The Vinland map ink is NOT medieval

ARTICLE *in* ANALYTICAL CHEMISTRY · MARCH 2004

Impact Factor: 5.64 · DOI: 10.1021/ac0354488 · Source: PubMed

Anal. Chem. **2004,** *76,* 863−865

Correspondence

The Vinland Map Ink Is NOT Medieval

In "Evidence That the Vinland Map Is Medieval"[1] Olin repeats her earlier speculations[2] that the anatase containing ink of the Vinland Map is a medieval iron gallotannate product. Olin believes that this titanium-bearing mineral could have been introduced into a 15th century ink as an inadvertent impurity through the use of oil of vitriol and the iron−titanium ore mineral, ilmenite. In reiterating this argument, no new evidence is presented and an abundance of previously published evidence to the contrary has been either totally ignored, seriously misinterpreted, or inaccurately described.

The Vinland Map has been a source of controversy since it first appeared on the scene in the late 1950s. The 1974 microanalytical discovery[3] in the ink of the mineral anatase (TiO_2) having the form, the crystallinity, and the narrow particle-size distribution[3−5] of modern pigment anatase together provided strong evidence that the map is a cleverly done early 20th century forgery. Subsequent work in the 1980s, although incapable of confirming the anatase mineralogy, identified the presence of titanium as a major element concentrated in the ink and not distributed over the parchment.[6,7] Yet, doubts about the forgery have persisted although more recent Raman spectroscopic analyses[8] have reconfirmed that the ink does, indeed, contain anatase and the anatase is, indeed, restricted to the ink. Now, despite the obvious and likely possibility that a clever forger would use a blank 15th century parchment, doubts have again been rekindled in the wake of a carefully done radiocarbon dating of the parchment to the mid-fifteenth century,[9] an appropriate date for a genuine article.

For almost 30 years, Olin has been among the more persistent proponents of authenticity, primarily because of her 1974 experimental preparation of a simulated medieval ink containing titanium. Poorly crystalline anatase was identified in this ink by X-ray diffraction and confirmed as a very finely divided colloid by transmission electron microscopy (TEM).[7] She prepared this ink using oil of vitriol (sulfuric acid) and a plausible medieval contaminant, the iron−titanium mineral ilmenite ($FeTiO_3$).[1,2,10] It is important to point out that the degree to which this ink actually simulates a medieval iron gallotannate ink or resembles the ink found on the Vinland Map rests almost entirely on her forthright self-assessment of it as such. The available evidence is slim. One TEM photo of the precipitate[7] and one neutron activation analysis of it (only titanium was reported)[2] have been published. Her X-ray diffractometer traces, or even a table of *d* spacings and relative intensities, of this material have never been published. Thus, the possible presence of other mineral phases, e.g., residual ilmenite, in her simulation remains unknown. Olin has never disclosed the iron content or even the Fe/Ti ratio of her ink. Values for copper, zinc, aluminum, sulfur, or any element other than titanium have not been reported nor have ultraviolet or infrared studies of her ink-on-parchment been made. Nevertheless, relying on what limited information is available, it is clear that the anatase in Olin's preparations differs substantially from the anatase found on the Vinland Map. Her simulated ink is directly comparable to the initial hydrated precipitates of modern titanium oxide pigments before they are calcined at elevated temperatures above 600 °C. The crystallites found on the Vinland Map are in the 50−500-nm range.[3−5,7] Olin's simulated ink viewed in the transmission electron microscope is that of a hydrolysate. It is a colloidal precipitate that consists of fine-grained aggregates of crystallites in the 4−5-nm range.[7,10] In evaluating these data, Olin[1] seriously misinterprets the transmission electron micrographs that compare the two hydrolysates.[7] Olin confuses aggregates of particles with particles themselves. She tries to equate her simulated ink *aggregates* (Figure 4 in ref 7) with the anatase *particles* from the Vinland Map ink (Figure 2 in ref 7). Astonishingly, Olin completely ignores both the text discussion of these micrographs and the figure legends describing each. The relevant text (p 85, ref 7), with emphasis added, reads, "Poorly crystalline anatase *aggregates* with a *particle*-size distribution overlapping that found in the Vinland Map's inks have been prepared under plausible 15th century conditions. However, these preparations display broadened X-ray diffraction maxima for anatase, indicating poor crystallinity and/or very fine crystallite sizes. Transmission electron microscope study of such simulated preparations reveals that the *particles* are *aggregates*, each made up of numerous fine crystallites, characteristics that compare most favorably to the initial precipitate stage of modern pigment preparations (compare Figure 4 with Figure 1)." Furthermore, the legend of Figure 4 instructs the reader to "Compare with Figure 1" because both Figures 1 and 4 are published at the same magnification.

* Present address: 230 West Adams St.; Tennille, GA 31089-1403. E-mail: ken.towe@alumni.duke.edu.

(1) Olin, J. S. *Anal. Chem.* **2003**, *75* (23), 6745−6747.
(2) Olin, J. S. *Pre-Columbiana* **2000**, *2* (1), 27−36.
(3) McCrone, W. C. *Chemical Analytical Study of the Vinland Map*; Report to Yale University Library; Yale University: New Haven, CT, 1974.
(4) McCrone, W. C. *Anal. Chem.* **1988**, *60*, 1009−1018.
(5) McCrone, W. C. *Morphology of Ground vs Precipitated Anatase*; Report to Yale University Library; Yale University: New Haven, CT, 1975.
(6) Cahill, T. A.; Schwab, R. N.; Kusko, B. H.; Eldred, R. A.; Möller, G.; Dutschke, D.; Wick, D. L.; Pooley, A. S. *Further Elemental Analyses of the Vinland Map, the Tartar Relation, and the Speculum Historiale*; Report to Yale University Beinecke Rare Book and Manuscript Library; Yale University: New Haven, CT, 1985.
(7) Towe, K. M. *Acc. Chem. Res.* **1990**, *23*, 84−87.
(8) Brown, K. L.; Clark, R. J. H. *Anal. Chem.* **2002**, *74* (15), 3658−3661.
(9) Donahue, D. J.; Olin, J. S.; Harbottle, G. *Radiocarbon* **2002**, *44*, 45−52.
(10) Towe, K. M. *The Vinland Map Revisited: An Analysis of the McCrone Reports and an Evaluation of the Problem of the Map's Authenticity*; Report to Yale University Library; Yale University: New Haven, CT, 1982.

10.1021/ac0354488 CCC: $27.50
Published on Web 01/07/2004

Olin attempts to challenge the criticism of Brown and Clark[8] that the anatase in her simulated ink yields "broad diffraction lines by XRD". She asserts[1] that "The references given by the authors [Brown and Clark] to "broad diffraction lines by XRD" for the anatase in Olin's simulated 15th century ink are not published in the McCrone references cited in their paper." This is not accurate. In Brown and Clark's ref 5 (ref 4 here), McCrone not only cites Olin specifically for her "private communication" on the subject, he describes her experimental material on page 1016: "...the product consisted of extremely finely divided, almost amorphous, anatase—unresolved by PLM and *giving very broad powder diffraction lines by XRD*" (emphasis added). Olin is thus not only negligent in failing to tell the reader that her own X-ray diffractometer traces made in 1974, used to identify the anatase in her simulated ink, showed substantial line broadening, she also attempts to mislead the reader by failing to note that this information has appeared in other sources.[7,10] The following statement appears in my 1982 report to Marjorie Wynne of the Yale University Library:[10] "The Olin hypothesis, which had been so attractive [prior to visits to NL Industries and the Beinecke Library], became substantially compromised by the fact that initially precipitated anatase is poorly crystalline and must be calcined to a high temperature (600−900 °C) and then milled to achieve its commercially useful properties. Mrs. Olin's precipitates were poorly crystalline anatase showing broad X-ray diffraction lines. The particles that we had observed in the transmission electron microscope were, on reexamination, aggregates of very fine crystallites similar to those seen in commercially precipitated but unheated anatase." Olin has never challenged this and even if Olin's "medieval" precipitate could somehow have been heated in a second step to the necessary temperature it would, in a third step, have to be milled to disaggregate the recrystallized precipitate before its use as ink. This is an improbable scenario.[4]

Olin's assertion that her simulated anatase-containing iron gall ink provides a plausible explanation for the ink on the Vinland Map inexplicably fails to discuss, or even recognize, another important body of physical evidence. In 1967, an experienced British Museum team examined the Vinland Map as well as its accompanying documents, the *Tartar Relation* and the *Speculum Historiale*. Principal Scientific Officer A. D. Baynes-Cope published some of the results in his paper as part of a symposium[11] devoted to the Vinland Map convened at the Royal Geographical Society in February 1974. Excerpts from this paper are decidedly relevant:

"...the ink of the map was found to have a peculiar structure unlike that of the accompanying textual documents or of the ink which has been found on other manuscripts of the period or on a number of drawings of the same reputed locality and date which were examined. *It certainly has not the appearance characteristic of a faded iron gall ink*." (emphasis added).

"Further evidence that the [Vinland Map] ink was not of the iron gall type was obtained when infra-red photographs of the map were taken; *the reaction of the ink was not consistent with an iron gall ink*." (emphasis added).

"The behaviour of the ink under ultra-violet light was of particular interest. Iron compounds quench the fluorescence induced in the background by ultra-violet light and for this reason, faded iron gallo-tannate ink, yellowish-brown by daylight, will appear black against a bluish or yellowish fluorescent background under this form of lighting. The inks used in both the *Tartar Relation* and the *Speculum Historiale* showed this phenomenon whereas the ink used both for the outline of the [Vinland] map itself and for the text on the leaf did not show this phenomenon."

Unaccountably, no such ultraviolet or infrared studies of Olin's simulated ink on parchment have been reported for direct comparison with the ink of the Vinland Map.

As the name implies, iron is a major element in medieval iron gall inks.[12,13] Even an ink derived from ilmenite would begin with 36.8% Fe in the $FeTiO_3$ crystals. In this connection, Olin has written[1,2] unabashedly: "The presence of iron as a major constituent in some areas of the Vinland Map ink has been established"; "The presence of iron in the ink of the Map is acknowledged...", and "Although iron is not present in all of the areas of the ink of the Vinland Map, it is present." These are all truthful but very misleading statements of support for her conjecture. Medieval iron gall inks are rich in iron, commonly with Fe contents ranging from 7000 to 57 000 ppm in numerous nondestructive proton-induced X-ray emission (PIXE) analyses.[12−14] Additional analytical evidence that the ink on the Vinland Map is not an iron gall ink exists in the "global" chemical analyses made by Cahill et al.[6] in 1985. Cahill et al. examined the map and the two accompanying documents using the PIXE milliprobe technique. Their results revealed that the iron gall inks of the accompanying *Tartar Relation* and *Speculum Historiale* did not contain titanium (above the level of detection), and as expected, both contained substantial iron, copper, and sulfur. They wrote (p 24, ref 6): "The ink of the *Tartar Relation* and the *Speculum Historiale* contain levels of Fe, Cu, and S 10 to 20 times greater than in the Vinland Map." This stands out in marked contrast to their similar analysis of the Vinland Map where titanium was the most frequently found element in the ink. Iron, certainly to be expected if it were present as an iron gall ink derived from ilmenite, was found together with titanium in only 24% of the samples. Cahill et al. analyzed paired samples of the Vinland Map ink-plus-parchment and parchment-alone by PIXE (Table 1, ref 6) with Ti and Fe in the ink itself being determined by difference. Of the 37 pairs studied, only 13 samples had more iron in the ink than in the parchment itself. Nineteen samples actually had more iron in the parchment! Furthermore, the mean Fe/Ti ratio of the ink on the Vinland Map[6] is only 0.3 (Table 2, p 17). In other numerous medieval iron gall inks studied by PIXE, when titanium is found above the level of detection, the average Fe/Ti ratio is over 300[14]—3 orders of magnitude higher. Olin recognizes this inconsistent iron distribution on the map but rationalizes it "...as a consequence of the deterioration of the

(11) Wallis, H.; Maddison, F. R.; Painter, G. D.; Quinn, D. B.; Perkins, R. M.; Crone, G. R.; Baynes-Cope, A. D.; McCrone, W. C.; McCrone, L. B. *Geogr. J.* **1974**, *140*, 183−214.

(12) Vodopivec, J.; Budnar, M. In *Proc. Iron Gall Ink Meeting*; Brown, A. J. E., Ed.; University Northumbria Newcastle upon Tyne, 2001; pp 47−52.

(13) Budnar, M.; Simcic, J.; Ursic, M.; Rupnik, Z.; Kolar, J.; Strlic, M. In *AIP Conference Proceedings*; Duggan, J. L., Morgan, I. L., Eds.; American Institute of Physics: St. Louis, MO, 2003;, Vol. 680 (1), pp 436−439.

(14) Budnar, M., personal communication.

ink."[1] This, too, is inaccurate and misleading. It is true that ferrous iron oxidation is a common cause of deterioration of iron gall inks,[15] but the absolute amount of iron in the ink does not change significantly.[14] Furthermore, a loss of paper or parchment substrates is the result of this oxidation, especially in the vicinity of the drawn lines.[15] Little or no such deterioration is seen on the Vinland Map parchment.[8] Olin[1,2] has apparently ignored all of this evidence. None of it supports her contention.

Olin offers a "strawman" suggestion[1] that "...it is unlikely that a forger would use an opaque white pigment to prepare an ink that would imitate a medieval ink." On the contrary, it is readily conceivable that a forger using a yellow organic medium to simulate an aged iron gall ink[16] might need to adjust the tint through the addition of small amounts of an off-white material such as was the anatase of early commercial preparations. The presence of such an organic medium in the ink is supported by the analyses of Cahill et al.,[6] who wrote (p 12), "...most of the [Vinland Map] ink consists of elements lighter than sodium" and by Brown and Clark,[8] who wrote, "Spectra [Raman] taken from the yellow areas [of the ink] were extremely fluorescent, suggestive of the presence of organic materials on the parchment surface...."

(15) Banik, G. In *Proc. European Workshop on Iron-Gall Ink Corrosion*; Windt, H. van der, Ed.; Rotterdam Museum Boijmans van Beuningen, Netherlands Institute for Cultural Heritage, Rotterdam, 1997; pp 21−27.

(16) McCrone, W. C. *Microscope* **1999**, *47*, 71−74.

In summary, no new evidence is offered by Olin to support her long-held opinion that the Vinland Map is medieval. What is presented is a "rehash" that is too often biased, misleading, or inaccurate. No data presently exist to support the notion that medieval iron gall ink containing well-crystallized anatase was used to draw the Vinland Map in the 15th century. An abundance of analytical evidence exists to refute it. Unfortunately, most of this evidence is neither cited nor discussed in Olin's papers. With or without anatase, none of Olin's arguments is even moderately consistent with the theory that the ink of the Vinland Map is an iron gallotannate product.

ACKNOWLEDGMENT

I acknowledge the help of the late David Baynes-Cope, Dr. Milos Budnar, the late Walter C. McCrone. Dr. R. J. H. Clark and Ms. Kirsten Seaver kindly reviewed early draft versions of the manuscript and offered helpful suggestions for its improvement.

Kenneth M. Towe

Department of Paleobiology, Smithsonian Institution, Washington, D.C. 20013-7012

AC0354488