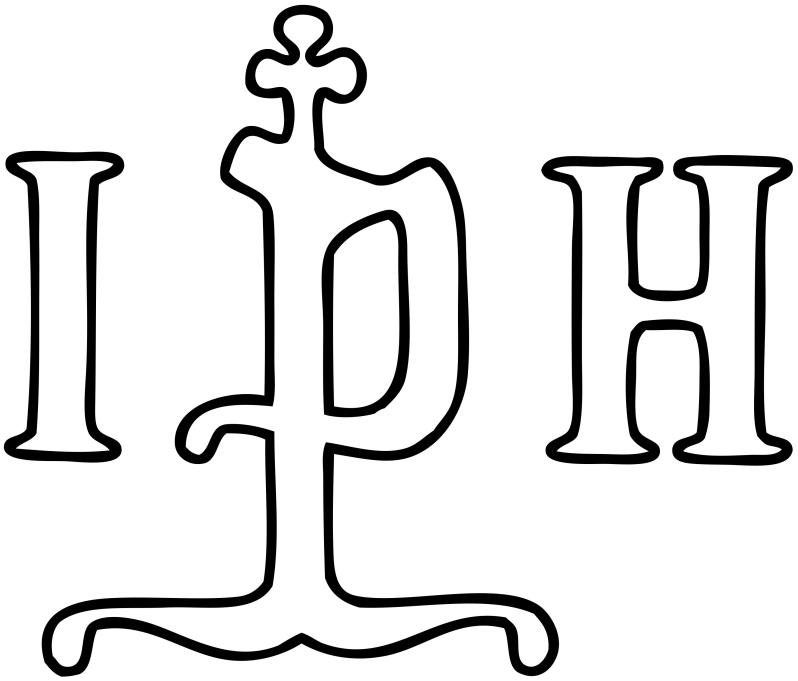
Volume 25, Year 2021, Issue 1



PAPER HISTORY

Journal of the International Association of Paper Historians

Zeitschrift der Internationalen Arbeitsgemeinschaft der Papierhistoriker

Revue de l'Association Internationale des Historiens du Papier

www.paperhistory.org

ISSN 0250-8338

A CLOSER LOOK INTO OLD PAPERS - CHEMICAL ANALYSIS OF THREE PAPERS FROM THE 14TH CENTURY BY ATR-IR AND MICRO-RAMAN SPECTROSCOPY

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ABSTRACT

ATR-IR and Raman microscopic measurements were used to analyse the chemical composition and structure of three old Italian papers dating from the second half of the 14th century. The IR spectra showed the general composition of the papers. More specific information on the different paper components and their distribution in the paper were obtained by Raman microscopic measurements. The resulting Raman images revealed the detailed chemical structure of the papers including the main paper components such as the paper fibres from rags and the gelatine size as well as substances that were not intentionally added but formed during the production process such as calcium carbonate.

The results of paper analysis are discussed in connection with the different steps in the paper production process and certain manufacturing techniques. The study demonstrates the use of spectroscopic analysis methods to help paper historians elucidate practices of early papermaking or confirm hypotheses about it.

Keywords: paper analysis, chemical composition, paper history, ATR-IR spectroscopy, Raman imaging

1. Introduction

The art of papermaking was brought to Europe by the Arabs in the 11th century. They established paper mills in Muslim Spain and began producing paper using techniques they had learned from Chinese papermakers as early as the 8th century. From Spain, the manufacture of paper then spread to Italy in the 13th century and subsequently expanded throughout the rest of Europe [1,2].

It is generally accepted that early Italian papermakers from the region of Fabriano made fundamental improvements in the craft of papermaking at the beginning of the 14th century [3]. While the raw fibre material from which paper was made remained the same, i.e. linen and hemp from old textiles, the Fabrianese papermakers introduced major technological inventions such as the application of improved beating techniques with sets of stamping hammers to reduce the rags to pulp, the use of lime for rag treatment and the sizing of the paper with gelatine (or animal glue) instead of starch.

While the general outline of these developments has already been established by paper historians, the details of this technological evolution have still not been elucidated completely [1,2]. This is mainly due to the fact that the literature and written documentation of papermaking is sparse until the mid-18th century [4] when the first books about papermaking were published [5,6]. Due of the lack of written evidence, paper historians have to rely on the examination of historical paper specimens themselves to learn about early papermaking technologies and their changes in the Middle Ages.

The analysis of the papers is conducted primarily by visual and microscopic inspection to discover traces resulting from the production process and the handling of the paper. It also includes the measuring and comparing of different sizes and thicknesses of papers, its haptic feel and even the sound of the paper when shaken [7,8]. Moreover, material analytical methods have been used more and more often in the past several years to investigate the material composition of old papers [9,10,11,12]. Infrared (IR) and Raman spectroscopy, in particular, have great potential for a detailed and very specific chemical characterization of paper [10,13,14,15,16]. Raman microscopy, especially, offers

new possibilities for chemical paper analysis [16,17,18]. Raman measurements have a high chemical specificity and the use of an excitation laser in combination with an optical microscope provides for a very high lateral resolution of less than 1 µm. The Raman imaging technique allows the chemical structure of the paper to be visualized, i.e. the presence and distribution of different paper components on the surface or along the cross-section [16]. This includes different fibres, sizing compounds and other substances. Besides the components intentionally added to the paper, other substances can be detected and identified that were introduced as trace particles together with the main components in the paper or were formed during the production process.

In this study, three old Italian papers from the second half of the 14th century were analysed using ATR-IR und micro-Raman spectroscopy to find chemical substances and their distribution in the papers that can be correlated to the different steps in the paper production process and to certain manufacturing techniques.

2. Research aim

The general objective of our research is to consistently use spectroscopic methods to analyse the detailed chemical structure of paper. The study presented in this work shows the suitability of ATR-IR and Raman measurements for the chemical analysis of paper. In particular, the Raman imaging technique provides new insights into the chemical composition and structure of old papers. The results of this research could help to broaden the understanding of past papermaking practices and to change and improve the hypotheses about the facts and the knowledge relating to old papers and how they were made.

3. Material and methods

3.1. Paper samples

Three samples of old papers were investigated. The samples were small paper strips which had been taken from documents archived in the library at the University of Graz. The samples were provided to Papiertechnische Stiftung (PTS) by the Austrian paper historian Dr. Gottfried Schweizer (1927-2014) in 2001. They were obtained from documents which originally came from the libraries of monasteries in Austria and are dated to the second half of the 14th century. Because paper mills outside of Italy were only established in the late 14th century (e.g. 1390 in Nuremberg, Germany) [1,2] it is almost certain that the paper samples came from Italian paper mills [19,20].

Table 1
Paper samples from the second half of the 14th century.

Sample ID	Origin of document
K1-H4	unknown
K1-H5	monastery of Seckau (Austria)
K1-H9	monastery of St. Lambrecht (Austria)

3.2. Scanning electron microscopy (SEM)

The SEM images were produced and recorded using a JSM-6510 scanning electron microscope (JEOL) with the accelerating voltage set to 15-20 kV.

3.3. ATR-FTIR measurements

The IR measurements were performed with an FT-IR spectrometer Tensor 27 (Bruker) combined with an ATR (Attenuated Total Reflection) accessory PIKE Miracle in the spectral range from 4000 to 600 cm^{-1}. Three IR spectra were acquired for each side of the paper to calculate corresponding average spectra. As the penetration depth of the infrared radiation in ATR measuring mode is only about 2 µm, one must bear in mind that only the surface of the paper was analysed. The IR spectra in Fig.1 were normalized to the maximum of the cellulose band at 1030 cm^{-1}.

3.4. Raman microscopic measurements

The Raman measurements were performed using a Raman microscope WITec alpha 300M+ with a 532 nm laser. The laser power on the samples was 10 mW. The spectra were acquired with one scan and with integration times of 500 to 700 ms. The step size of all mapping measurements was 1 µm. The paper cross-sections were prepared by simply cutting the paper with a razor blade using a self-made apparatus. Data analysis including the generation of the Raman images was conducted with spectral imaging software that was developed in-house based on MATLAB (The MathWorks Inc.). All spectra were smoothed with a 5-point Savitzky-Golay function and were baseline-corrected.

The Raman images presented in Fig. 3 are representative images of two measured images per sample. The paper components, i.e. their Raman spectra, were detected using principal component analysis (PCA) and searching for known characteristic Raman bands. The detected substances were colour-coded by using the intensities of one of their characteristic bands. The colour coding used only indicates the presence of the substances and does not contain any quantitative information.

4. Results and discussion

4.1. ATR-IR measurements

The IR spectra were measured on both sides of the paper

and turned out to be very similar. Therefore, only one spectrum of each paper is shown in Fig.1. The figure presents the IR spectra in the so-called fingerprint region below 1800 cm^{-1} where the characteristic bands of most paper components can be found.

The IR spectra of the papers are dominated by the intensive, broad bands of the cellulose in the paper fibres. Within these bands, a double band with maxima at 1369 and 1362 cm^{-1} is characteristic of rag fibres (linen, hemp or cotton) [21].

Additional bands were observed at around 1650 and 1540 cm^{-1} which are assigned to the protein bands amide I and amide II [22], respectively, and show the gelatine sizing of the papers. A closer inspection of this spectral region reveals two distinct maxima at 1577 and 1541 cm^{-1} which can be clearly attributed to calcium stearate. Calcium stearate is often associated with gelatine and can be formed by calcium ions in the water and stearic acid which is a component of triglycerides in animal fat.

It is well known that mineral fillers were not used in early papermaking. The use of kaolin as a filling and whitening component in paper only developed at the beginning of the 19th century [1]. Nevertheless, one often finds small traces of kaolin in old papers which shows a very characteristic IR band at 3692 cm^{-1}. This is also the case for the two paper samples K1-H4 and K1-H5 (not shown in Fig.1). Apparently, the kaolin is introduced together with other mineral material from the water in the paper [16].

Furthermore, there is a weak band at about 875 cm^{-1} in all three spectra. This band is also very characteristic. Despite being weak, it can be unambiguously assigned to traces of calcium carbonate, more precisely to the crystalline form of calcite. Moreover, an additional band is observed at 856 cm^{-1} in the spectra of the two papers K1-H5 and K1-H9 and can be assigned to the calcium carbonate crystalline form of aragonite.

The presence of calcium carbonate in old papers is not unusual. The use of lime, calcium hydroxide, in the stamping treatment of the rags introduced calcium ions and formed alkaline conditions which induced the lime to react with atmospheric carbon dioxide to produce calcium carbonate particles [23]. The calcium carbonate precipitated as finely distributed particles on the fibres and even in the lumens or cell walls of the fibres as can be seen in the SEM images of the paper cross-sections in Fig. 2 (white particles and areas in images A and B). The images also show greater deposit clusters which suggest that most of the calcium carbonate precipitated after the paper sheet had formed and while the paper was drying.

The alkaline character of the old papers is considered to be one major reason for their high permanence und durability until today [11,24,25]. Dabrowski [23,25] and Barrow [24] reported on old papers that were made before 1600 with calcium carbonate contents of 2 to 3 % and high pH values of up to 9. After 1600, most European papers became more acidic due to the introduction of alum, aluminium potassium sulphate, into the gelatine size [24]. The Italian papermakers continued not using alum, and the alkaline character continued to be characteristic of Italian papers [25].

While deposits of calcium carbonate are very common in old paper, the presence of calcium carbonate in its crystalline form of aragonite in the papers K1-H5 and K1-H9 is unexpected. Aragonite is a metastable polymorph of calcium carbonate and tends to transform to the stable polymorph calcite. The formation of aragonite during precipitation from aqueous solutions is favoured by higher temperatures and low ion concentrations [26]. This would support the conclusion that most of the calcium carbonate deposited in the

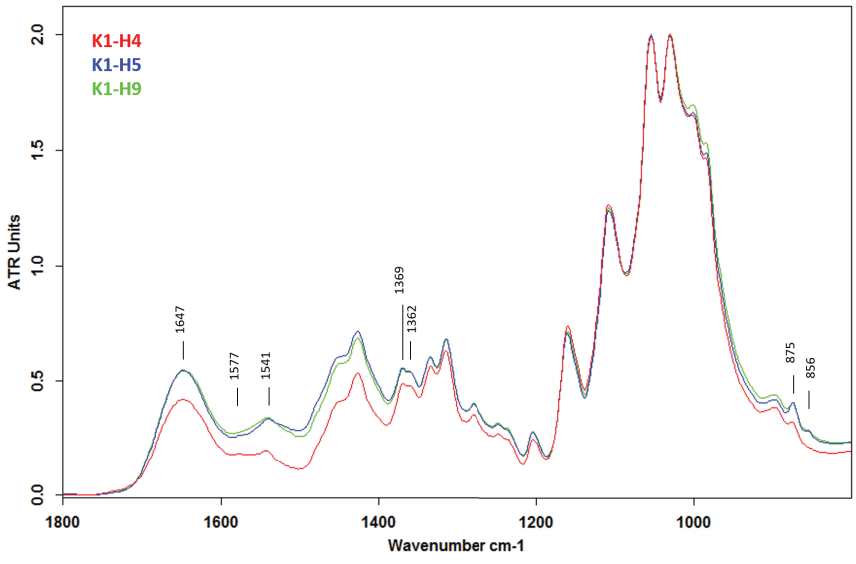

Fig. 1. IR spectra of the three paper samples

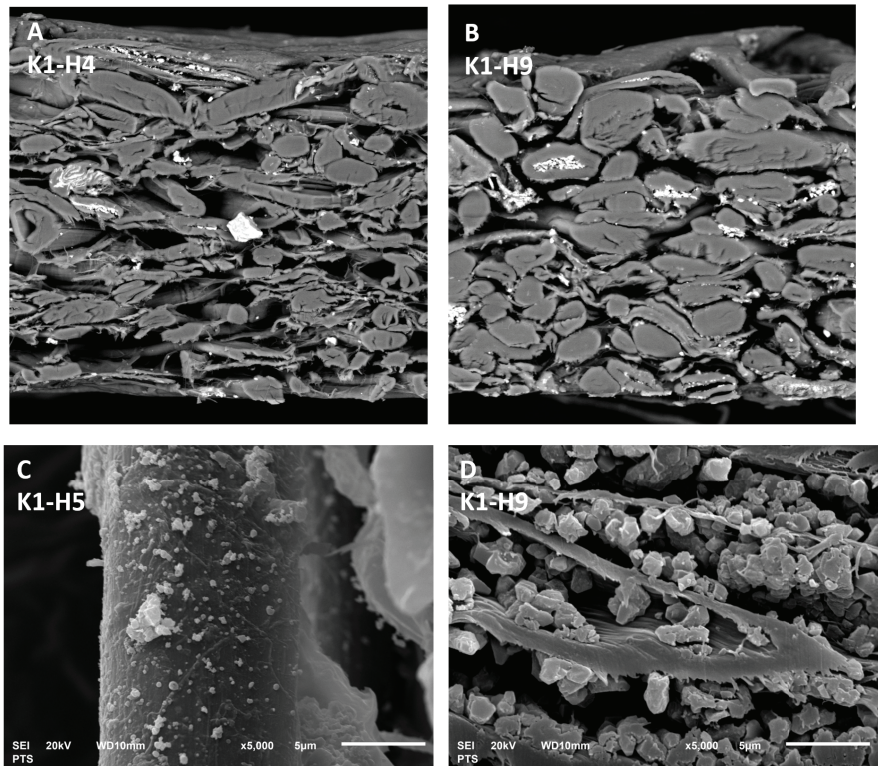

Fig. 2. SEM images from the cross-sections of the three paper samples. Images A and B in backscattered electron mode, images C and D in secondary electron mode

papers after the paper sheet had formed and during the subsequent drying step once the papers had been dipped into the boiled gelatine size. More investigations on old paper from this period or even experiments with modern handmade papers could help to further elucidate the actual nescessary conditions for the formation of aragonite.

4.2. Raman imaging measurements

Raman measurements were conducted on the paper cross-sections over areas of about 110 x 85 µm. Figure 3 shows the resulting Raman images of the three papers revealing the fibre structure, the detected chemical components and their distribution. An initial observation is that the gelatine had penetrated well and is distributed throughout the entire thickness of the papers. This fact tells us something about how these papers were sized.

The Arab papermakers used to size their papers with rice or wheat starch. The starch was applied in a thick solution by spreading it over the surface. After the starch had dried, the surface was then polished with a smooth stone. [3]

In Italy, instead of using starch size, gelatine size which was made from boiling animal skins or bones was introduced about 1300. Gasparinetti [27] and Hill [3] suggest that the papermakers in Fabriano probably began using gelatine for sizing in accordance with suggestions given by the local tanneries. At first, like the starch used by the Arabs, the gelatine size was brushed or smeared onto the surface resulting in polishing or brushing marks on very early Italian papers. Hill observed on Italian papers dated after 1370 that the sizing became more even and that this improvement was continued after this date. He suggests that these papers were sized with a dipping technique as was later described in books about papermaking [4,5,6]. The paper sheets were then piled and placed in a press. The press was brought into action and the gelatine size was forced uniformly through each paper in the pile. The homogenous distribution of the gelatine size found in the three investigated papers would confirm this procedure.

The connections of the Italian papermakers to the tanneries would suggest that they used predominantly skin scraps to prepare the gelatine size. In this respect, the detection of an apatite $Ca_5[OH/(PO_4)_3]$ deposit in a fibre lumen in the Raman image of the paper K1-H5 is interesting because this is proof that animal bones which consist mainly of apatite were also used in preparing the gelatine.

An additional substance associated with the gelatine sizing is found in the Raman image of paper K1-H9. Again, in a fibre lumen, one finds a deposit of calcium stearate. This substance is included in triglycerides in fat, i.a. animal fat, and was already detected in the IR spectra.

The Raman images also show the calcium carbonate deposits in the fibre lumen and between the fibres. Furthermore, the high lateral resolution of the Raman measurements allowed the detection and identification of few aragonite particles in the papers K1-H5 and K1-H9.

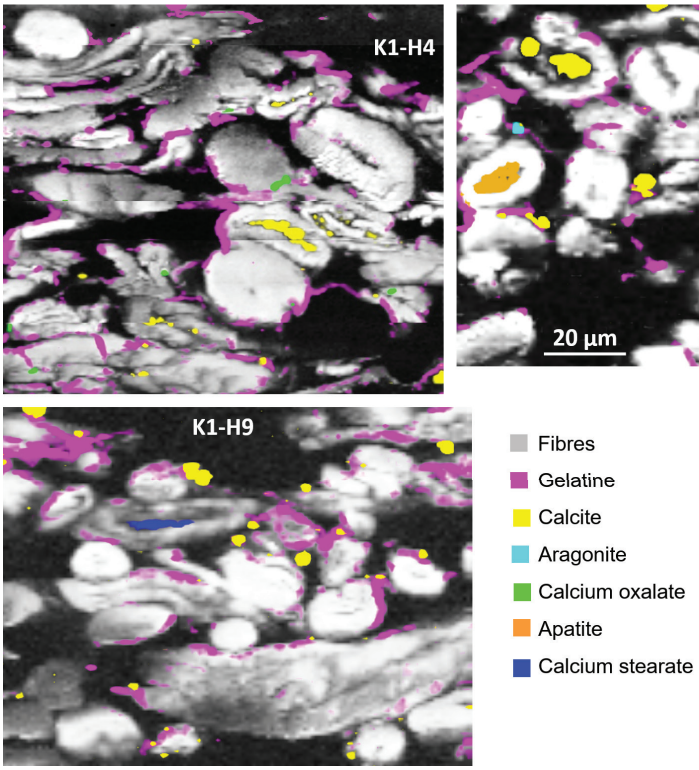

Fig. 3. Raman images of the cross-sections of the three paper samples

Traces of calcium oxalate were also detected in the paper K1-H4. Calcium oxalate is often found in old papers [16]. This substance is a product of biological activity and is produced by moulds and other microorganisms [28,29]. Calcium oxalate exists in two forms: the monohydrate $CaC_2O_4 \cdot H_2O$ (whewellite) and the dihydrate $CaC_2O_4 \cdot 2H_2O$ (weddellite). Small particles of both forms were detected in the paper based on their characteristic Raman spectra [29] (see Fig. 4).

5. Conclusions

In this study ATR-IR and micro-Raman spectroscopy were used to analyse the chemical structure of old papers, most probably Italian, from the second half of the 14th century. In particular, Raman microscopic measurements allowed the detection and identification of the different paper components and the visualization of their distribution in the paper. The information thus obtained could be correlated to different steps in the paper production process and to certain manufacturing techniques.

The study demonstrated the use of spectroscopic methods to help paper historians elucidate practices used in early papermaking or to confirm hypotheses about them. The importance of material analytical methods in the study of paper history was recognized at the end of the 19th century by the Austrian botanist and paper historian Julius von Wiesner (1838-1916) who was one of the first to conduct material analyses on old papers. He stated as early as 1911: "Only through the combination of historical and natural scientific studies can one obtain deeper insights into the true history of paper." (translated from German, [30]). In the last few years, renewed efforts have been undertaken to investigate the materiality of old papers [12,31,32,33]. This is due largely to the technical progress that has been made in the analytical methods which currently allow highly specific analyses using non-destructive methods. IR and Raman spectroscopic measurements, in particular, offer several advantages to a detailed and specific chemical characterization of old and historically important papers. IR and Raman measurements conducted on the paper surface are non-invasive. Raman microscopic measurements on the paper cross-section can be performed on very tiny paper strips with a width of 1 mm or even less. Furthermore, ATR-IR measurements can be conducted very quickly and an experienced analyst can extract the chemical information from the spectra just as fast [21].

The results and findings of this study open up new perspectives for the investigation of old historical paper and its making and encourage further studies in this direction.

Acknowledgements

The author would like to express his thanks to Pia Schenke (Papiertechnische Stiftung (PTS), Heidenau, Germany) for performing the SEM measurements. I am also grateful to Bryan McEwen (Munich) for the translation of the Wiesener statement.

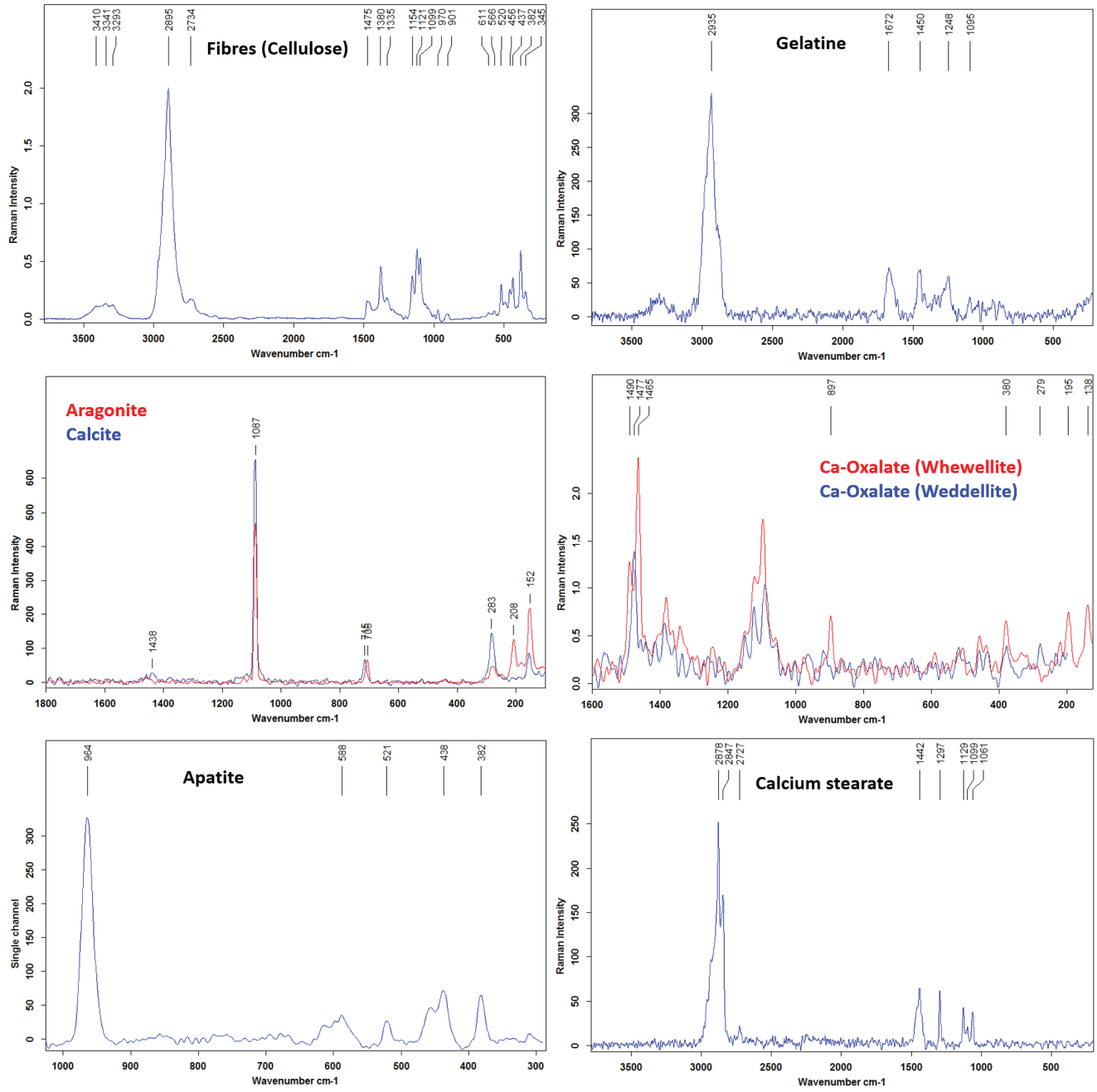

Fig. 4. Raman spectra of the detected paper components

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