

# 3D Synchrotron x-ray microtomography of paint samples

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## ABSTRACT

Synchrotron based X-ray microtomography is a novel way to examine paint samples. The three dimensional distribution of pigment particles, binding media and their deterioration products as well as other features such as voids, are made visible in their original context through a computing environment without the need of physical sectioning. This avoids manipulation related artefacts. Experiments on paint chips (approximately 500 micron wide) were done on the TOMCAT beam line (TOMographic Microscopy and Coherent rAdiology experimenTs) at the Paul Scherrer Institute in Villigen, CH, using an x-ray energy of up to 40 keV. The x-ray absorption images are obtained at a resolution of 350 nm. The 3D dataset was analysed using the commercial 3D imaging software Avizo 5.1. Through this process, virtual sections of the paint sample can be obtained in any orientation. One of the topics currently under research are the ground layers of paintings by Cuno Amiet (1868-1961), one of the most important Swiss painters of classical modernism, whose early work is currently the focus of research at the Swiss Institute for Art Research (SIK-ISEA). This technique gives access to information such as sample surface morphology, porosity, particle size distribution and even particle identification. In the case of calcium carbonate grounds for example, features like microfossils present in natural chalks, can be reconstructed and their species identified, thus potentially providing information towards the mineral origin. One further elegant feature of this technique is that a target section can be selected within the 3D data set, before exposing it to obtain chemical data. Virtual sections can then be compared with cross sections of the same samples made in the traditional way.

Keywords: Synchrotron microtomography, 3D x-Ray imaging, Cuno Amiet, Paintings, Ground.

## 1. INTRODUCTION

The study of cultural heritage in general and of fine arts in particular has, in recent years, seen an increase in interest within the scientific community. This has lead to a better understanding of the chemistry and physical behaviour of artist's materials, to the development of dedicated analytical tools, and to the establishment of improved conservation strategies.

Established research methodology of paint samples can be separated into bulk and cross section analysis. Bulk analysis is usually performed on a scraping of a single paint layer whereas for the preparation of a cross section, samples containing one or more paint layers are embedded in a transparent resin and polished to expose its stratigraphy.

The bulk analysis of paint samples provides detailed chemical compositional data. 2D analysis of cross sections applying light microscopy, imaging FTIR, imaging SIMS and SEM is able to give spatially resolved information and has been proved highly insightful in the study of paint composition and reactivity phenomena [1,2]. Recently, ion polishing has greatly improved the cross section surface preparation allowing much higher magnification and improved image resolution [3].

The combined use of these techniques is fundamental in understanding artists' paint chemistry, however, the surface of a cross section represents only one image of the whole compositional distribution. While alterations during the process of its preparation cannot be excluded, the data gained through such a study is always limited to two dimensions. Synchrotron x-ray microtomography collects three-dimensional data at a resolution of 0.350 microns on complete, unmanipulated paint samples and can therefore provide important complementary information.

Synchrotron x-ray microtomography has been successfully applied to the study of otherwise inaccessible internal features of fossils [4] and of changes in the internal structure of materials such as cement samples [5]. Paint samples from artwork are of heterogenic nature, consisting of inorganic pigment and filler particles, organic binding media, and phases resulting from the reaction of pigment and binding media. The high resolution of the above technique and the contrast in x-ray absorbance between the different paint components enhances the potential of a successful application of the technique to such multi-phase materials.

Easel paintings often have a complex build up. The support, mostly a linen canvas, is sealed with a layer of sizing before a ground layer is applied to prepare for painting. The subsequent build up might comprise an underdrawing, isolation layers, multiple paint layers and a varnish.

The samples selected for this synchrotron x-ray microtomography pilot study are simple in build up and composition and include only the ground layer(s) taken from the unpainted margins.

All examples were collected from the early oeuvre of the Swiss artist Cuno Amiet (1868-1961). At the time of interest (late 19<sup>th</sup> century to early 20<sup>th</sup> century) commercial canvases were available prepared with a sizing and ground layer. Yet artists did also prepare their own to obtain desired colour and absorbency qualities. A number of observations including the surface smoothness, the layer's even thickness and the fact that the priming covers the whole extent of the canvas including turnover edges, suggests that the priming or ground of the *Winter in Oschwand* is a commercial priming i.e. applied by the manufacturer (figure 1a-b).

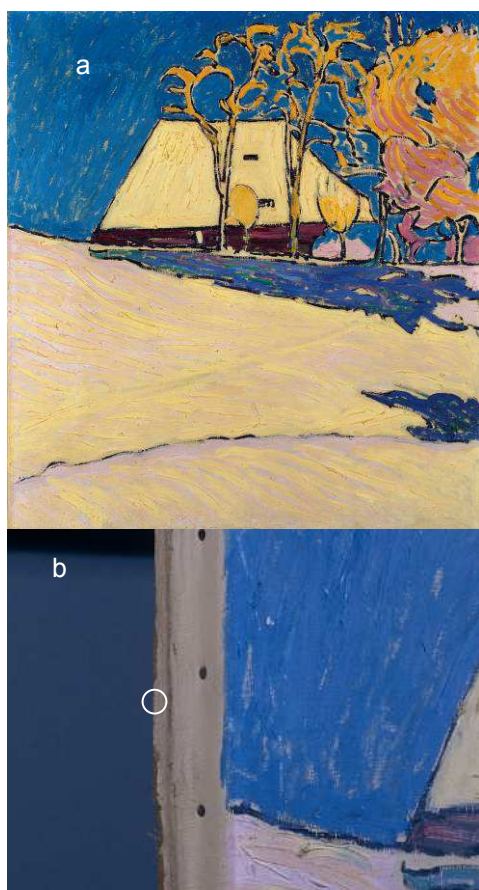


Figure 1a. Cuno Amiet, *Winter in Oschwand*, 1907, oil on canvas, 60.5 x 54 cm, private collection. b) sampling location of the commercially primed canvas

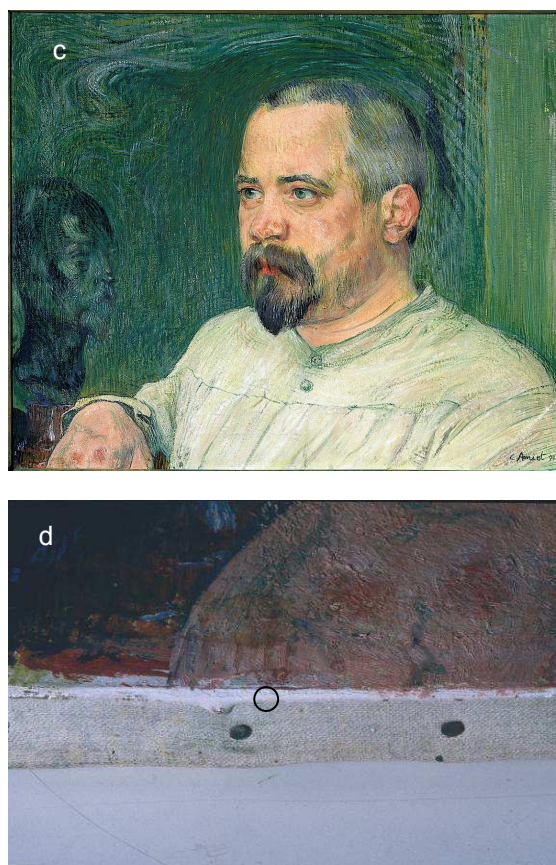


Figure 1c. Cuno Amiet, *Portrait of Max Leu*, 1898, oil on canvas, 73.5 x 84 cm, Kunstmuseum Solothurn. d) sampling location of the manually prepared priming.

In the second case (*Portrait of Max Leu*, 1898, figure 1c-d) the canvas was first fixed onto the stretcher and then the ground was applied probably by the artist himself. With the aid of micro tools, small samples (diameter < 700 microns) were collected from the edges of the canvases (figures 1b and 1d).

## 2. EXPERIMENTAL

### 2.1. Sample preparation

Sample 1 was collected from the turnover edge of the painting entitled *Winter in Oschwand* (1907). FTIR bulk analysis suggests this to contain lead white and barium sulfate as pigments with traces of silicates and aluminium silicates in an oil binding medium. Sample 2 was collected from the edge of the painting *Portrait of Max Leu* (1898). Here bulk analysis suggested it to be a calcium carbonate ground bound with a proteinaceous medium. Traces of clay minerals were also found.

The samples were attached to a specially designed sample holder with the aid of a small drop of two component epoxy glue. The sample holder consists of a 500 mm steel flat top rod, 500 micron wide at the sample level fixed onto an aluminium base.

### 2.2. FTIR analysis

Sub samples were analysed by Fourier Transform Infrared Spectroscopy.

FTIR was performed in a Perkin Elmer Fourier Transform Infrared Microspectrometer (Perkin Elmer System 2000) with IR/vis microscope (Perkin Elmer i-series). Samples were analysed in a diamond cell.

### 2.3. Synchrotron measurement and reconstructions

Microtomographic scans were performed at the Swiss Light Source (SLS) in Villigen (Switzerland) on the MS-X02DA-TOMCAT beamline [6]. Experimental settings were sample size and composition dependent. Settings for sample 1 were: 1501 projections at 38 keV with an angle step of  $0.12^\circ$  and an exposure time of 2300 ms per step. The sample was cooled during measurement. Settings for sample 2 were: 1501 projections at 15 keV with an angle step of  $0.12^\circ$  and an exposure time of 800 ms per step. All images were acquired at a pixel resolution of  $0.350\text{ }\mu\text{m}$  on a 2048 px CCD camera equipped with a 20x magnification optical objective.

Tomograms were computed using the Filtered Back Projection algorithms in use at the SLS. The reconstructed data cube of images was processed and analysed in the commercial software AVIZO 5.1.

### 2.4. Cross section preparation

In order to expose a selected plane of the sample it was removed from the sample holder and embedded in light curing resin Technovit 2000 LC. After careful orientation the sample was dry polished using micromesh cloths until approximately 5 microns from the target plane. Subsequently it was ion polished. The ion polishing was performed on a JEOL cross section polisher using ultra pure argon under high vacuum conditions with an acceleration voltage of 6 kV and an ion current of  $150\text{ }\mu\text{A}$ .

### 2.5. SEM EDX

SEM in association with high energy dispersive X-Ray Spectroscopy was performed on a XL30 SFEG high vacuum SEM equipped with an EDX detector. SE (Secondary electron) images of the samples were obtained with an accelerating voltage of 10 kV and a spot size 3 (2.2 nm beam diameter). Samples were gold coated (2 nm) to improve conductivity.

## 3. RESULTS AND DISCUSSION

3D X-Ray microtomography is performed under atmospheric conditions on unmanipulated samples, thus eliminating sample preparation and instrumental artefacts and allowing the study of vacuum sensitive samples.

### 3.1. Surface characteristics

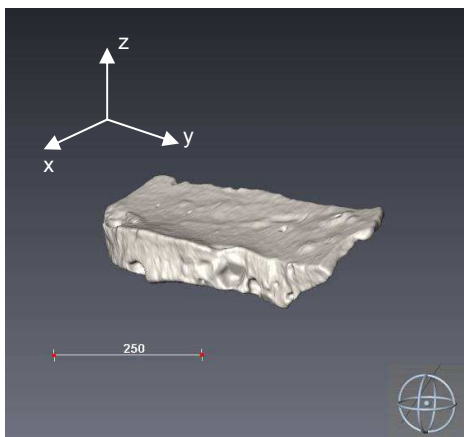


Figure 2a. Surface reconstruction of the ground sample (1) taken from *Winter in Oschwand*, 1907. Scale in microns. Painting surface at the top.

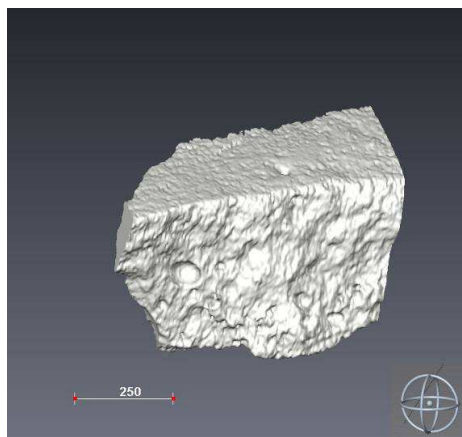


Figure 2b. Surface reconstruction of the ground sample (2) taken from the edge of *Portrait of Max Leu* 1898. Scale in microns. Painting surface at the top.

X-ray microtomography data allows the reconstruction of the sample surface morphology in detail as can be seen in figures 2a and 2b. It is clear from the top surface appearance that the two samples have distinct characteristics. The sample taken from the commercial ground (figure 2a) has a top surface with a smooth appearance with the occasional protuberance whereas the self prepared ground has a rougher overall quality.

### 3.2. Single slice analysis

Figures 3a, b and c represent single slice images of sample 1. The quality of imaging of the individual particles is hindered by the extremely fine particle size and the smaller particles cannot be individually imaged at the resolution of the technique (350 nm). Other experiments have also shown that the long exposure times required to image lead containing samples might increase the sample temperature and induce the mobility of certain phases [results not shown]. Sample cooling does improve the image quality and further work is underway to optimise conditions for highly absorbing materials such as in sample 1. This figure shows that this ground is composed of two distinct layers: a lower layer measuring in average 50 microns and a top one measuring 25 microns in average. In contrast, sample 2 consists of a single layer over 400 microns thick (figures 3d and e).

SEM-EDX analysis was performed on a cross section of a separate chip from the same location as sample 1. The lower layer is composed mainly of barium sulfate and zinc sulfide (lithopone) with fine particles of lead white, aluminium silicates and larger particles of silica. The top layer is composed mainly of lead white with a few particles of barium sulfate and aluminium silicates.

Figures 3a, 3b and 3c demonstrate how useful it is to look at more than one cross section of a sample. This is demonstrated by selecting three different slices from the same sample. The three images describe different features. Whereas the first slice shows apparently undisturbed layers, the second slice clearly shows a large agglomerate probably formed as a reaction between the pigments and the medium. This phenomenon has been often observed in different paint systems with lead containing pigments or additives in an oil medium [7]. The identification of the nature of the agglomerate requires chemical characterisation. Very different interpretation of the current chemistry of this ground would arise from the study of only one of the different single 2D cross sections as done by the traditional methodology. Furthermore, the two distinct layers vary in thickness throughout the whole sample. The measurement of a layer thickness based on a single 2D plan is always an approximation.

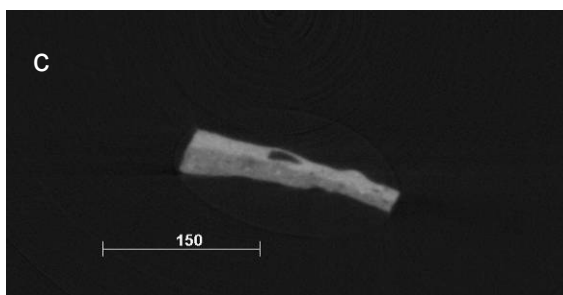
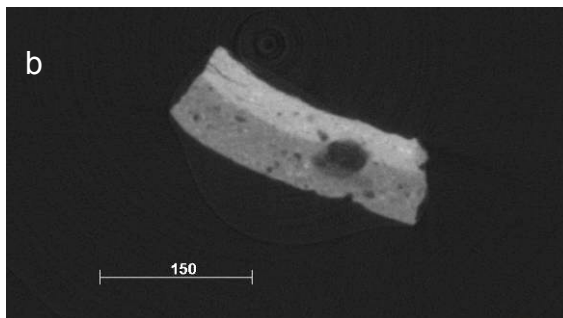
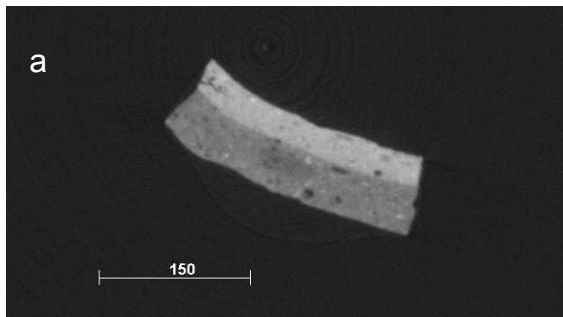


Figure 3a, b and c. XZ single image (a slice number 854 c 943) reconstructed from the tomographic data of the sample taken from *Winter in Oschwand*. Scale in microns.

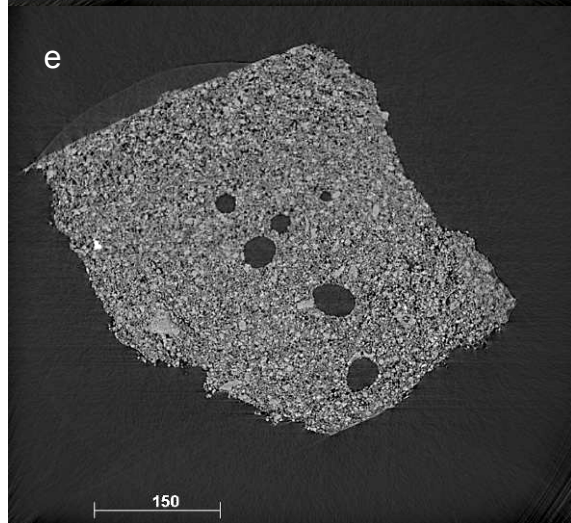
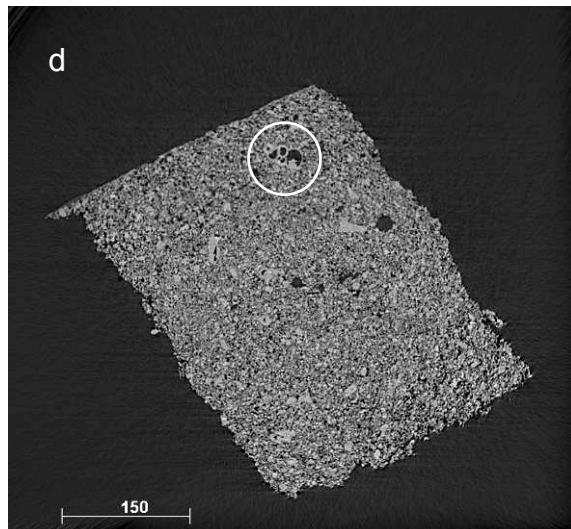


Figure 3d and e. XZ single image (b 1095 d 1919) reconstructed from the tomographic data of the sample taken from *Portrait of Max Leu*. Scale in microns.

### 3.3. Voids

3D X-ray microtomography can provide information on the degree of porosity throughout a sample. The high contrast between the calcium carbonate particles and the void spaces (seen on figure 3e) allows the reconstruction of the empty volumes by segmentation and we can visualise the location and size of the pores inside the ground chip as imaged in figure 4b. We can see that trapped air created pores predominantly in the lower part of the ground layer.

Voids are filled with debris during the preparation of cross sections by dry polishing or new voids can be created by removal of large particles. Even finishing off the cross section surface polishing by ion milling doesn't always sufficiently clear the debris (figure 4d). The virtual cross section (figure 4c) helps to recognise the voids in the real cross section.

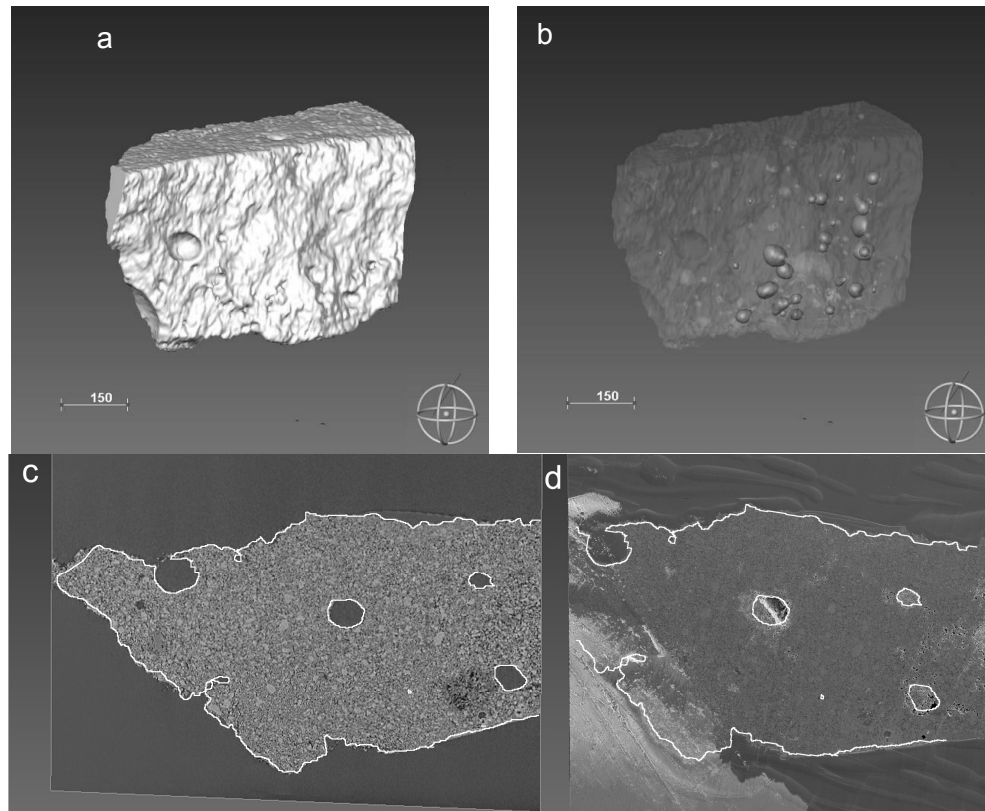


Figure 4. *Portrait of Max Leu, 1898.* a) Surface reconstruction. b) Reconstruction of the internal empty volumes i.e. pores seen through the transparent sample reconstructed surface. c) oblique slice extracted from the reconstructed x-ray tomography dataset. d) SEM-SE image of the surface exposed through a combination of dry polishing and ion milling.

### 3.4. Microfossils

Smaller features such as microfossils naturally present in chalk can be imaged. If such foraminifera can be documented, the calcium carbonate in the ground is identified as natural chalk. Their size, density and possibly species determination may provide some information towards the origin of the natural chalk mineral. Throughout the chip of sample 2, the total number of completely or partially recognised foraminifera microfossils approached 50.

The identification of foraminifera in palaeontology delivers a range of information with respect to the ancient sedimentary environment. In translation to the ground chalk applied to a painting, the geographic origin of the source rock could possibly be traced back by way of classification of the microfossils. Based on the images in figure 5, the foraminifera can be classified as planktonic, biserial possibly Late Cretaceous, Campanian-Maastrichtian. Furthermore, the foraminifera may belong to the Genus *Heterohelix*, however, the species is difficult to determine due to insufficient definition of the wall texture at 350 nm resolution [Spezzaferri, S., University of Fribourg, Department of Geosciences, Ch du Musée 6, 1700 Fribourg, personal communication (2008)]. A possible source could be Cretaceous sediments, very finely textured, rich in foraminifera and calcareous nanoplankton. In Switzerland, such rocks are common in the Helvetic Nappe for example, a long belt oriented North-East to South-West starting south of St. Gallen and crossing all of Switzerland. However the commercial sources of best quality chalk at the time of the painting are mainly known from northern Europe. Additional work towards the identification of the different species present in the sample is currently underway to elucidate the potential source rock more precisely.

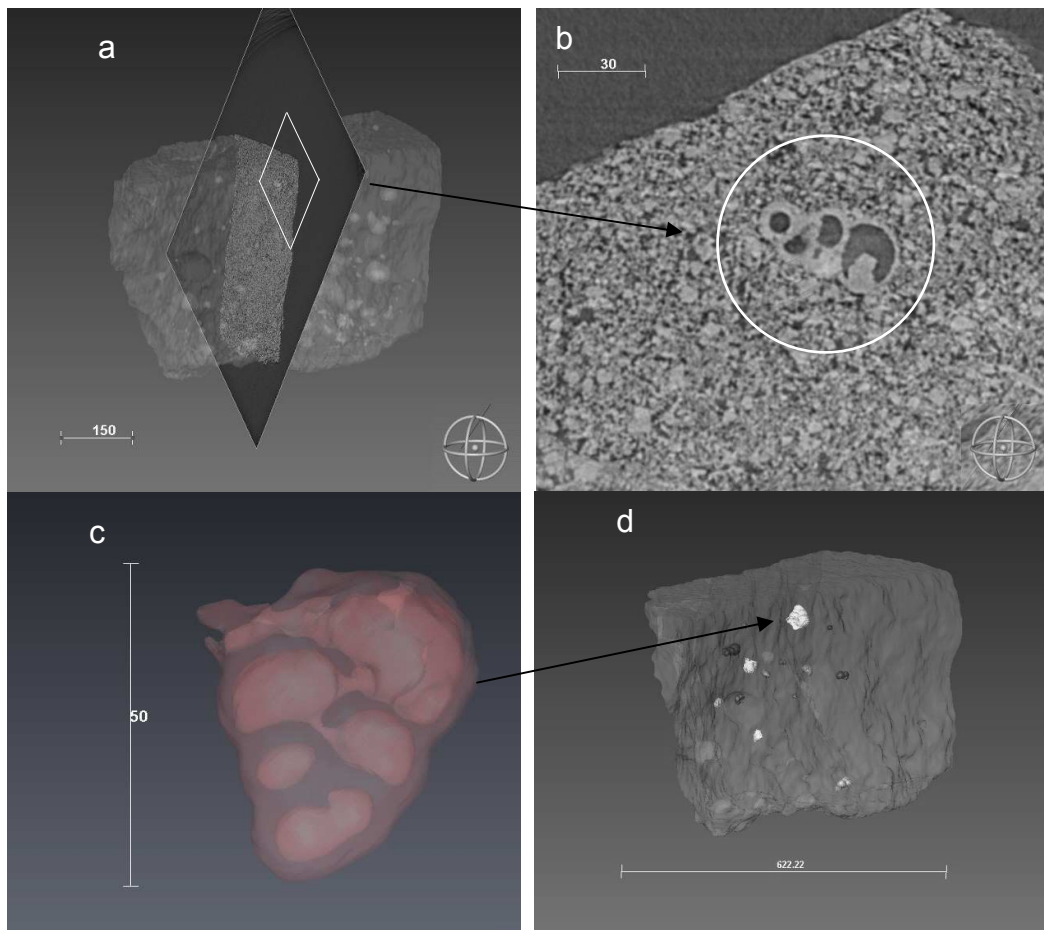


Figure 5. Detail (5b) of a XZ slice (5a) containing a foraminifera fossil (Video1) <http://dx.doi.org/10.1117/12.827511.1> 5c) (Video 2) The 3D reconstruction of the whole fossil. <http://dx.doi.org/10.1117/12.827511.2> 5d) The distribution of a selection of reconstructed foraminifera microfossils. Scale in microns

One advantage of supplementing the conventional techniques with 3D-Synchrotron X-ray microtomography is that the chemical data gained through the study of a selected cross section can now be interpreted in the context of the whole sample. Furthermore, particularly structural and morphological information that is otherwise inaccessible can be inferred from the 3D x-ray microtomographic data, like i.e. the recognition of microfossils clearly illustrates.

## 4. CONCLUSIONS

### 4. Conclusions

Samples collected from paintings are sources of information on the paint composition and its condition, as well as the materials and methods applied by an artist. Because sampling a painting is always an invasive and destructive act, samples are precious and a maximum of information should be extracted from them.

In traditional cross section studies, only a single plane is studied and the information present in the remaining sample is often not accessible. In addition the preparation of the cross section itself may alter the exposed surface. 3D X-ray microtomography can elegantly overcome these drawbacks and

provide complimentary information since the whole, unmanipulated sample is imaged and studied before further steps are taken.

The reconstruction in 3D of features observable in X-ray absorption images can reveal sample properties such as the surface morphology and porosity levels. For example in the case of the commercial ground (sample 1), a smooth surface with a low porosity level was observed. In contrast, the manually applied ground (sample 2) reveals larger and heterogeneous particle sizes. This is reflected by a rougher surface and a higher porosity resulting in a more absorbent ground layer. The use of an absorbent ground is anticipated to achieve a matt paint effect. Also the study of multiple XZ single-plane orthoslices through the 3D sample reconstruction can provide information on the number and dimensions of the different layers in a more representative manner than a traditional cross section. Similarly the particle distribution within a single layer can be easily elucidated in an XY image plane - information that is not accessible in traditional cross section observation.

Finally, the reconstruction of the 3D morphology of the several microfossils present in the chalk of sample 1) provides information on their species and thus potentially may assist with the establishment of the origin of the source rock.

Within the 3D data set a target section can be selected before grinding the sample down to expose it and obtain chemical data. The virtual section remains an important reference towards interpreting data gained from the cross section.

In conclusion 3D X-ray microtomography of paints in combination with traditional methods brings a whole new wealth of information that has so far been inaccessible.

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