Dating of a unique six-colour relief print by historical and archaeometric methods*

ARMIDA SODO[a], LUDOVICA RUGGIERO[b], STEFANO RIDOLFI[c], ELIZABETH SAVAGE[d], LUCA VALBONETTI[e], MARIA ANTONIETTA RICCI[f]

Abstract

The aim of this work is the historical and archaeometric investigation of a unique six-colour single-sheet relief print on paper belonging to a private collector. It is undescribed, undated and unsigned, and it depicts Charlemagne enthroned in Aachen Cathedral. The print was tentatively dated to the 16th century based on the style and iconography. This study offers a revised dating based on stylistic analysis of the design and archaeometric investigation of the six printing inks. The methodology consists of the complementary use of imaging and spectroscopic techniques, which are entirely non-invasive and non-destructive due to the rarity and fragility of the object. In particular, preliminary unaided visual analysis, UV fluorescence and IR reflectography were used to investigate the surface condition of the impression and to select the most promising areas for further analysis. Raman spectroscopy and XRF were used to identify pigments and treatments. Our results show that the paper support is in good condition. The pigments of all six inks have been identified. Results suggest that this impression was printed after 1850 and before 1900. In its conception and production, this artwork used then-modern methods and materials to pay homage to the styles and production techniques of the earliest German colour woodcuts.

Key Words

Printing ink
Colour printing
Woodcuts
Relief print
Archeometric methods
German colour woodcuts

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Armida Sodo[a], Ludovica Ruggiero[b], Stefano Ridolfi[c], Elizabeth Savage[d], Luca Valbonetti[e],

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Introduction

Relief prints are artefacts created by removing voids ("white" areas, which are not to be printed) from an object so that only the design remains, and then impressing the surface on a substrate. The object was normally a woodblock and the substrate was usually paper in pre-industrial Europe, but relief printing can involve different materials for both blocks and substrates to create different final effects. Relief printing appeared in Europe, in particular in the Netherlands, France and Germany, first through manual techniques (for example, blockprinting on fabric) by the 14th century, and then with letterpress after Johannes Gutenberg created moveable type and the relief printing press to print the *Gutenberg Bible* in 1455. Woodcut book illustrations could be cheap alternatives to the much more expensive illuminated manuscripts, but single-sheet woodcuts were also produced and collected as fine art. The most influential early modern printmaker, Albrecht Du¨rer (1471–1528), is often crediting with transforming woodcut into a fine art. Many millions of individual impressions of woodcuts were printed during his lifetime, when printing fuelled social and cultural revolutions including the protestant reformation. They were printed in black. Possibly tens of thousands were printed in colour (that is, not painted after having been printed). Today, several hundred German single-sheet colour woodcut book illustrations survive from the sixteenth century, almost all in black and red on white paper. Only five or six dozen German single-sheet woodcuts from this time survive in at least one colour-printed impression. Many are extraordinarily rare or the unique colour impression of a print [1].

Recently, a private collector acquired at auction a unique impression of a previously unknown and undescribed single-sheet relief print depicting Charlemagne enthroned in the Aachen Cathedral (fig. 1). This artefact is unde-scribed, undated and unsigned. It is a relief print, as the design is impressed into the substrate; the reverse is true of intaglio prints (*e.g.*, etching and engraving), and the design is coplanar with the surface in planographic printing (*e.g.*, lithography). However, the lines are finer and of a more consistent width that would be expected of wood. The print was tentatively dated to the 16th century based on the style and iconography. The use of novel materials (colour inks) indicate this print was created as an exceptional production. In particular, the use of six colour inks would make it one of the most complex colour prints of the first 350 years of printing (from Gutenberg's invention of printing around 1450 until Jakob Christoff Le Blon's invention of trichromatic process printing around 1700). However, further analysis of the style of the design and unusual aspects of the manufacture suggests that it was designed and produced in the late 19th century, following the artistic influence of the Pre-Raphaelite Brotherhood, called the "Pre-Raphaelites" (founded in 1848). In particular, the design of the two female figures and kneeling man, namely the idealised facial profiles and locks of hair, are typically Pre-Raphaelite. The style of this English artistic collective was influential especially from the 1850s through the 1890s, so stylistic grounds suggest that the print was produced in that time period.

The red and black designs are from freely drawn lines of varying widths, so the draughtsmanship would suggest etching. However, etching is an intaglio technique, but the "ink squash" indicates that this impression is from relief. Woodcut is the most common form of relief printing for imagery, but it is improbable that a block of wood could be cut with lines as fine, curvilinear, and calligraphic as the red and black designs. In principle, they could be from conventional relief etching, which William Blake (1757–1827) is credited with inventing. That involves sketching the designs onto a metal plate with a resist, eating away the rest of the plates' surface in an acid bath so that the design is effectively "raised", and then printing them in relief. However, the accidental duplication of elements of the red and black designs, for example between the eagles' necks and wings, suggests that the black and red designs were taken from the same "original". It is improbable that one surface was used for both impressions using frisket sheets with inaccurately cut holes. The shape of the holes, especially around the feathers, would be too complex to be stable. Given the freehand nature of the black and red designs, the accidental duplication of areas of both colours, and the difficulty of deriving both colours from one surface using frisket sheets, the most likely explanation is that the red and black designs were produced with a photomechanical process —perhaps involving relief etching— that transferred a design to a relief printing surface. A photomechanical process would also date the design of this print to the late nineteenth century.

In order to confirm the dating of the print, we necessarily adopted a multi-disciplinary approach. The methodology had to be non-invasive and non-destructive due to the rarity and fragility of the object. We used complementary imaging and spectroscopic techniques, corroborated by stylistic, art historical analysis. Preliminary unaided visual analysis, UV fluorescence and IR reflectography were used to investigate the support and the conditions of the impression, and also to select the most promising areas for further analysis. Raman spectroscopy and Energy Dispersive X-Rays Fluorescence (EDXRF) were then used to identify pigments and substrate treatments.

Materials and methods

The single-sheet relief print measures 21 × 29.3 cm. It represents Charlemagne enthroned in the Aachen Cathedral (fig. 1) and was printed on paper in six colours: red, yellow, blue, green, black and "gold". The full order of printing could not be determined, but the black ink was the first to be applied (see *Results and discussion* below). Since each colour requires a different block, six blocks were designed and then printed with great skill in register (alignment). The additional work of the colour printing attests the high quality of the production of this unique artefact.

Visual observation confirms that the paper and ink films are in good condition, except for discolouration and warping in the central part (especially visible on the verso) and a cut in the lower margin. It did not require any conservation work before analysis commenced.

Photos in visible and ultraviolet (UV) light were taken with a Canon EOS 500D camera equipped with 18–55 mm lens. The photos in UV were collected by illuminating the artefact with a wood's lamp (E27, 160 W). Macro photos were taken with a Nikon D200 and a Tamron SP AF 60 mm optics. Photos in infrared (IR) were acquired in the range 400–1100 nm with a MICRO IR 20 camera equipped with a charge-coupled device (CCD) with a silicon detector CCD and a VIS filter of IR80.

Preliminary visible, UV and IR photos of the artefact have been collected in order to determine the conservation condition of the print, to evidence potential inhomogeneities and to select areas to be further investigated. These preliminary observations showed that each colour ink is homogeneous thus revealing that for each colour the same pigment or mixture have been applied. For this reason, we decide to investigate by EDXRF a total of 20 points: 16 points from the verso side and 4 from the recto. Each EDXRF measurement has been repeated three times. In particular, the investigated areas on the recto are reported in fig. 2 and depict the blue ink near the gems and the tapestry, the green on the floor area, the red on the scrolls and on the coat of arms, the yellow on the eagle's paws, the black on the writing and the gold in the area of the throne. Raman measurements have been performed on the same areas investigated by EDXRF.

EDXRF spectra were acquired using an Amptek Mini-X X-Ray tube with a gold anode (working voltage 38 kV and working current 0.1 mA) and an Amptek X123 Silicon Drift Detector Peltier cooled. Energy resolution is about 168 eV. The spatial resolution is less than 1 mm [2].

Raman spectra have been collected in the region 200–4000 cm−1 by using a Horiba LabRAM μ-spectrometer equipped with three different laser sources: a solid state 532 nm laser (output power 1W), a 633 nm HeNe laser (output power 18 mW), and a solid state 785 nm laser (output power 300 mW). Neutral filters were used to reduce the laser power on the print. The illumination and collecting optics consist of a confocal microscope. Most of the Raman spectra reported in this article were collected by using an objective lens with 20 magnification. The system achieves the high contrast required for the rejection of the elastically scattered component by an edge filter. The backscattered light is dispersed by a 1800 line/mm grating, and the Raman signal is detected by a Peltier cooled (70 ◦C) 1024 256 pixel CCD detector. LabSpec and Origin software were used to analyze the raw data, including a baseline adjustment by a polynomial fit as well as smoothing and spikes removal when necessary.

Results and discussion

Stylistic investigation

Stylistic analysis revealed that many elements of the design derive from sixteenth-century sources, especially prints by Du¨rer. However, they are not careful imitations. Instead, they comprise a pastiche: only certain aspects of Du¨rer’s designs are emulated, and Du¨rer’s figures are "cut and pasted" to be presented in a new context. This form of imitation of earlier artworks and styles, which often involves recontextualising or modernising certain aspects, was uncommon in the 16th century but relatively common in the mid-to-late 19th century. The antiquarian revival of late medieval/early Renaissance forms at that time is linked to the neo-Gothic movement, which took hold in Germany especially after unification in the 1870s. The design of the figures, particularly the facial profiles, shows influences of the English pre-Raphaelite movement, which was influential especially from the 1850s through the 1890s. Analysis of the paper treatment and printing inks was required to refine this re-dating to the mid-to-late 19th century.

Archaeometric investigations

Images were obtained using macro photography, a technique that allows a maximum magnification of 10:1. These images gave us some clues about how this artwork was manufactured, including the conventional black-first order of printing (fig. 3).

To determine the physical condition of the print, evidence potential inhomogeneities and select areas to be further investigated, images under UV and IR radiation were acquired. We want to stress that both these techniques were used only for a preliminary investigation, so only general remarks can be derived from the results (fig. 4). The UV fluorescence reveals that unprinted areas (both on the margins and within the borders) have a homogeneous bluish fluorescence. Red details change to a red-purple yellowish tone. This can be attributed to the presence of an organic pigment that has not been revealed by spectroscopic investigation. The green and the blue areas did not turn to black, which excludes the use of copper-based compounds. The "gold" ink turns to black, thus not giving any clues for its identification. The discoloured areas show a halo with a whitish fluorescence [3]. IR radiation, which penetrates below the ink films and surface of the paper, reveals details that otherwise cannot be observed. The infrared reflectography of the upper part of the artwork reveals that the scrolls were made directly on the paper without any reference of black ink. The images do not reveal alterations below the superficial ink films [3–5]. Both these techniques evidence that the artefact is in a good state of conservation and suggest a homogeneous preparation of the paper before printing.

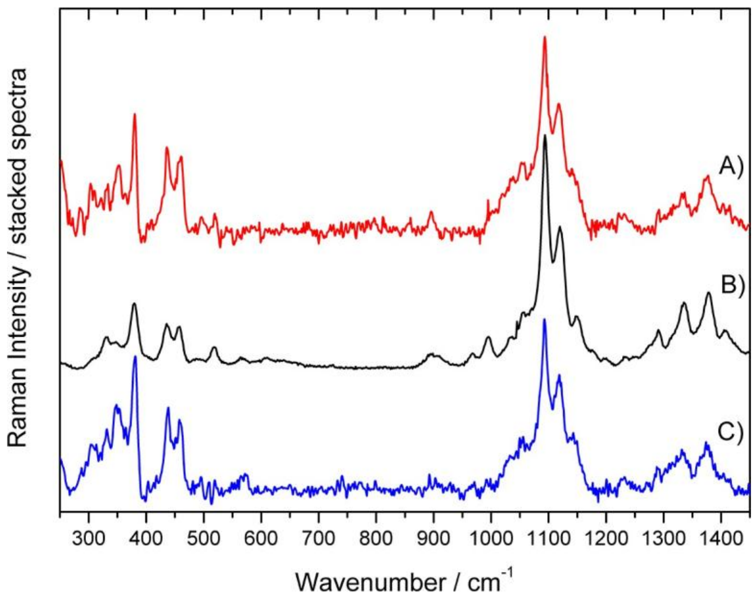

Fig. 5. Raman spectra collected from (A) paper area; (B) standard cellulose; (C) white background area.

After these preliminary observations, the relief print was subjected to further investigation by Raman spectroscopy and EDXRF to identify ink components (specifically, pigments) and materials involved in the paper treatment. EDXRF spectra were collected from several points across the full surface of the print, allowing the identification of elements involved in the inks' composition and the paper's treatment [6]. Raman spectroscopy was performed on the same selected points, which had been investigated by EDXRF investigations, to yield information about the molecular composition of the materials [7].

Usually the superimposition of layers with different pigments complicates EDXRF measurements. In this case, the stratigraphy is very simple, and spots with only one pigment layer were chosen to avoid interference. EDXRF spectra collected on the paper (in the upper area of the print) showed peaks of Ca and Fe, probably from the preparation of the paper [8–10]. Raman spectra collected on the same points did not identify the salts, due to an intense fluorescence, but showed the spectra of cellulose (fig. 5(A)).

The background and the two figures in the central part of the impression were realized with a white material. EDXRF revealed the presence of Zn as the main element, suggesting the use of a zinc compound (probably zinc white, ZnO, a modern pigment that was manufactured from 1850 [11, 12]). Raman spectra collected from the same area were consistent with that collected directly on the support: a cellulose-based compound (fig. 5(C)) with no evidence of Zn compounds. This is likely due to the most intense Raman band of zinc white being positioned at 441 cm^{-1}, in a spectral range full of cellulose bands [9].

In the black inks, EDXRF showed the presence of Fe, Zn, Ba and Cu. As reported above, Fe is associated to paper preparation. Zn and Ba are present in all EDXRF measurements of the coloured inks, but no zinc or barium or zinc/barium compound could be detected in any of the collected Raman spectra. Our hypothesis is that Zn and Ba compounds could have been used to whiten the paper or prepare it for printing. Zn and Ba compounds were used as pigments [11–13] or paper treatments [14, 15]. In particular, the presence of Zn has been detected on paper sheets produced since 1770 and associated to white zinc oxide used during paper making. The presence of Ba, indeed, can be attributed to a paper coating treatment or to a deacidification restauration treatment. In the first case, the use of barium sulphate was already reported in documents from the beginning of the XIX century for paper coating and in very rare instances it might be reported as a filler [14]. The second hypothesis is that Ba was used during a restoration treatment. In fact, for many decades, the aqueous solutions of calcium, magnesium, and barium hydroxide have been widely used as conventional paper deacidification processes [15].

Raman measurements unambiguously show the typical bands of carbon black (1325 and 1596 cm^{-1}), indicating that the black ink is a carbon-based pigment. The presence of Cu will be discussed below.

In all the red areas (volutes, scrolls and the background of the coat of arms), EDXRF detected Pb, Hg, Cr, Zn, Cu, Ba, Ca and Fe. Again, Ca and Fe can be linked to paper preparation. Raman revealed in each investigated point the presence of vermillion (HgS, bands at 255, 287 e 345 cm−1), present either as pure or in mixture with minium (Pb_3O_4, bands at 121, 150, 315, 337, 390 and 548 cm−1) and chrome yellow pigment (bands at 138, 340 and 828 cm−1) (fig. 6). In this work we identify the chrome yellow pigment by comparing our spectra with [16], but some more recent works [17] suggested that this spectrum could be due to degradation products.

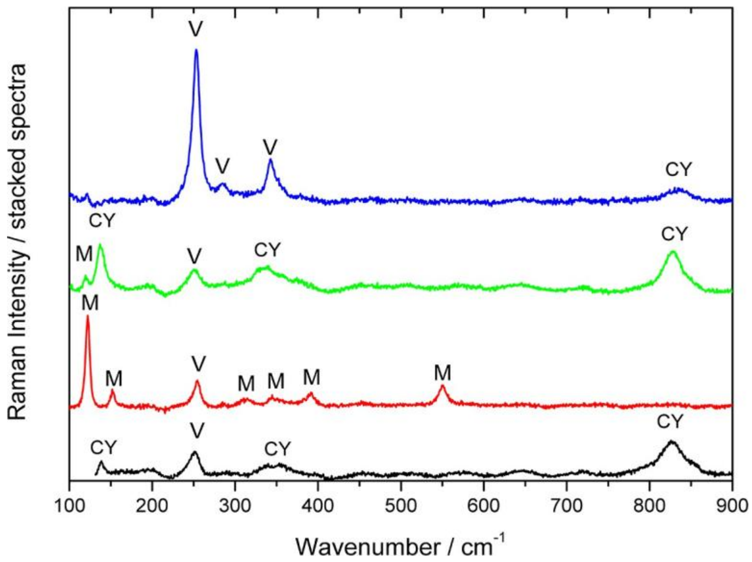

Fig. 6. Raman spectra collected from different red areas; labels evidence bands attributed to M = minium, V = vermillion, CY = chrome yellow.

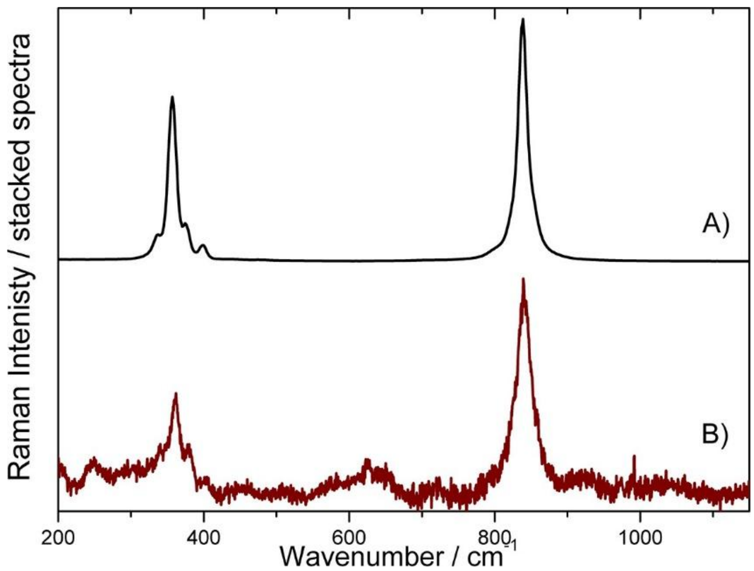

Fig. 7. Raman spectra collected from (A) standard chrome yellow [16] and (B) yellow area.

The correct and unambiguous identification of the huge category of “chrome yellow” pigments is a hard work, especially due to several conflictual information reported in literature, its not easly controlled laser degradation and also due to the commercialization of several synthetic products with different name and molecular composition. For this reason, we are confident to assume that the ink was made by a generic “chrome yellow pigment” without any further specification, as reported in other literature paper [18] that shows the same spectra we obtained.

Vermillion and minium are pigments that have been used since antiquity [19], but the chromate-based pigments were first synthetized in 1809 [20, 21] and commercially available from the first quarter of the 19th century [22]. Only on the eagle’s body, in particular on the claws, it is possible to observe a yellow pigment. In this area, EDXRF detected Pb, Cr, Zn, Cu, Ba, Hg and Fe while Raman showed the typical bands of chrome yellow, $PbCrO_4$, positioned at 339, 360, 375 and 841 cm^{-1} (fig. 7). This pigment was also first synthetized in 1809 [20]. The presence of Hg could be associated to the presence of red inks nearby.

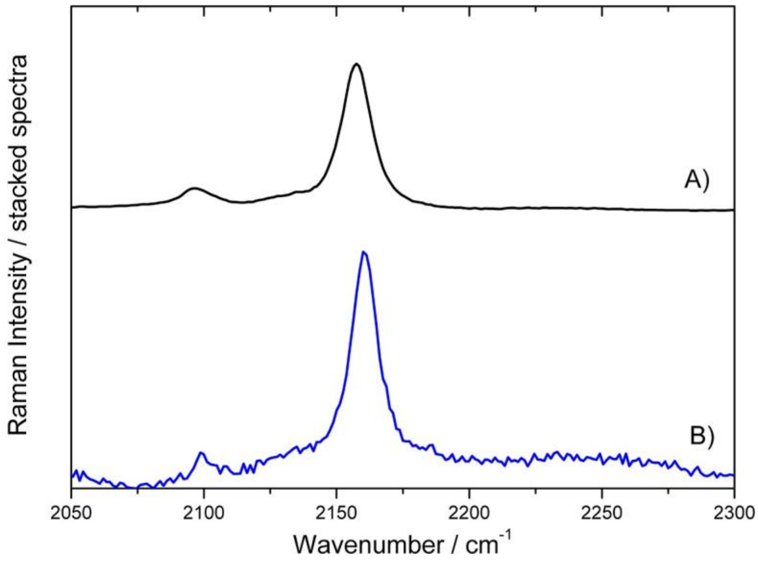

Fig. 8. Raman spectra collected from (A) standard Prussian blue [16] and (B) blue area.

Blue ink is used on some of Charlemagne's jewels and the tapestry below the throne. EDXRF evidenced the presence of Fe, Zn, Ba and Cu. Raman showed the typical spectrum of Prussian blue, $Fe_4 [Fe (CN)_6]_3$, a synthetic pigment that was introduced in 1724 [23, 24]. In particular, the Raman spectrum presents the typical band at 2160 cm−1 ascribable to the CN stretching mode (fig. 8).

Green ink is present on the floor. EDXRF revealed the presence of Pb, Fe Cr, Zn and Ba. Raman spectroscopy showed that it was not a true green pigment but a mixture of chrome yellow and Prussian blue.

"Gold" inks are present in several areas, especially on the architectural elements and throne. EDXRF showed Cu, Zn and Pb but not Au, confirming the preliminary observation by UV fluorescence. Raman spectroscopy revealed the typical spectra of copper oxides, suggesting the use of a cheap imitation of gold. In particular, this ink could be made of "Orone", an ancient Italian word meaning "bad gold", which is a brass powder made of Cu, Zn and sometimes Pb [25].

In all of these colour inks, EDXRF measurements show the presence of Cu. This is not justified by a copper-based pigment. It could suggest that matrix was not a woodcut but made of copper [26, 27]. Copper would be a surprising choice for relief printing because the soft metal cannot hold up to many impressions under the great pressure of a relief printing press, and relief etching is relatively unusual. It might have been produced using one of the many industrial printing processes that were introduced in the late 19th century.

Conclusion

A multi-disciplinary and multi-technique approach were used to study a unique six-colour relief print in a private collection. Our work re-defined the dating from the 16th century to the late 19th century. UV fluorescence and IR reflectography showed that the artefact is in a good state of conservation and helped the selection of the measurement points. EDXRF and Raman spectroscopy revealed that two printing inks were produced with formulations that were introduced in 1809. Stylistic analysis and art historical research, as well analysis of the paper substrate, indicate a dating of after 1850. The results of the art historical and instrumental analyses suggest that this impression was printed after 1850 and before c.1900. The upper limit is suggested by historical analyses: in fact, the Pre-Raphaelite style was highly influential from the 1850s through the 1890s, but then it fell out of favour. From an art historical perspective, stylistic evidence suggests a dating of between 1848 (when the Pre-Raphaelite Brotherhood was founded) and the 1890s (when the style fell out of fashion). In its conception and production, it used then-modern methods and materials to pay homage to the styles and production techniques of the earliest German colour wood-cuts.

Endnotes

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[a] Dipartimento di Scienze, Universit`a degli Studi Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy e-mail: armida.sodo@uniroma3.it

[b] Dipartimento di Scienze, Universit`a degli Studi Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy e-mail: ludovica.ruggiero@uniroma3.it

[c] Ars Mensurae, Via Comparini 101, 00188 Roma, Italy e-mail: stefano@arsmensurae.it

[d] Institute of English Studies, School of Advanced Study, University of London, London, UK e-mail: elizabeth.savage@sas.ac.uk

[e] Facolt`a di Bioscienze e Tecnologie Agro-Alimentari e Ambientali, Universit`a degli Studi di Teramo, Campus universitario di Coste Sant'Agostino, via R. Balzarini 1, 64100 Teramo, Italy e-mail: lvalbonetti@unite.it

[f] Dipartimento di Scienze, Universit`a degli Studi Roma Tre, Via della Vasca Navale 84, 00146 Roma, Italy e-mail: mariaantonietta.ricci@uniroma3.it

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List of Figures