Mineralogy of Supports and Selected Pigments in Mediaeval Churches of Slovenia

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INTRODUCTION

Mortar in ancient structures is a composite material which has exhibited excellent durability through time. It is constituted of a binder, such as lime (CaO) and/or gypsum, and aggregates, such as sand, grit, marble or lime-rock. The composition of mortars varies greatly and they are commonly divided into lime, gypsum and mixed ones, depending on the binding material. The most common one is lime mortar, in which slaked lime is used as a binder. The calcination of calcite rock (calcium carbonate, $CaCO_3$) at 800-900°C produces burnt lime (calcium oxide, CaO) and, after cooling, the hydration process of lime yields the hydroxide $Ca(OH)_2$ also known as slaked lime. After a carbonation process in air, the hydroxide in the mortar yields calcium carbonate agan.

Fresh mortar is the basic ground for a fresco wall painting, a painting technique in which only natural inorganic pigments - earths and minerals, can be used. After drying, slaked lime evolves the pigment particles, converting all together in a hard and durable surface, which is one of the principle characteristics of mural painting. *(Wehlte 1967, Knoepfli et al. 1990, Brachert 2001, Mora et al. 2001)*

OBJECTIVES

The present research was dedicated to the analysis of selected murals from different parts of Slovenia, covering the period from the 13th till the 15th centuries *(Höfler 1996-2004)*. The principal objective was to obtain information on the composition of mortars and pigments applied. Among the pigments, only mineral ones were selected, as malachite, azurite or cinnabar. Due to their high cost, they can be rarely found on Slovene murals.

ANALYTICAL METHODS

All the paintings were first studied in situ, next, samples of mortars and pigments were carefully extracted. They were analysed by different analytical techniques *(Matteini, Moles 1984, Kriznar 2006)*, prepared as finely grounded powder or as cross-sections. The principal exam for the mortar composition was carried out by X-ray Diffraction (XRD), a Siemens D-501 diffractometer with CuK (α) Ni-filtered radiation. The results provided the information about crystalline phases of mortars as well as information about the grade of impurity of used lime and sand. The second technique applied was scanning electron microscopy (SEM), using a Jeol JSM-5400. The accompanying energy dispersive X-ray analysis (EDX) was performed under the SEM equipment using an Oxford Link analyser with Si (Li) detector and Be window. Due to a small amount of pigment samples, for their identification mostly SEM-EDX was used and samples were analysed as powder or as cross-sections.

RESULTS

Mortars

The results showed that in the Slovene mediaeval mural painting several kinds of mortars were used, which can be divided, on the basis of aggregates, into three principal groups.

1. Mortars of lime and sand

The majority of mortars are made by standard procedure by mixing lime and sand *(Knoepfli et al. 1990, Mora et al 2001, Kriznar 2006)*. The composition may vary, depending on the quantity of lime and on the cleanliness of the sand used. The elaborated cross-sections permitted to observe the calcite matrix and sand grains of different colour, dimension and form *(Fig, 1a)*. The XRD analysis *(Fig. 1b)* showed if the mortars contain mostly calcite ($CaCO_3$) or there is more quartz. In some samples, dolomite, feldspars and some clay minerals, as minor crystalline phases were also identified.

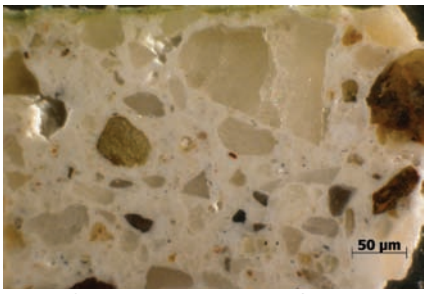

Fig. 1a. Selected optical micrograph of a cross-section (x25) of a typical mortar made of lime and sand. Famlje (1450-60).

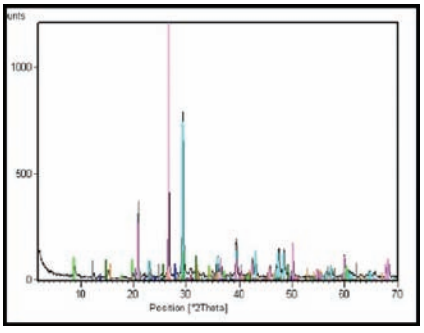

Fig. 1b. Corresponding XRD diagram for mineralogical analysis of powder sample.

If there is more lime than sand in the mortar, it is of better quality and more resistant. When mortars have little lime and are overfilled with sand, the quality is poorer and a mortar tends to pulveri-

palabras clave: Pintura Mural Medieval, Morteros, Pigmentos, XRD, SEM-EDX

key words: Mediaeval Mural Painting, Plasters, Pigments, XRD, SEM-EDX

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se. The sand for the plaster used to be taken from the nearby location, which is why the quality of mortar depends mostly on the geological characteristics of the territory and not so much on the workshop itself. However, the grade of washing the sand is also important. The cleanest sand with rounded small grains was found in mortars applied in churches near rivers or lakes.

2. Mortars of lime and crushed marble or lime-rock

n fewer cases a mortar made of lime and crushed marble or lime-rock was found. This mortar of high quality is very suitable for the fresco buono technique *(Knoepfli et al. 1990, Mora et al 2001, Brachert 2001)*. In this kind of plasters the presence of calcite has two origins: *a)* as a binder and *b)* as an aggregate. It has a typical white colour, which can be well observed on cross-sections *(Fig. 2a)*, where white, slightly transparent grains are mixed with white lime. The XRD analyses *(Fig. 2b)* show the presence of calcite ($CaCO_3$) and some dolomite ($CaMg(CO_3)_2$), while in some other cases of mortars also a small quantity of quartz was appreciated.

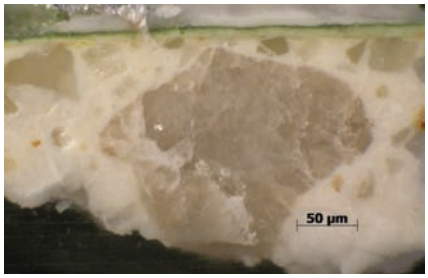

Fig. 2a. Cross-section (x25) of a mortar made of lime and crushed lime-rock or marble. Selo near Zirovnica (around 1430).

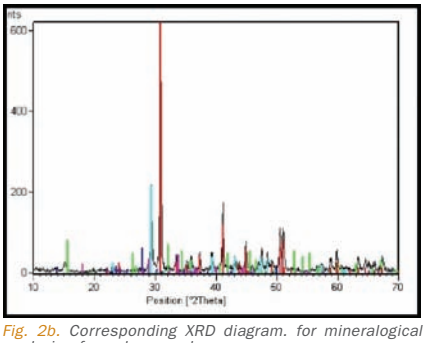

Fig. 2b. Corresponding XRD diagram. for mineralogical analysis of powder sample.

It is a kind of mortar that was used in Italian Tre-and Quattrocento for a fresco buono technique, however in Slovene territory was mostly related to those murals that are stylistically connected to the North-Alpine regions.

3. Mortars with organic additives

Only in the case of one group of mural paintings, limited to the north-east Slovene area of Prekmurje, the results showed the specific construction of mortars *(Kriznar 2006)*. To the mixture of lime and sand also organic fibres were added, in order to improve the quality of the mortar and to give it more solidity by increasing the mechanical strength. The fibres were best observed on the SEM image *(Fig. 3)*.

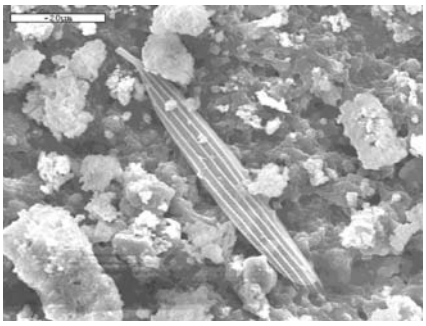

Fig. 3. SEM image of an organic fibre on the surface of the mortar sample from Martjanci (x200).

This composition of mortar is unique in Slovene territory and was not found in any other monument of this investigation.

Pigments

The principal mineral pigments applied were malaquite ($Cu_2CO_3(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$) and cinnabar (HgS), identified by EDX on the bases of their characteristic chemical elements *(Wehlte 1967, Knoepfli et al. 1990, Montagna 1993, West Fitzhugh et al. 1987-2007)*. The first one was very rarely found and was applied in smal areas like lips or drapery decoration. It is always related to murals ordered by a rich doner, due to its high cost. When cinnabar is obtained from the mineral, it is considered one of the most expensive pigments. That is why it was soon replaced by an artificial one, called vermilion, with the same chemical compositon *(West Fitzhugh et al 1987-2007)*. Malaquite was applied more often, however, Slovene mediaeval painters prefered to use much cheaper, but less covering green earth. The most used pigment obtained from the mineral was azurite, which can be found on vast areas for sky or vestments of important figures, like Virgin Mary. As beeing a semiprecious mineral, the pigment was underlayed by gray (veneda) or reddish (morello) colour, in order to use it as less as possible (Knoepfli 1990, Mora et al, 2001).

CONCLUSIONS

The research work on selected mediaeval mural paintings confirmed that the principal mixture for mortars was the most common one, made of lime and sand. In fewer cases, lime plaster was applied, and only in the northeastern region of Slovenia also organic fibers were found in the mixture, in order to give more solidity to the plaster. Pigments, made of minerals, were less used than earths, nevertheless the analysis identified that cinnabar, malachite and especially azurite formed the palette of painters. Mortars were mostly characterized by XRD, while pigments, due to small amount of sample, by SEM-EDX.

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REFERENCES

Brachert, T. (2001): Lexikon historischer Maltechniken Quellen-Handwerk-Technologie-Alchemie, Callwey Verlag, Manchen.

Höfler, J. (1996-2004): Srednjeve.ke freske v Sloveniji, Vol. I-IV, Dru.ina, Ljubljana.

Knoepfli, A., Emmenegger, O., Koller, M., Meyer, A. (eds.) (1990): Reclams Handbuch der künstlerischen Techniken, Vol 1-3. Philipp Reclam jun., Stuttgart.

Kriznar, A. (2006): Slog in tehnika srednjeveskega stenskega slikarstva na Slovenskem, Filozofska fakulteta Univerze v Ljubljani, Zalo.ba ZRC SAZU, Ljubljana.

Matteini, M., Moles, A. (1984): Ciencia y Restauración: Método de investigación, IAPH, Nerea, Sevilla.

Montanga, G. (1993): I pigmenti,: Prontuario per l´arte e il restauro, Nardini editore, Firenze.

Mora, P., Mora, L., Philipot, P. (2001): La conservazione delle Pitture Murali, Editrice Compositori, Bologna.

Wehlte, K. (1967): Werkstoffe und Techniken der Malerei, Otto Maier Verlag, Ravensburg.

West Fitzhugh, E., Feller, R., Roy, A., Berrie, B.H. (1987-2007): Artist´s pigments, A Handbook of their history and characterisation, (Eds. E. West Fitzhugh, R. Feller, A. Roy, B. H. Berrie.), Vol. 1-4, National Gallery of Art: Washington, Oxford University Press:New York, Oxford.