

# Ancient Parchments: Structural Diagnostics and Visualization of Textual Fragments of Manuscripts—A Natural-Science Approach

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**Abstract**—The analytical diagnostics of art objects and items of cultural value have become increasingly sought for in modern interdisciplinary studies. Within the natural-science approach, a manuscript is considered as a physical object consisting of materials of two types. The first type comprises various substrates for writing (papyrus, paper, parchment, palm leaves), and the second type includes writing materials (soot ink, iron gall ink, or red lead ink). Textual fragments of ancient parchment manuscripts, including hidden textual fragments, are elementally mapped and digitally imaged with X-ray fluorescence. The collagen structure of the parchment and ink composition are diagnosed.

**Keywords:** X-ray fluorescence, synchrotron radiation, small-angle X-ray scattering, collagen, parchment, X-ray fluorescence imaging

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## INTRODUCTION

Natural-science methods have become increasingly topical in the practice of humanities research [1, 2]. The state-of-the-art scientific expertise of cultural-heritage objects employs an interdisciplinary approach based on the combined use of methods of historical and material analysis and state-of-the-art natural-science methods and technologies, because only this integrated approach can lead to more authentic results [3]. We note that in recent years, methods and analytical tools based on state-of-the-art synchrotron radiation sources show the highest dynamics in the study and scientific expertise of cultural-heritage objects. New methods of synchrotron X-ray imaging, based on the physical phenomena of X-ray dynamic scattering, phase contrast, and X-ray fluorescence, are currently used to analyze new cultural-heritage objects. The goal of this paper is to develop a nondestructive method for diagnosing the state and degree of degradation of ancient parchments and to develop and test methods for the digital X-ray imaging of textual fragments, faded and erased, of medieval parchment manuscripts.

## EXPERIMENTAL

Elemental mapping and digital imaging of the textual fragments of a parchment manuscript was con-

ducted at the REFRA X-ray fluorescence analysis station [4, 5], of the dedicated Kurchatov synchrotron radiation source. A bright beam of broadband synchrotron radiation (SR) from a deflecting magnet with a field of 1.5 T was employed. Measurements were performed in air at room temperature. The sample was mounted at a 45° angle to the direction of the synchrotron beam and to the detector. Several methodological problems were solved to adapt the station’s experimental equipment to the study of parchment-manuscript fragments. A KT&C KPC-4300PH video camera with a 5.0–50-mm Daiwon Optical varifocal lens and a D6-5-650-5-P low-power semiconductor visible laser were used to determine where the beam hits the sample. A thin glass mirror was installed along the path of the synchrotron beam between the sample and a collimating slit device at a 45° angle to the beam and to the laser ray. The SR beam went through the mirror, and the light from the laser was reflected. The laser was calibrated so that the laser ray reflected by the mirror aligned with the SR beam visualized on a lumino-phore. Thus, the red light from the laser and SR hit the same area of the sample. The X-ray fluorescence emission from the test sample, excited by the SR beam, was recorded by a BDER-KI-11K semiconductor detector, connected to an SU-06P spectrometer with a resolution of 245 eV on a 5.9-keV line and a sensitive region of 12 mm<sup>2</sup>. Special software was written to

process the experimental X-ray fluorescence spectra. As a result, a map of the relative concentration of the chosen chemical element of the sample surface was obtained. Reference Cu, Fe, Pb, and Sn metal samples were used for energy calibration. The SR beam was collimated by slits with diameters ranging from 0.1 to 1.5 mm, depending on the experimental problems posed. Fluorescence emission of the chemical elements was detected beginning with Ca, whose spectral  $K_{\alpha}$ -line energy is 3.7 keV. The X-ray fluorescence signal of lighter elements was absorbed by air. The distance from the sample to the detector changes from 3 to 5 cm, depending on the experimental problems posed. The sample was installed on motorized high-precision mobile devices with a path of 50 mm horizontally and 90 mm vertically. A computer program was specially written to scan the given region of the parchment-manuscript fragment with a collimated SR beam at a preset pitch. The program stopped measuring automatically when radiation overaccumulated and renewed measuring under favorable conditions. Exposure was prolonged automatically as the current dropped in the storage ring.

X-ray small-angle scattering and diffraction experiments were conducted at the DICS station [6] of the dedicated Kurchatov SR source. A SR beam that came from the storage ring hit a monochromator, crystal Ge(111). The wavelength of the monochromatic SR beam,  $\lambda = 0.162$  nm, corresponded to a photon energy of 7.62 keV. The beam was focused in the sagittal plane using the monochromator and in the meridional plane using a polysectional system of mirrors; the beam-flare region on the sample was about  $0.4 \times 0.6$  mm. The detector was DECTRIS Pilatus3 1 M with a resolution of  $1043 \times 981$  pixels, a wide dynamic range of 20 bit, and zero noise level. The detector was built on pixel-array technology, the intensity of each pixel being a number of photons with an energy higher than the threshold one (the threshold was chosen to be two times lower than the beam energy) recorded during exposure. The typical exposure time was 5 min. The current rate of the beam in the SR source was 70–100 mA. To calibrate the scale of scattering angles, an X-ray diagram of silver behenate powder was taken.

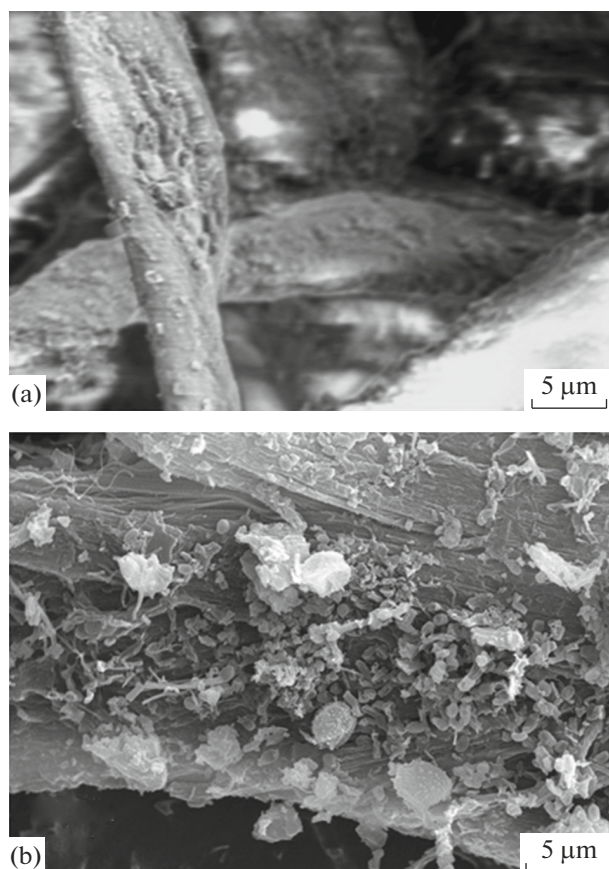
## RESULTS AND DISCUSSION

**The structure of ancient parchments.** Parchment is a unique natural nanostructured material with a high strength due to a special hierarchical organization of protein-collagen molecules, which make its basis. Parchment is produced by special processing of the skin of calves, sheep, or goats. Before paper had been invented, parchment was the main material for writing, and practically all the main handwritten artifacts of medieval Europe were written on it. The condition of these historical media depends on many environmental factors and storage conditions (temperature, humidity, and lighting) and is determined primarily by

the degree of collagen degradation at various levels of its structural hierarchy.

In this paper, we used an interdisciplinary approach to understand collagen degradation and a complex of nondestructive analytical methods (optical microscopy, scanning electron microscopy, small-angle and large-angle synchrotron X-ray diffraction) to analyze the various levels of structural hierarchy. Figure 1a shows an image of the collagen structure of a medieval parchment manuscript from the collection of the State Historical Museum (SHM). The image was made by a Versa 3D scanning electron microscope (SEM) in the low-vacuum mode (70 Pa). For comparison, Fig. 1b is also a SEM image of the collagen structure of a historical parchment from [7], which explicitly shows fibers with bacterial clumps on the surface, destroying the collagen structure and leading to the parchment's biodegradation and destruction. We note that the image in Fig. 1a shows no bacteria, which is probably associated with the storage conditions optimal for this parchment-manuscript sample from the SHM collection. Efficient tools for studying and diagnostics of the condition and degradation of the collagen structure of parchments are methods based on X-ray diffraction. The small- and large-angle ranges were used. Measurements were made at the DICS station of the dedicated Kurchatov SR source. Figures 2a and 2b show examples of the small-angle scattering for two parchment-manuscript samples from the SHM collection: sample 1 is Sin. Greek 9, Menology, the Byzantine Empire, 1063; sample 2 is Uvar. 289-4, Aprakos Gospel, Bulgaria, 13th century. The absence of diffraction peaks for sample 2 in Fig. 2c and the wide diffuse halo in Fig. 2b allow us to conclude that the collagen of parchment sample 2 is in the process of gelatination. Such integral assessments of the collagen structure conditions of medieval parchments are important characteristics in monitoring the parchment structure in general and to improve conservation and storage processes for parchment manuscripts.

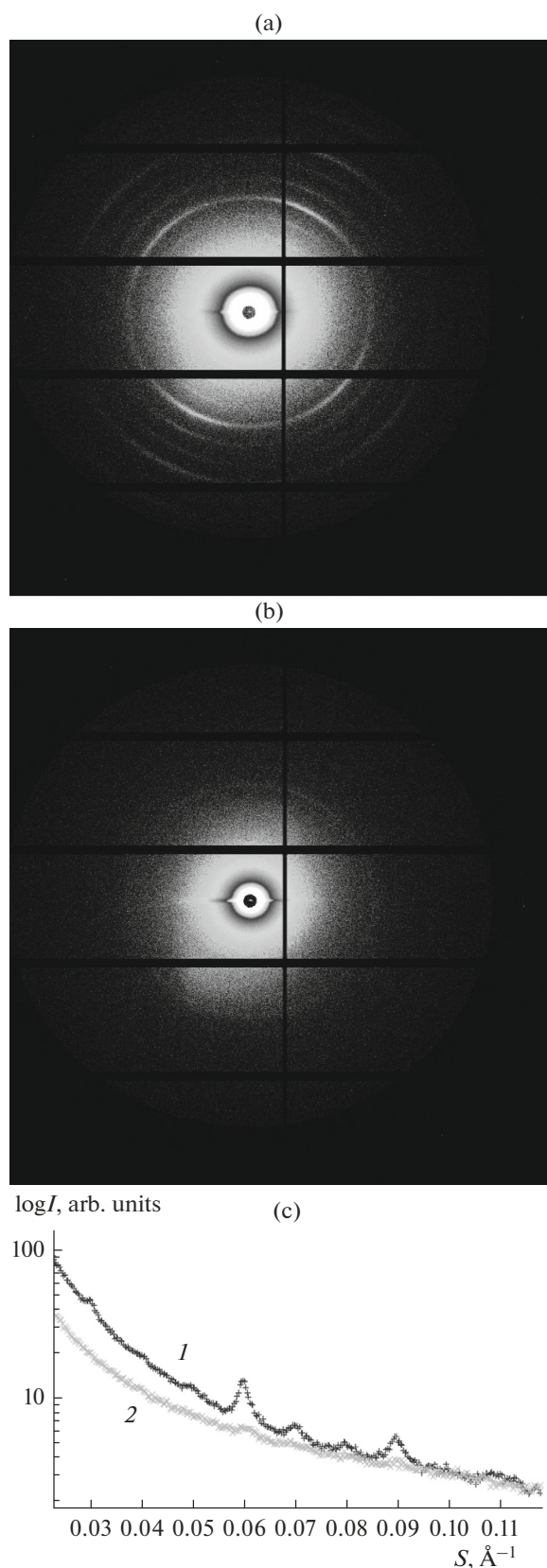
**X-ray fluorescence imaging of textual fragments.** The possibility of reading ancient decayed or rejuvenated texts, as well as palimpsests [8, 9], arouses great historical interest. Ink penetrates into parchment sufficiently deep, and often contains heavy elements, such as iron, mercury, and lead. SR excites the intense X-ray fluorescence of these elements during photoelectric absorption, and the semiconductor detector records this fluorescence. This opens up a unique opportunity to identify nondestructively the chemical composition of ancient ink [10, 11] and to visualize digitally with X-rays hidden or faded historical texts by scanning the surface of manuscripts with a collimated synchrotron beam. Thanks to the extremely high intensity of synchrotron radiation, it is possible to record negligibly small concentrations of elements and to map the distribution of these elements on the sample surface during scanning.



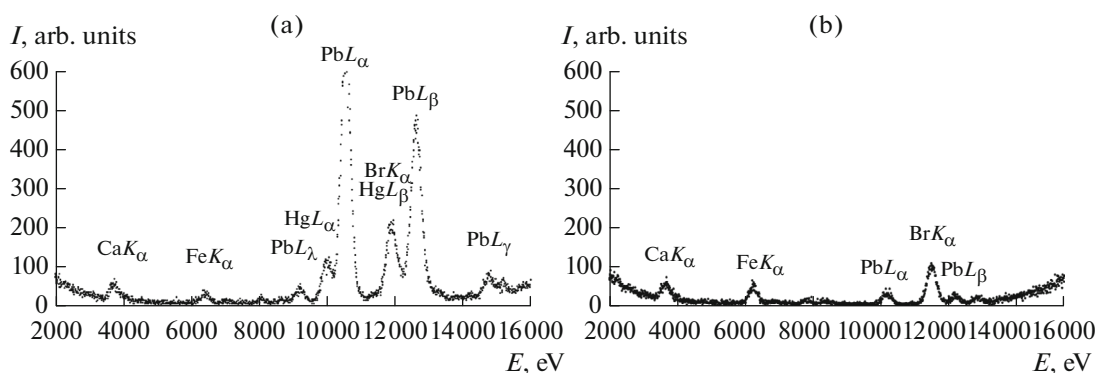
**Fig. 1.** SEM images of the collagen structure of a medieval parchment: (a) a parchment sample of a medieval manuscript from the SHM collection; (b) a parchment sample from [7]; the image shows collagen fibers with bacterial clumps.

A small fragment of a parchment sheet of a medieval manuscript with text on both sides, taken out of the binding of a 15th-century code, was used for study. The experiment was carried out at the REFRA X-ray fluorescence analysis station of the dedicated Kurchatov SR source. X-ray fluorescence elemental analysis was conducted traditionally, when the content of various chemical elements in a sample is determined on the basis of detection and further analysis of the energy spectrum of X-ray fluorescence. The text was scanned by a “white” SR beam. Absorbers were not used to ensure the maximal output of the X-ray fluorescence; therefore, several experiments to test the thermal effect of the SR “white” beam were conducted on parchment samples specially prepared for testing before scanning the historical parchment. Damages to the samples were not detected during the experiments; therefore, absorbers were not used.

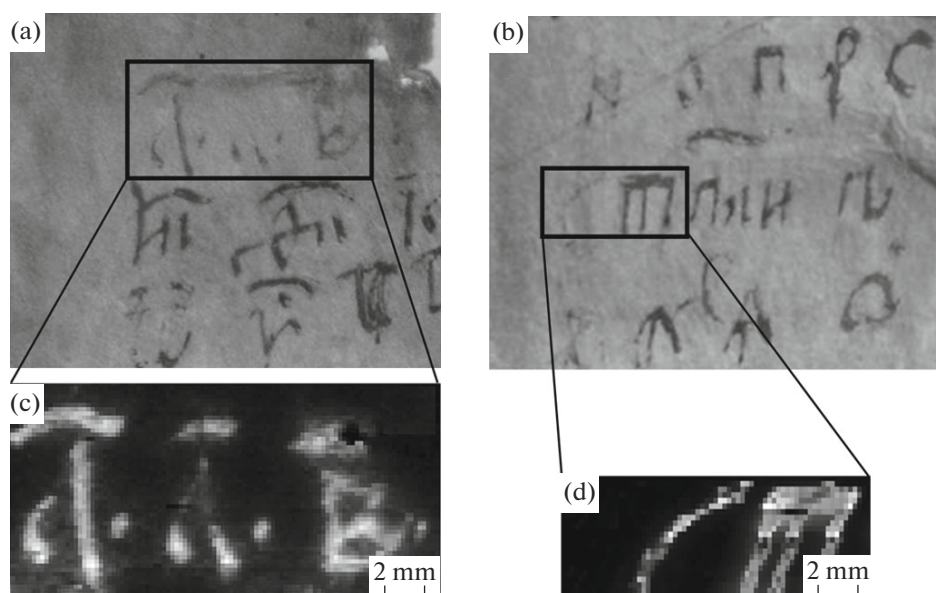
To determine the possibility of obtaining an X-ray digital image of the text and the composition of the medieval ink, the first stage was to choose a region with visually readable red letters. Figure 3 shows the



**Fig. 2.** (a, b) Azimuthal and (c) radial distributions of small-angle X-ray scattering on parchment samples of medieval manuscripts from the SHM collection: (a) sample 1; (b) sample 2; (c) samples 1 (1) and 2 (2).



**Fig. 3.** Experimental spectra of synchrotron X-ray fluorescence emission of (a) the parchment with red ink and (b) the parchment without text.



**Fig. 4.** Images of textual fragments, including faded textual fragments of the medieval parchment manuscript with red ink: (a, b) optical photographs in the visible wavelength range; (c, d) reconstructed digital X-ray fluorescence images. The scan regions are marked by rectangular frames.

experimental spectra of the synchrotron X-ray fluorescence emission from a parchment with red ink and a parchment without ink. The presence of intense lead lines in the main elemental composition of the red ink used allows the conclusion that the main component of the ink with which the text was written was minium.

The second stage of research was to visualize digitally with X-rays faded fragments of handwritten text. Figures 4a and 4b exemplify the optical photographs of text fragments in visible light; Figs. 4c and 4d show digital X-ray fluorescence images of the same text fragments obtained using the X-ray spectral lead line, which show well the reconstructed images of faded/erased fragments. We note a rather good correspondence between the optical and X-ray images, demonstrating the pos-

sibility of visualizing the text of parchment manuscripts using X-ray synchrotron radiation.

### CONCLUSIONS

The conducted studies demonstrated experimentally the efficacy of SR diffraction methods, including the small-angle region, and scanning electron microscopy to diagnose parchment degradation processes. The integral data about the condition of the collagen structure, obtained by the method of small-angle X-ray scattering and SR diffraction, are important characteristics to monitor the parchment condition in general and to improve the conservation and storage processes of parchment manuscripts. The text fragments written with red ink on medieval parchment

were elementally mapped. The chemical composition of the red ink was identified, and a conclusion was made on this basis that the main component of the ink with which the text was written was minium. The complete correspondence of the text fragment written with red ink to its digital image in the X-ray wavelength range was shown, and it was experimentally demonstrated that it is possible to visualize digitally faded (erased) fragments of texts handwritten on parchment using synchrotron X-ray fluorescence emission.

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