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Dr. Roman Skála
Chair of the PhD Board of Examiners
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Charles University, Prague

Padova, 15 February 2015

Dear Dr. Skála

Concerning your invitation to review the PhD thesis of Dr. Zdeňka Čermáková, with the title “Mineralogical analysis of historical paintings”, I am pleased to report that the material presented in the dissertation is certainly suitable for the defense. Indeed the quantity and quality of experimental work is such that the criteria for the awarding of the PhD degree are comfortably met. This is clearly supported by the number of scientific articles already published in peer-reviewed international journals.

Enclosed you may find a list of suggestions for discussion during the defense.

Please let me know if you need further information.

Sincerely yours

Prof. Gilberto Artioli

Dr. Zdeňka Čermáková

PhD dissertation - “Mineralogical analysis of historical paintings”

Comments and suggestions for discussion:

- 1) The dissertation contains a variety of experimental data focused on the characterization of pigments from paintings and wall frescoes, mostly of post-Medieval age. Indeed the combined use of diffraction and spectroscopic techniques is one of the strong aspects of the reported investigation. Understandably the study makes good use of state-of-the-art laboratory instrumentation, although in a few cases the use of intense laboratory micro-sources or synchrotron radiation for diffraction might have warranted higher quality data.
- 2) Given that the samples are from important art works, I would have liked to see a few pictures of the original paintings/frescoes. Only 2-3 pictures contained in the articles in the appendixes are present.
- 3) Vivianite:
 - a. It could be nice to discuss the relationship between the rare use of vivianite in paintings and the local availability of vivianite mineral sources
 - b. The widespread use of the term “structure analysis” in place of “phases characterization” is possibly inappropriate, since structure analysis is normally intended to define the detailed atomic and crystallochemical analysis of the crystal structure of the investigated phases
 - c. The presence of Mn in the vivianite present in the art-works points to local natural occurrences such as the German or the Czech ones. Specifically the German occurrence (Hagendorf) possibly also has the proper sedimentary environment, although it seems not to be a possible provenance by the authors. This should be discussed.
 - d. The investigation of the alteration/decomposition of vivianite is very interesting
- 4) Antozonite: this is a very interesting study showing the important relationship of the Raman bands with the chemical impurities and defects in fluorite.
 - a. Did you consider possible sources in the Ardennes area?
 - b. Did you deposit the measured Raman spectra in the RRUFF database? They might be very useful to other researchers!
- 5) Crocoite:
 - a. I could find no discussion of possible sources of crocoite from Middle Age mines, although crocoite occurrences are reported from Slovakia (Brezno, Jelšava)
 - b. As far as I know there are no reports of mimetite as natural alteration of orpiment in nature. As a matter of fact also the association of orpiment and mimetite is rare. I think the proposed alteration of orpiment in mimetite should be carefully investigated on experimental basis.
- 6) Hoganite:
 - a. Given that the investigated compound (mixture of Cu-acetate and organics) is not visible by XRD, the spectroscopic data should be carefully interpreted with reference to available data for Cu-resinate, which is also commonly obtained by organic interaction with verdigris (for example see: Conti et al., J. Raman Spectr. 45, 1186-1196, 2014).