

# Analysis of Pigmentary Materials on the Vinland Map and Tartar Relation by Raman Microprobe Spectroscopy

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**Studies by Raman microprobe spectroscopy have shown that the black ink defining each feature on the controversial Vinland Map consists of carbon that overlays a yellow line containing anatase. This material was not detected elsewhere on the map. Since anatase has not been found on medieval artifacts, and such yellow lines are only naturally produced by iron gallotannate inks, a modern (post 1923) origin for the Vinland Map is strongly indicated. The ink of the Tartar Relation is different and probably consists of an iron gallotannate mixed with a small proportion of carbon. The rubrication is established to be vermilion.**

The Vinland Map (VM) and Tartar Relation, held in the Beinecke Rare Book and Manuscript Library of Yale University, are historically significant and have been at the center of a controversy since they first came to light in 1957. The items had been bound together in a modern binding (19th or 20th century), but are now separate. The Tartar Relation (of the 15th century) consists of a previously unknown account of the expedition of Friar John de Plano Carpini to the Mongols in 1245–47. The VM is a world map on parchment measuring 28 cm by 40 cm which includes, significantly, representations of Iceland, Greenland and the north-eastern seaboard of North America ("Vinland"). Some time after 1959, when they were originally offered for sale, both were purchased and later given to Yale University by an unknown benefactor who was subsequently revealed to be Paul Mellon. On October 11, 1965, the day before Columbus day, facsimiles and transcriptions were published<sup>1</sup> along with claims, based on cartographical, paleographical, and philological analysis, that the VM had been drawn from two different prototypes around 1440, possibly in Basle, Switzerland, thereby predating by some 50 years, the discovery of America by Columbus.

It is now well-known that the Vikings did indeed reach the new world<sup>2,3</sup> – evidence of their settlement has been discovered in Newfoundland (L'Anse aux Meadows) and elsewhere, but the sudden appearance of a manuscript with a clear depiction of the

north Atlantic seaboard but no apparent origin or provenance, was destined to cause controversy.

Several attempts to verify the suggested origin of the map have been made with the sanction of Yale University, but the conclusions have not been in agreement with one another. Polarized light microscopy (PLM), micro-X-ray diffraction (XRD), and scanning electron microscopy (SEM)/energy-dispersive X-ray analysis (EDX) by McCrone Associates have, in 1974 and 1991, indicated the presence of anatase,<sup>4–6</sup> the least common form of titanium dioxide found in nature, in the yellow lines. Transmission electron microscopy (TEM) of the anatase on the VM showed it to be in the form of uniform, well-rounded, single crystals  $\sim 0.1$ – $0.3 \mu\text{m}$  across and with the narrow size distribution which is characteristic of synthetic calcined anatase but not of the mineral. The latter, when ground, forms as irregular, jagged particles of widely varying dimensions. Since off-white cream-yellow anatase could not be synthesized until  $\sim 1920$ , and white anatase, until  $\sim 1923$ , McCrone concluded that the implication of this discovery is that the VM itself must be post  $\sim 1920$  (though the parchment may be earlier).<sup>5</sup> Subsequent analyses by Cahill et al. using particle-induced X-ray emission (PIXE),<sup>7</sup> another elemental technique, have also led to the detection of titanium on the map but to the conclusions that (a) the anatase is not confined to the lines on the VM and (b) titanium (to a maximum of  $10 \text{ ng cm}^{-2}$ ,  $\sim 0.0062\%$  by mass) and other heavy elements are present only in trace amounts in the inks. Cahill et al.,<sup>7</sup> therefore, concluded that the VM should be reevaluated and reaffirmed their opinion in 1995.<sup>8</sup> However, the interpretation given to the PIXE results has been robustly challenged by McCrone.<sup>9</sup> Moreover, the results of a small-sample carbon-dating study, which would relate only to the parchment, have never been published, whereas palaeographical studies seem to support or cast doubt on any or all of the proposed dates, depending on who conducts them.<sup>10–12</sup>

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Figure 1. The Vinland Map, scanned from ref 1 by Jim Siebold, Cartographic Images, at [www.henry-davis.com/MAPS](http://www.henry-davis.com/MAPS). The red boxes indicate those areas from which Raman spectra were obtained.

The black pigment in the ink has also not previously been identified, but several possibilities have been considered, including carbon black and iron gallotannate. McNaughton<sup>11</sup> has proposed that a printing ink based upon chromite ( $\text{FeCr}_2\text{O}_4$ ) was used. This black material must be heated to c. 90 °C in order to be fixed to a substrate; in the absence of such treatment, the black fraction may flake off, an apparent explanation of the deterioration of the VM.

The aim of this study was to examine both the VM and the Tartar Relation by Raman microprobe spectroscopy, a highly sensitive and specific in situ technique which often makes it possible to identify common pigments and their whereabouts with certainty, even in subnanogram quantities.<sup>13,14</sup> It was hoped that this study would allow the components of the inks on both objects to be identified and the surfaces to be studied for evidence of pigments and any other substances that might be present. The results resolve some of the discrepancies relating to the conclusions previously drawn about the date of the VM and provide new information on the Tartar Relation.

## EXPERIMENTAL SECTION

The map and manuscript were analyzed by Raman microprobe spectroscopy using a Renishaw System 100 with a 632.8-nm laser

and fiber-optic probe. Laser powers of between 0.5 and 5 mW at the sample were used over accumulation times of up to 800 s. The laser spot size was  $\sim 5 \mu\text{m}$  in diameter using a 10 $\times$  lens as the probe objective.

Areas of study were selected on the basis of pigment density or other specific features of interest.

## RESULTS

**The Vinland Map.** The Vinland Map (Figure 1) is not in good condition, apparently suffering from considerable pigment loss, which is unsurprising for a manuscript of its postulated age.

The ink lines appear to be composed of two parts, a yellowish line which strongly adheres via absorption to the parchment and an apparently overlaid black line from which >90% of the black pigment has flaked off; indeed, in some places the black has been almost entirely lost. (Figure 2) The parchment itself is dull fawn, in reasonable condition and clean, with an additional strip of parchment securing the spine and small squares of parchment patching over a number of small holes.

Raman spectra of the blank areas of the parchment were essentially featureless. However, those from the points on the VM indicated in Figure 1 did yield Raman spectra. Analysis of the black ink on six areas of the map and its legends gave rise in each case to a poorly defined but nevertheless characteristic Raman spectrum of carbon (Figure 3), the broad bands attributable to defect (D) and graphitic (G) carbon being evident at  $\sim 1325$  and  $\sim 1580 \text{ cm}^{-1}$ .<sup>14</sup> Chromite ( $\text{FeCr}_2\text{O}_4$ ), which is a reasonably good scatterer (Figure 4), was not detected in any of the lines on the map.

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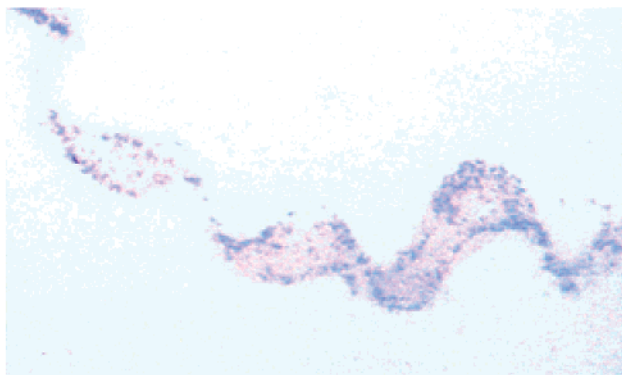


Figure 2. Black ink with yellow under-layer, from the Vinland Map.

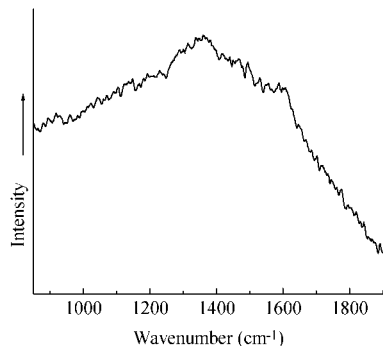


Figure 3. Black ink from the Vinland Map.

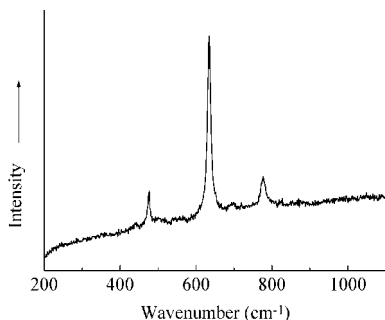


Figure 4. Chromite ( $\text{FeCr}_2\text{O}_4$ ) from a specimen sample.

Anatase was shown by Raman microprobe spectroscopy to be present in the yellow lines in five areas, traces also being found in places where the black ink coincides with the yellow lines. The most intense band characteristic of anatase (at  $143\text{ cm}^{-1}$ )<sup>15,16</sup> is clearly present, despite the proximity of the low-wavenumber cutoff of the notch filter assembly of the fiber-optic probe. The weak, broad band that is evident at  $\sim 398\text{ cm}^{-1}$  is also characteristic of anatase (Figure 5) and, among other features, distinguishes it from rutile, its polymorph.

Spectra taken from the yellow areas were extremely fluorescent, suggestive of the presence of organic materials on the parchment surface, possibly gelatin, as proposed by McCrone.<sup>9</sup>

It was first suggested in the 1970s and subsequently reiterated<sup>17–19</sup> that anatase could have been formed during the medieval

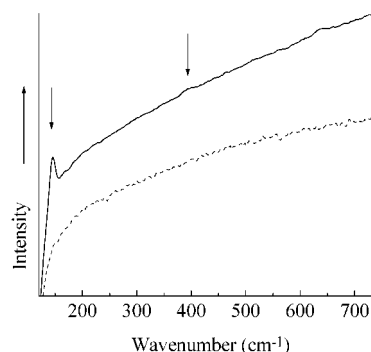


Figure 5. Anatase and plain parchment from the Vinland Map; solid line, anatase in yellow line; dotted line, plain parchment.

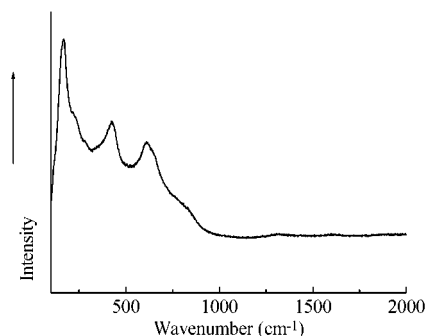


Figure 6. Ilmenite ( $\text{FeTiO}_3$ ) from a specimen sample.

production of iron-based inks from iron/titanium ores (ilmenite,  $\text{FeTiO}_3$ , being the principal ore of titanium) and incorporated into the ink during the production process. Given the imprecise nature of medieval iron gall ink recipes, a residue of ilmenite would be expected to remain in the ink had any been present. However, no ilmenite could be detected (see Figure 6, which relates to a West Australian sample of air-floated ilmenite, possibly partially oxidized).

Furthermore, the procedure outlined<sup>19</sup> is known to yield finely divided, almost amorphous, anatase which is unresolved by PLM and which gives very broad powder diffraction lines by XRD.<sup>4–6</sup> To convert this material to the form identified on the VM by McCrone via PLM and TEM requires a calcination step ( $800\text{--}1000\text{ }^\circ\text{C}$ ) unknown in the 15th century. The ilmenite suggestion would, moreover, appear to be irrelevant, since the dominant pigment in the black ink is here identified to be carbon rather than iron gallotannate or ilmenite (and neither is it chromite, see above).

**The Tartar Relation.** The ink on the Tartar Relation is of two colors. The red material in the rubric proved to be vermilion (Figure 7), as made evident by the presence of the three characteristic bands of  $\text{HgS}$  at  $252$ ,  $282$ , and  $343\text{ cm}^{-1}$ .<sup>14</sup> The black ink gave only a very weak spectrum of carbon, suggestive of its presence in only very small amounts, together with intense fluorescence. Such fluorescence can result from the binders, substrate, or organic components in the ink itself. However, it is a common feature of an iron gallotannate ink, supporting the visual evidence in that assignment.

## DISCUSSION

For this study, it was unfortunately not possible to gain access to a Raman microscope but to a fiber-optic probe system, with its

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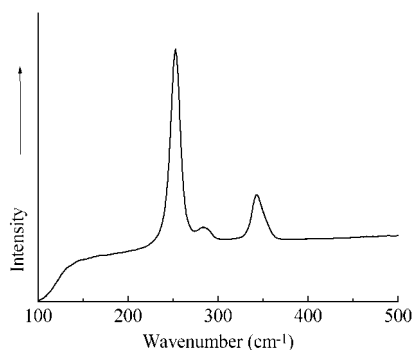


Figure 7. The rubrication of the Tartar Relation, indicative of vermilion.

inherently poorer spatial and spectral resolution and poorer signal/noise ratios. Probe systems also have problems associated with vibrations of the probe head, but do have the advantage of permitting the investigation of all positions on an awkwardly shaped or large object.<sup>20</sup>

The weakness of the carbon signals in the spectra of the ink on the Tartar Relation shows that the ink contains very little carbon and this observation, along with the fluorescence and the general appearance of the ink (brown-black), is suggestive of an ink which is essentially composed of iron gallotannate. The black ink on the VM, however, is not of the same composition, as it is carbon-based. This would seem to suggest that the two documents were not produced by the same hand in the same time frame. In addition, it is noteworthy that the ink used for the legends on the VM is the same as that used for the map itself.

The rubrication of the Tartar Relation was found to be composed of vermilion, which is entirely in keeping with expectation for works of the mid-fifteenth century, the accepted date for this manuscript.<sup>1</sup>

Anatase was identified in the yellow lines and, in some cases, in the vicinity of the black ink, presumably from the underlying yellow line. It was not found elsewhere on the surface, as would be expected if its presence were to be attributed to outside contamination from, for example, dust from white ceiling paint, which might conceivably contain (just) detectable quantities of anatase. This strongly indicates that anatase was a deliberate component, with organic binders (gelatin<sup>9</sup>), in the yellow lines. Anatase is comparatively rare and is the least abundant of the three polymorphs of titanium dioxide (anatase, brookite and rutile) that are present in the earth's crust.<sup>21</sup> When found in nature, it is usually as black or dark gray tetragonal crystals, less often as brown or indigo crystals, and very rarely as yellow crystals. It is important to emphasize that anatase was detected solely in the ink lines and not elsewhere on the parchment; i.e., it is not uniformly distributed over the surface of the map and so must be an integral part of the yellow line. Moreover, the results relate to material at the surface only and not to that within the body of the parchment, since the laser beam is unlikely to penetrate by more than  $\sim 1 \mu\text{m}$ . The present results thus confirm, by a technique unrelated to those used previously, the presence of anatase dispersed in the yellow lines.

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It is generally accepted that prior to the development of the printing press, manuscripts were written in either carbon-based or iron gallotannate inks. A common means of differentiating between them is by the identification of erosion of the parchment or paper substrate by iron ions leeching from the iron gallotannate inks. This causes considerable discoloration and embrittlement of both paper and parchment, often leading to brown or yellow staining and, sometimes, considerable loss of the fabric of the manuscript. This trait is not evident in manuscripts produced with carbon-based inks, which are inherently more stable than iron gallotannates. Had the VM been drawn in a medieval iron gallotannate ink, a yellowing at the borders of the ink such as that seen on the map might have been expected. Knowing that such yellowing is a common feature of medieval manuscripts, a clever forger may seek to simulate this degradation by the inclusion of a yellow line in his rendering of the map. However, this study has shown that (a) the black ink on the VM is carbon-based making the natural occurrence of such a feature impossible and (b) that the VM shows no evidence of embrittlement of the parchment or associated parchment loss. Moreover the presence of anatase in a genuine medieval ink is extremely unlikely and has not been detected by us on any other such manuscript prior to this study.<sup>22</sup> It seems that the appearance of yellow borders to the black ink on the VM is only possible if the VM had been produced by laying down on the parchment first a yellow line, followed by the black ink. The presence in this yellow line of quantities of anatase indicates that the VM is a 20th century product.

## CONCLUSIONS

The use of Raman microprobe spectrometry has conclusively identified the materials used in the construction of two significant historical documents, the Vinland Map and the Tartar Relation. Although the inks used for the Tartar Relation are entirely appropriate for the period of its construction, one of those used to draw the Vinland Map is not. The presence of a yellow line containing anatase, closely associated with a stable carbon ink, indicates that the VM is a modern forgery.

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