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Conservation of ancient manuscripts: with or without oxygen?

It is generally accepted that paper deterioration in ancient manuscripts due to the presence of iron gall inks results mainly from two phenomena: hydrolysis and oxidation. Recently, scientists from the Centre de Recherche sur la Conservation des Collections (Muséum national d'Histoire naturelle/CNRS/ministère de la Culture et de la Communication) and Antwerp University in Belgium, have just shown that the main cause of degradation in manuscripts is oxidation. This phenomenon could be inhibited by a drastic oxygen-free conditions. Carried out notably on the SOLEIL and HASYLAB synchrotrons, these studies have just been published in the journal *Analytical Chemistry*.

Iron gall inks are generally composed of iron salts, gum arabic and water-soluble extracts of oak gall nuts. In the West, these black inks have been widely used for writing since the Middle Ages until the early Twentieth century. Under certain conditions, they cause a significant deterioration of the paper, which becomes brown and brittle, sometimes as far as collapsing into dust. The information carried by the manuscripts, often an important part of our heritage, is then lost.

The degradation of paper is usually explained as the result of two phenomena: acid hydrolysis of cellulose, favoured by moisture and the acidity of the paper, and oxidation of cellulose, due to ambient oxygen and exacerbated by the presence of ferrous ions (Fe^{2+}). The teams of Véronique Rouchon, at the Research Centre for the Conservation of National Collections (CRCC, CNRS/MNHN/ministère de la Culture et de la Communication) and Koen Janssens, in the Chemistry Department at Antwerp University set out to identify whether it was hydrolysis or oxidation that was the main process that caused manuscripts written with iron gall inks to deteriorate.

Paper models, impregnated with iron gall inks, were stored for several months in humid and less humid environments and with varying oxygen concentrations. An originality of this study lies in the fact that the paper degradation was sufficiently fast to be observed at room temperature. On inked paper, the oxidation of iron, namely the transformation of ferrous ions (Fe^{2+}) into ferric ions (Fe^{3+}), was measured versus time by X-ray absorption near-edge spectrometry on the DIFFABS and "L" beamlines, two experimental setups at the SOLEIL (St Aubin, France) and HASYLAB (Hamburg, Germany) synchrotrons.This was to assess whether there was a direct link between the ferrous concentrations and the degradation of the paper.

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The results show that the degradation of cellulose is dependent on the presence of oxygen and completely independent of relative humidity. Thus, oxidation is the dominant mechanism in the deterioration of manuscripts. This cellulose oxidation is directly related to the presence of iron in the paper. However, it seems to have little correlation with the oxidation state of iron, namely the ferrous (Fe^{2+}) or ferric (Fe^{3+}) ion content, which depends directly on the presence of both oxygen and humidity.

This research also discuss about the use of anoxia techniques, that is to say decreasing the amount of oxygen, for the preservation of manuscripts. It also shows the value of studying "antioxidant" methods for treating the most damaged manuscripts.

Example of damaged manuscript.
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Samples and experimental setup.
on the left: experimental setup (DIFFABS- SOLEIL)
on the right: general view of prepared samples
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Bibliography

Room temperature study of the degradation of iron gall ink impregnated paper under various oxygen and humidity conditions - time-dependent monitoring by viscosity and X ray Absorption Near Edge Spectrometry measurements. Rouchon V. et al., *Analytical Chemistry*, DOI: 10.1021/ac1029242 (2011).

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