Without Comparative Studies of Inks, What Do We Know About the Vinland Map?[1]

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Abstract. *The element titanium has been identified in a number of inks from historical documents. However, no further analyses of these inks have been carried out in order to determine in what molecular form the titanium is present. This paper emphasizes the need for further studies of historical inks and provides information about their preparation, which suggests that the compound anatase might be present as a component of medieval inks. The reported presence of anatase in the Vinland Map ink has previously been forwarded as evidence of the modern manufacture of the map. Other elements, such as copper, zinc, and aluminum, that are present in the Vinland Map ink, are shown to be consistent with the medieval method of preparation of green vitriol, a known component of inks, which strongly suggests that the Map's ink is medieval.*

Historical documents such as maps have not been extensivel analyzed as physical objects. This situation is in contrast to that regarding other cultural artifacts. Paintings studies, for example, have involved investigations of pigments, media, canvases, and stretchers, and underpaintings and underdrawings have both been studied. As a consequence of the dearth of such studies of documents, including maps, we are faced with a lack of compatative data for materials analysis. One map that *has* been studied is the Vinland Map (Figure 1). The ink has been especially extensively investigated; the parchment has received less study.

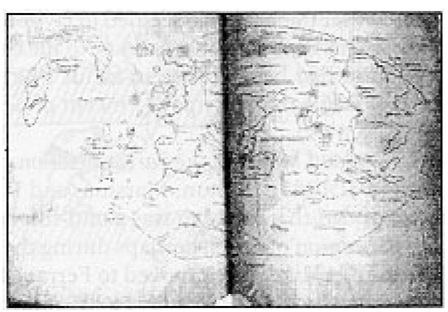

Figure 1. The Vinland Map (from the collection of the Beinecke Library, Yale University) is drawn on a 285-by-210 millimeter parchment bifolium.

The Vinland Map

In 1957, the Vinland Map (see Lamprecht 2000, in this issue) was first brought to the attention of Thomas Marston, CUrator of Medieval and Renaissance Literature at the Yale University Library, by the late New Haven antiquarian bookseller Laurence Witten. It was bound with the Tartar Relation (TR), an account of John de Plano Carpini's mission to the Mongols in 1245-1247. Like the Vinland Map, the Tartar

Relation had remained unknown to scholarship since the late Middle Ages. The binding of the Vinland Map and Tartar Relation is relatively recent, possible of the nineteenth century (Skelton, Marston, and Painter 1965) or of the twentieth century (Parker 1971).

In April 1958, Marston received an advance copy of a new catalogue of a London bookseller and noted listed therein a manuscript of a portion of Vincent of Beauvais' *Speculum Historiale* (SH), at a very modest price. He promptly ordered the manuscript, which arrived about three weeks later. He showed the manuscript to Witten, who then borrowed it and subsequently identified it as the key to the puzzle of the Map and the Tartar Relation. Both Marston and Witten determined that the hand in which the TR was written was the same as that of the SH. The men also observed that the worm-holes, which are evident in, and which had been repaired on, the Vinland Map, matched the worm-holes of the SH. They concluded that the Map, TR, and SH had at one time been bound together, the map at the front having been followed by the *Speculum Historiale*, with the Tartar Relation at the back.

Confirmation of the relation of the Tartar Relation to the *Speculum Historiale* was provided by Allan Stevenson of the British Museum in 1962. Stevenson stated the following letter to Thomas Marston: "You seem to be in luck regarding the paper in the Tartar Relation and the Vincent de Beauvais. For these manuscripts apparently consist of long runs of a single paper manufactured (except for a sheet or so), on one pair of moulds, in the same state or related states and thus belonging to one short period in the work of the moulds." Stevenson stated that the evidence seemed to favor Basel, Switzerland, as the source of the paper. This observation was a key to the conclusion that the Map and the Tartar Relation had been copied in about 1440, by an unknown scribe, from lost originals. into a manuscript of Vincent of Beauvais's *Speculum Historiale*.

Publication of *The Vinland Map and the Tartar Relation* by Yale University Press occurred in October of 1965 (Skelton, Marston, and Painter 1965). The authors of this book concluded that the Map was a mid-fifteenth-century work of a copyist working in the region of Basel, perhaps during the Council of Basel, which commenced there in 1431 and then moved to Ferrara-Florence in 1438-39. The map had been acquired, sold, and donated to the Yale University Library under circumstances of secrecy, which led to considerable controversy following the publication of the book the day before Columbus Day.

The following year, a conference was held at the Museum of History and Technology of the Smithsonian Institution, organized by Wilcomb Washburn, chairman of the Department of American Studies (Washburn 1971). At the conference, the authenticity of the Vinland Map was questioned, and numerous speakers suggested that physical and chemical tests of the ink and parchment should be undertaken.

The Map's Ink

During the following few years, the Vinland Map was analyzed and the ink was determined to contain titanium dioxide, in the form of the mineral anatase (McCrone 1974; McCrone and McCrone 1974). Anatase did not become commercially available until about 1920. This report of the presence of anatase, in 1974, created a new round of controversy regarding the Vinland Map. While this new evidence did not deter some people who believed the Map to be authentic, others developed new doubts about its authenticity. Chemist Walter McCrone claimed that since the form of titanium dioxide, the precipitated or chemically produced variety known as anatase, was not manufactured until the twentieth century, the Map was unquestionably a twentieth-century forgery. There exists, however, a possible alternative explanation for the presence of anatase in the ink of the Map. This explanation is based on the fact that titanium frequently occurs with iron in nature, and the anatase could be present in the ink through a natural process. In modern practice, when anatase (TiO_2) is manufactured from the mineral ilmenite ($FeTiO_3$), green vitriol ($FeSO_4$<>$2H_2O$), the iron component of medieval inks, is produced as a byproduct (Heslop and Robinson 1967: 639). The reverse could also have been true. Therefore, the association of anatase with a medieval ink seems quite plausible, and its presence need not prove that the Map is a forgery. Figure 2 shows vitriol-bearing solutions being collected from ancient heap-leaching galleries, as it has been proposed took place at sulfide deposits.

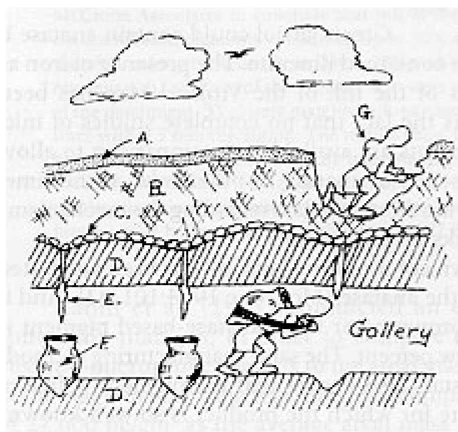

Figure 2. Sketch of ancient heap-leaching galleries. Vitriol-bearing solutions might be caught in pithoi, as shown: a) possible earth cover; b) crushed ore forming a leach pile; c) cobbles a base of leach pile, forming a permeable and porous bed; d) gallery roof and floor of impervious nonmineralized rock; holes were made to allow drainage into gallery; e) vitriol stalactite; f) pithos to collecto dripping solutions; g) man turning over the ore pile and breaking up lumps. (Reprinted, with permission, from Koucky and Steinberg[1982: 167]; copyright 1982, Smithsonian Institution Press.)

Figure 3 shows the step at which green vitriol is produced as a by-product from the leaching process (Koucky and Steinberg 1982). Aluminum, copper, zinc, titanium, and iron have been identified in the ink of the Vinland Map (McCrone 1988), and their presence is consistent with the production of green vitriol as shown in Figure 3. White vitriol (aluminum sulfate) and blue vitriol (copper sulfate) are shown as products, and zinc would be a likely element in the minerals being processed. Aluminum is a short-lived nuclide and would not have been detected in the neutron-activation analysis of document 2 described in this paper but may be present; copper, zinc, iron, and titanium are present and have been detected (Table 2).

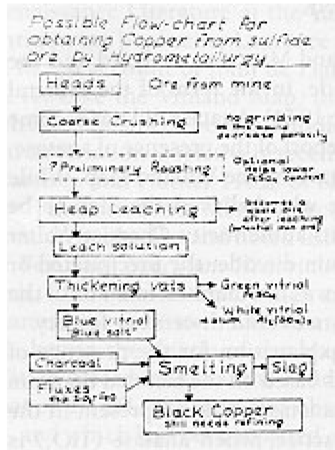

Figure 3. Possible flow chart of byproduction of green vitriol in the heap-leaching process. (Reprinted, with permission, from Koucky and Steinberg [1982: 168]; copyright 1982, Smithsonian Institution Press.)

Koucky and Steinberg quited Biringuccio's sixteenth-century account of the production of vitriol, which describes how ore heaps were "exposed to the weathering of the rains, the cold, and the sun for five or six months... [and later] left to stand for another six or eight months..." Biringuccio described how the ore was then washed, the wash solution was decanted off, and this solution heated in large vats. The thickened solution was finally used to produce the vitriol (Biringuccio 1959: 95-98).

Green vitriol could contain anatase if it were produced from an ore which contained ilmenite. The presence of iron as a major constituent in some areas of the ink of the Vinland Map has been established. Especially important is the fact that no complete studies of inks from other authentic period documents are available for comparison to allow confirmation or denial of the presence of anatase in other inks of the time. Specifically lacking for comparison are reference data regarding the mechanisms and products of deterioration of inks on parchment.

The yellow or yellowish-brown color of the Map's ink has been attributed to the presence of ilmenite iron in the anatase (McCrone 1994: 101-02). And it has been noted that "a yellowish brown color in an anatase-based pigment is usually due to iron impurities of a few percent. The same manufacturing methods that produce unifore anatase crystals also ensure that the pigment is free of impurities giving the brilliant white for which the product is so well known" (Cahill et al. 1987: 832). The presence of iron in the ink of the Map is acknowledged, and the yellowish color of the anatase is attributed to ilmenite iron. The size of the anatase particles in the Map has been attributed to modern manufacturing methods (Towe 1990). Did manufacturing methods that did not ensure that the anatase pigment was free of impurities produce the Vinland Map's anatase particles or were they produced by a reaction in the formation of green vitriol? It is important to examine inks from authentic period documents, inks that contain titanium, in order to determine in what form it is present. This might then suggest alternative explanations for the reported size and form of the anatase particles on the Map, and might provide an explanation other than they were produced by modern manufacturing methods.

Initially, the ink of the Map was studied by taking exceedingly small samples and analyzing them using a variety of techniques that are used by specialists in ultramicroanalysis. Then in 1987, in their paper in *Analytical Chemistry* entitled "The Vinland Map, Revisited: New Compositional Evidence on Its Inks and Parchment," Thomas A. Cahill of the University of California, Davis, and his colleagues, presented the results of a study of the Map's ink using a method known as PIXE or proton-induced x-ray emission spectroscopy. They had previous experience with PIXE for this kind of examination, having done an extensive study of the printing inks of the Gutenberg *Bible*. The use of PIXE requires that the document be placed in a specially designed holder and that a beam of protons be focused on the area to be analyzed. The beam can be focused down to about 500 microns or 0.5 millimeters, about the width of an ink line. Analyses were made on 159 different areas of the Map's ink and parchment.

The abstract of their paper reads,

The Vinland Map, once considered the first cartographic evidence of the North American continent, purportedly dated from the mid-15th century. In 1974 compositional evidence derived from microparticles removed from its surface led McCrone Associates to conclude that ink in the Map was made up of 20th century titanium-based pigments containing up to 50% anatase (TiO_2) and that the Map was therefore a forgery. Recently at Davis, 159 multielemental PIXE (particle induced X-ray emission) analyses of the Vinland Map were performed, including spatial analyses of the parchment, 33 closely matched ink-parchment pairs, and transects across inked lines with 0.5 mm resolution. The results show that titanium and other medium and heavy elements are present in only trace amounts in the inks, with titanium reaching a maximum value of 10 ng/cm^2, or about 0.0062% by weight. In light of these results the prior interpretation that the Map has been shown to be a 20th-century forgery must be reevaluated. (Cahill et al. 1987: 829)

Cahill et al. (1987) conducted an experiment using synthetic inks containing titanium, in order to compare the relative values obtained using electron-microprobe analysis to the areal mass values obtained using PIXE. One point that must be made regarding this comparison of data is that the calculation of 27,600 ng/cm^2 as the average areal mass value based on McCrone's average composition of 12% titanium in the ink of the Vinland Map, is based on these measurements. The 27,600 ng/cm^2 figure came from the synthetic ink containing titanium prepared by Cahill et al. and measured using PIXE and the 12% figure for the average titanium concentration measured by electron-microprobe analysis. It is difficult to make a true comparison of electron-microprobe and PIXE analysis, however. Electron microprobe analyses were made on particles removed from the ink. PIXE analyses included parchment in the samples volume.

No further analyses of the elemental concentrations of the ink of the map have taken place to date. McCrone (1988: 1014) reported that the "titanium content of the TR and SH inks was estimated to be a maximum of about 200 ppm and averaging about 100 ppm" and that "the TR and SH inks contained at least 2 orders of magnitude less titanium than the VM inks."

The paper by Cahill et al. (1987) in Analytical Chemistry prompted a reply from Walter McCrone (1988). For a further understanding of this matter, I refer the reader to the two papers.

My Experiments and Analyses

I stated earlier that inks of the fifteenth century might have contained anatase as an impurity. I have prepared such an ink, containing titanium in the form of anatase, using the iron ore ilmenite. A sample of this ink on parchment has been analyzed and will be referred to as Document 1. Another occurrence of titanium in an ink is that of an old undated document fragment (Document 2). Document 2 (Figure 4) was provided from the study collection of a Late Medieval art historian at the Institute of Fine Arts, New York University. These samples were analyzed using neutron-activation analysis. A sample of approximately one square centimeter of ink on parchment (Figure 5) was analyzed, thus requiring that the concentrations by expressed as parts per million per weight of sample and not of ink alone. Bothe parchment with ink and parchment without ink were analyzed, and the elemental concentration of the parchment were subtracted from those of the parchment plus ink. The concentrations of the analyzed elements were expressed in terms of the weight of the sample of parchment plus ink, as it was not possible to ascertain the mass of the ink on the sample analysed. This is not precisely comparable with analyses of samples of ink.

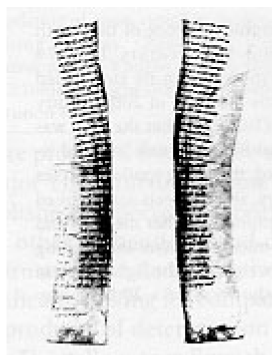

Figure 4. Document 2, showing both sides of the fragment after the samples had been taken for analysis.

Figure 5. The sample of document 2 that was used for neutron-activation analysis; the weight of the sample of parchment-plus-ink was 21.38 milligrams.

An estimation of the amount of ink present is necessary in order even to approximate the concentration of titanium. The amount of titanium in the ink of the analyzed 21.38-milligram sample of Document 2 is .00132 milligrams. If the ink on the document were estimated to be approximately 1/100th the weight of the sample or .2138 milligrams, the concentration of the titanium would be 0.62%. This value would lie between the two concentrations reported for titanium in the ink of the Map. It is understood that this is not a very satisfying calculation of concentration, and neutron-activation analysis of a weighed sample of ink is not feasible as a method of analysis of documents; the amount of sample required would be too large. The titanium concentrations obtained on the two documents using neutron-activation analysis and the concentrations reported for the Vinland Map, Tartar Relation, and *Speculum Historiale*, are given in Table 1. Although there are difficulties in comparing the data from different methods of analysis, all of the inks contain titanium. Three different units of concentration are used: parts per million, percentages (%) and nanograms per square centimeter (ng/cm2). Three different analytical methods were employed: neutron-activation analysis (INAA), electron-microprobe analysis (EMA), and proton-induced x-ray-emission analysis (PIXE). The samples taht were analyzed were different in each case. With INAA, ink and parchment were analyzed; eith EMA, a sample of ink was removed from the parchment and analyzed; and with PIXE, the ink on the parchment was analyzed. As stated above, there are numerous difficulties in comparing the results from these different methods of analysis. However, as also stated above, one may say that, based on the data in Table 1, titanium occurs in all of the inks that were analyzed and is evidence that further analysis of inks to determine in what form the titanium is present is necessary in order to evaluate the significance of the presence of anatase in the Vinland Map ink.

Concentration of Titanium in Inks Showing the Range and the Differences Obtained Using Different Methods

Document	Method of Analysis	Ti Concentration
Document 1	INAA	300 ppm (1)
Document 2	INAA	61.7 ppm (1)
Vinland Map	EMA* PIXE**	10–40% (2) 0.0062% (3) or 2ng/cm² (4)
Tartar Relation	EMA*	100 ppm (2)
Speculum Historiale	EMA*	100 ppm (2)

* As reported in McCrone, W.C., *Analytical Chemistry*, 1988, 60, 1009-1016.
** Cahill, T.A., *Analytical Chemistry*, 1987, 59, 829-833.
(1) Wt. of titanium in ink expressed as ppm of analyzed sample.
(2) Wt. of titanium in ink expressed as % or ppm of ink sample.
(3) Not presently defined.
(4) Average wt. of titanium/square centimeter of ink on parchment.

Table 1.

Table 1. Concentration of Titanium Inks Showing the Range and the Differences Obtained Using Different Methods

The ratios of elements in inks can be used to make a comparison of inks from two different documents. Table 2 shows concentrations for four different elements in the ink of Document 2. There is about seventy times more iron than copper in Document 2s ink. Figure 6 shows that the ratio of iron to copper in both the Tartar Relation and in the *Speculum Historiale* is about one-and-a-half. This latter ratio is markedly different from that of the ink in Document 2. As discussed above, the papers in the TR and SH have been shown to have the same watermarks and the inks have similar iron-to-copper ratios. These comparisons provide two forms of evidence that support a close relationship between the TR (the manuscript bound with the Vinland Map) and the SH.

Neutron Activation Conditions and Concentrations in the Ink of the Samples for Document 2

Element	Product Nuclide	Half-life	E_{γ},kev	Length of Activation*	Elemental Composition
Ti	^{51}Ti	5.8m	320.0	8m	1.32μg (61.7ppm)
Cu	^{66}Cu	5.1m	1039.2	8m	0.17μg (8.0ppm)
Fe	^{59}Fe	44.6d	1099.3	10h	12.3μg (575ppm)
Zn	^{65}Zn	244d	1115.5	10h	0.29μg (13.6ppm)

Other elements of interest detected:

Ag, As, Au, Br, Ca, Cr, Hg, La, Sb, Sc

* In thermal neutron flux of 2.0×10^{13} n/cm² sec.

Table 2.

Table 2. Neutron Activation Conditions and Concentrations in the Ink of the Samples for Document 2

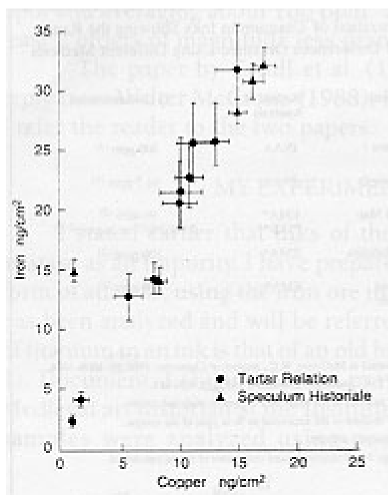

Figure 6. Relationship of copper to iron in the inks of the Tartar Relation and the Speculum Historiale*. Great similarities are seen in these inks, favoring a hypothesis of a common source for these two documents. Reprinted with permission, from Cahill et al. (1987: 831); Copyright 1987, American Chemical Society.*

A number of people concur with Cahill that the prior interpretation of the Map as a 20th century forgery must be reevaluated. One method of analysis, which is discussed by Thomas Marston in *The Vinland Map and the Tartar Relation*, is carbon-14 dating. In 1965, the large sample size that was required precluded carbon-14 dating the parchment of the Map at that time. However with recent advances in carbon-14 dating technology, it is now possible to date a much smaller sample (Stulik and Donahue 1992). I wish to conclude by saying that the parchment of the Map has now been sampled for carbon-14 dating. The results of this test will become an important part of the evidence. The age of the parchment on which the map is drawn will be known. If the parchment dates to the fifteenth century, the date alone will not prove absolutely that the Map was drawn at that time. However, if a precise date shows that the parchment dates to the mid-fifteenth century, the significance becomes very real. The evidence that the document with which the Map was bound when it was purchased by Yale University, the Tartar Relation, dated to the mid-fifteenth century was not published until after Yale had acquired the volume. This knowledge was based on the studies of the watermarks of the paper of the Tartar Relation referred to earlier. A twentieth century forger would have to have done this research as well in order to avoid detection of forgery and would not have known of the possibility of dating the Map's parchment.

The analysis of the ink on Document 2 by neutron-activation analysis (Olin and Cheng 1992) and the identification of the presence of titanium, prompted discussion regarding other possible methods of elemental analysis applicable to documents. A focusing neutron lens has been introduced successfully into a prompt-gamma-activation-analysis instrument placed at the exit of a cold neutron guide (Chen et al. 1995). This technique might allow for the analysis of areas of ink similar to those analyzed with PIXE, using prompt-gamma rather than neutron-activation analysis. However, elemental analysis alone will not suffice. Titanium has been identified in the inks of authentic documents. It is, in addition, necessary to identify the molecular form of the titanium. The titanium is present as anatase in the Vinland Map ink.

Conclusion: The Need for Technical Studies

It is important to be aware of the need for *technical studies* of documents of known age and origin, studies of both ink and parchment. What are technical studies? In conjunction with archaeological and historical research, objects and works of art in museums and other collections throughout the world are being studied using materials analysis. From these studies, new insights into production and exchange, the history of technology, artist's intent, and other aspects of material culture are being gained. There is a wealth of information that can be acquired from techincal studies, which adds important information to our understanding of collections and, through the study of these collections, to our interpretations of history.

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Notes

1. This paper is a modification of one presented on July 14, 1993, at the Yale-Smithsonian symposium "The Power of Maps." The paper was then solicited by Wilcomb Washburn for the second edition (1995) of The Vinland Map and The Tartar Relation but was ultimately not included in that book.

2. Renamed "Smithsonian Center for Materials Research and Education" (SCMRE) in 1997. The author is now affiliated with Olin Conservation, Inc., 9447 Rabbit Hill Road, Great Falls, VA 22066, and remains a research associate with SCMRE.

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See also The Vinland Map - Some "Finer Points" of the Debate, by J. Huston McCulloch, August 2001

See also Evidence That the Vinland Map is Medieval, by Jacqueline S. Olin, in Analytical Chemistry, Vol. 75, No. 23, December 1, 2003, pp. 6745-6747.