mortar the ratio of  $\text{Ca}/\text{CO}_3$  would have to be 2/3. Analysis of twelve lime mortars from the Mussbach church (see sample PH06 below) gave a average ratio of 0.67, however the individual values ranges from 0.58 to 0.75 with 3 samples lying above 0.68 and an other three below 0.64. In mortars with remaining not carbonized calcium hydroxide, this ratio should be higher than 0.66. In dolomitic lime mortars the ratio can theoretically be higher or lower than 0.66, depending on the products of the setting reaction, i.e. depending on the individual history of the mortar.

## EXAMPLES

For the following discussion we selected 5 samples.

### *PH06*

Is the Gothic intonaco from the church of Mussbach (near Neustadt/Weinstrasse, Germany). In this church all mortars regardless of their age are all very similar and they are pure lime mortars, probably manufactured by the same raw material. As a whole twelve samples have been analyzed and PH06 is here selected to represent one typical pure lime mortar sample.

### *RE2*

Is a 19th century plaster from the crypt of St. Appollinaris at Remagen (Germany). From this monument we have analyzed five samples of lime mortars containing volcanic material (tuff and pumice) that has partly reacted with the lime and RE2 is representative for this group of mortars.

### *30311, 302A, 302AoP*

Three dolomitic lime mortars come from St. Maximin, Trier (Germany). Their age is Romanesque or possibly older. These samples were selected out of twelve dolomitic lime samples on which wet chemical analysis were performed, from which however only the selected three could be analyzed any further. Sample 302A is the ground layer to sample 302AoP.

With the exception of PH06 the samples were analyzed by means of thin section microscopy, XRD and IR and on all samples a wet chemical analysis was performed. The results of these analysis are summed up in tables 3 and 4.

With the following discussion we intend to emphasize some of the problems that can arise, when it is the task to interpret analytical data on such mortars, taking into account the theoretical considerations outlined above.

Table 3 shows that only the dolomitic lime mortars do contain magnesium hydroxides, magnesium carbonates or magnesium hydrogen carbonates in detectable amounts. Whereas in the RE sample only other magnesium containing phases were observed. From the rather high magnesium content measured in this sample (table 4) it can be supposed, that some of the magnesium containing phases (volcanic glass) are at least partly soluble in hydrochloric acid. Thin section analysis revealed that both 302A and 302AoP contained shell fragments as part of the aggregate, so that we think that the aragonite found in these mortars by means of XRD comes from these shells and not from high temperatures during setting.

From table 4 it can be seen, that the pure lime mortar, which contains no dolomite fragments as part of the aggregate, has very low magnesium values. The magnesium content of the sample RE2 however is as elevated as the ones in the dolomitic lime mortars. From this it follows, that elevated magnesium concentrations alone are no indication for a dolomitic lime mortar. In fact only if the typical magnesium phases (table 1) are found, the mortar can be considered to be dolomitic lime mortar.

Typically the pH values of fully carbonized pure lime mortar samples lie below 9 and often below 8. If some calcium hydroxide still remains in the sample the pH will however be higher. All the reaction products of dolomitic lime mortars are alkaline, so that the pH usually is higher than 9. But again this is only an reliable indication if the relevant reaction products are actually detected.

If the gypsum content of the samples is calculated from the sulphate content the calcium ( $=\text{Ca}-\text{Ca}_{\text{gypsum}}$ ) and the "Rest" ( $=\text{"Rest"}-\text{H}_2\text{O}_{\text{gypsum}}$ ) can be recalculated so that the figures

listed in table 5 result. In this table it can be seen, that the ratio Rest/Mg varies a great deal for the three dolomitic lime mortars selected. The high ratio for sample 302AoP is somewhat disturbing, however when analyzing the thin section of this sample, certain very fine grained areas were detected which looked like former volcanic rock fragments that had completely reacted with the lime, so that we actually suppose, that this mortar originally was a mixture of dolomitic lime and puzzolana. This is also supported by the fact that the ratio Ca/CO<sub>3</sub> is higher than 0.66.

Table 3 *Types of mortar: lime=pure lime mortar; trass=mortar containing volcanic material; dolo.=dolomitic lime mortar.*

sample	type	Po	Cc	Ar	Do	Pe	Br	Mg	N/L	H/A	Gy	other
PH06	lime	-	+	-	-	-	-	-	-	-	-	-
RE2	trass	?	+		-	-	-	-	-	-	-	+
303/1	dolo.	-	+	-	-	-	+	?	?	-	-	-
302A	dolo.	?	+	+	+	-	+	+	?	?	+	-
302AoP	dolo.	+	+	+	+	?	?	?	+	+	+	?

Po=portlandite; Cc=calcite; Ar=aragonite; Do=dolomite; Pe=periclase; Br=brucite; Mg=magnesite; N/L=nesquehonite or lansfordite; H/A=basic magnesium carbonate; Gy=gypsum; other=Mg phases other than the ones previously mentioned in the table; ?=maybe present

Table 4 *Wet chemical analysis, all values in weight-%. (Sand=HCl insoluble aggregate; Sum=Ca+Mg+CO<sub>3</sub>+SO<sub>4</sub>+Sand; Rest=100%-Sum).*

sample	pH	Ca <sup>+2</sup>	Mg <sup>+2</sup>	CO <sub>3</sub> <sup>-2</sup>	SO <sub>4</sub> <sup>-2</sup>	Sand	Sum	Rest
PH06	7.8	7.1	0.1	10.1	<0.4	80.1	97.4	2.6
RE2	9.9	6.3	3.2	12.2	<0.4	65.5	87.2	12.8
303/1	10.0	8.1	5.2	13.9	3.7	55.3	86.2	13.8
302A	9.3	24.6	4.8	30.2	1.5	17.9	79.0	21.0
302AoP	10.1	14.3	2.6	18.9	1.0	44.2	81.0	

Table 5 *Recalculation of the analysis with regard to gypsum (see text) and ratios of calcium to magnesium, "Rest" to magnesium and calcium to carbonate.*

sample	Ca	Mg	CO <sub>3</sub>	Gypsum	Rest	Ca/Mg	Rest/Mg	Ca/CO <sub>3</sub>
PH06	7.1	0.1	10.1	0	2.6	71	26	0.7
RE2	6.3	3.2	12.2	0	12.8	2.0	4.0	0.5
303/1	7.0	5.2	13.9	6.6	12.4	1.3	2.4	0.5
302A	24.2	4.8	30.2	2.7	20.4	5.0	4.3	0.8
302AoP	14.0	2.6	18.9	1.8	18.6	5.4	7.2	0.7

The Ca/Mg ratio of the lime mortar lies very high and the results that we have gained until now do give the impression that this ratio cannot be used to distinguish dolomitic lime mortars from mortars containing other magnesium rich phases, that are soluble in hydrochloric acid.

## CONCLUSIONS

We are aware that the above outlined could not solve all analytical problems and problems of interpreting the analysis, however we do hope that we could show the major difficulties one has to face, when trying to analyze mortars other than pure lime mortars. Especially dolomitic lime mortars cannot be distinguished from other mortars containing magnesium phases by only performing a wet chemical analysis. To be sure that dolomitic lime was applied, it is necessary to know the mineral species present in the mortar. A very useful analytical method for this purpose is thin section microscopy. It allows to analyze the mineral phases but also to observe, whether these minerals are present as part of the aggregate or of the binding media, a differentiation which is crucial for the interpretation. Other analytical methods like XRD or IR are very helpful to give additional information on constituents that are too small in grain size to be analyzed by polarising microscopy. It has to be kept in mind though, that some products of the setting reaction of dolomitic lime mortars cannot be detected by these methods. As a conclusion it has to be stated, that there is not one single and simple method by the help of which such an analysis could be done, only the combination of several methods can give the desired results. For the further work it would be necessary to gain more information about mortars and plasters of known making and history, to be able to correlate the results of the different types of analysis with the original material and the setting history.

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