## Correspondence

# **Evidence That the Vinland Map Is Medieval**

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The Vinland Map has been proposed to date to the midfifteenth century and is significant in showing the north Atlantic area of what is now North America about 50 years before the voyages of Columbus. It has been confirmed by radiocarbon dating that the map was drawn on a fifteenth century parchment; however, controversy regarding the ink of the map has persisted. Analytical studies of the ink of the map have been interpreted to show that the map is a twentieth century forgery because of the presence of carbon and anatase in the ink. However, carbon is known to have been added to medieval iron gallotannate inks, and the presence of anatase in a medieval ink can be explained by examining the process of making medieval inks.

Two papers were published in 2002 on studies carried out on the Vinland Map, a map that includes representations of Iceland, Greenland, and the northeastern seaboard of North America.<sup>1,2</sup> The map has been dated to the mid-fifteenth century and, if authentic, demonstrates a European knowledge of the northeastern Atlantic 50 years before the voyages of Columbus.

In 2002, radiocarbon dating of the Vinland Map dated the parchment of the map to AD 1434  $\pm$  11 years.<sup>1</sup> This date is consistent with that obtained from a study of the watermarks of the paper of the Tartar Relation, a fifteenth century document with which the Vinland Map is bound.<sup>3</sup> Those watermarks were found to be associated with a mill that was established at Basel, Switzerland, about 1433 to supply paper for the Church Council, which took place there from AD 1431 to 1449. Thus, the map and the paper of the document, with which it is bound, both date to the mid-fifteenth century and provide evidence that the Vinland Map is a fifteenth century map. It is proposed that in the fifteenth century both the Vinland Map and the Tartar Relation were bound together with a copy of Vincent of Beauvais Speculum Historiale. The fifteenth century binding in which the Speculum is now bound has provided further evidence for the origin of the map. Writing found under the pastedowns of the binding include the name of Bartholomaeus Poignare, who was appointed notary to the Council of Basel on 16 September 1435.4

(2) Brown, K. L.; Clark, R. J. H. Anal.Chem. 2002, 74 (15), 3658-3661.

Also in 2002, the paper by Brown and Clark<sup>2</sup> reported on the analysis of the ink of the map. On the basis of their analyses, they claimed that the map is a forgery. Did a forger use a parchment for the Vinland Map that existed but which was blank in the fifteenth century? It is this possibility that disallows using the date of the parchment as conclusive proof that the map is authentic. The information needed to prove that the Vinland Map is medieval rests with the ink used to draw it.

#### IMPORTANCE OF REFERENCE TO HISTORICAL LITERATURE IN INTERPRETATION OF ANALYTICAL DATA FROM THE VINLAND MAP INK

It is the interpretation of the analytical data obtained on the ink that has aroused much of the controversy surrounding the Vinland Map.<sup>5,6</sup> The identification of titanium in the form of anatase titanium dioxide in the ink of the map caused McCrone to claim that the map was a forgery. This conclusion has been supported by Towe.<sup>7</sup> It must be recognized that it is unlikely that a forger would use an opaque white pigment to prepare an ink that would imitate a medieval ink. It raises many interesting questions that have not been addressed about the formulation of such an ink and what medium would have been used by a forger to suspend the anatase. The conclusion that anatase is present only in the ink of the map and not in the parchment alone<sup>2,8</sup> verifies that anatase did not accumulate on the map sometime in the twentieth century. Therefore, the ink of the Vinland Map does contain anatase. The concentration of anatase in the map's ink has been one of the controversial points but has been demonstrated to be the result of the fact that the samples analyzed differ from each other by a factor of 1000.8 This is due to the fact that PIXE analysis included the underlying parchment in the sample analyzed. The explanation for the presence of anatase in the ink of the Vinland Map is either that it was added by a forger in the twentieth century or it is present in the ink because of the materials used to make the ink. The source of the iron in medieval inks is green vitriol, an iron sulfate. It is significant that green vitriol would include anatase if the iron source from which it was made were the irontitanium mineral, ilmenite. In the modern production of anatase.

- (5) McCrone, W. D. Anal. Chem. 1988, 60, 1009-1018.
- (6) Cahill, T. A.; Schwab, R. N.; Kusko, B. H.; Eldred, R. A.; Moller, G.; Dutschke, D.; Wick, D. L. Anal. Chem. 1987, 829–833.
- (7) Towe, K. M. Acc. Chem. Res. 1990, 23, 84-87.
- (8) McCrone, W. C. Microscope 1999, 47, 271-74.

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<sup>(1)</sup> Donahue, D. J.; Olin, J. S.; Harbottle, G. Radiocarbon 2002, 44, 45-52.

<sup>(3)</sup> Skelton, R. A., Marston, T. E., Painter, G. D., Eds. *The Vinland Map and the Tartar Relation*, Yale University Press: New Haven, CT, 1995.

<sup>10.1021/</sup>ac034533c CCC:  $25.00\ \ \odot$  2003 American Chemical Society Published on Web 10/24/2003

<sup>(4)</sup> Washburn, W., Ed.; 1971 Proceedings of the Vinland Map Conference; Smithsonian Institution: Washington, DC; University of Chicago Press: Chicago, 15–16 November 1966.

green vitriol is produced as a byproduct.9 Based on this fact, Olin<sup>10</sup> has prepared a simulated fifteenth century ink using ilmenite for the preparation of the green vitriol. This ink contains anatase. Towe<sup>7</sup> has claimed that the crystallite size of the anatase in the ink of the map differs from that in the simulated ink. He has used transmission electron micrographs of anatase particles from the ink of the map and the simulated fifteenth century ink as evidence. In the publication of his data, he used  $25000 \times$  for the magnification of the anatase from the Vinland Map ink and  $170000 \times$  for the magnification of the simulated fifteenth century anatase. The micrograph of the ink produced by Olin shows what Towe called "poorly crystalline anatase" hydrate "aggregates" and the micrograph of the Vinland Map anatase shows "rounded crystallites". Taking into account the difference in magnification, the dimension of the aggregate shown in the published micrograph of the simulated fifteenth century ink matches the dimension of an anatase particle in the micrograph of the Vinland Map ink. Both are about the same size.

Titanium is present in other medieval inks. However, no studies of other medieval inks have been carried out to show in what form the titanium is present.<sup>10</sup> Although it has been recognized that precipitated anatase could have been produced and become part of an ink in the fifteenth century, it was assumed that its production would have had to have been intentional.<sup>5</sup> It has been assumed that it would be either ground mineral anatase or an anatase pigment. This is not what the historical literature would suggest is a possible source of the anatase. As stated earlier, precipitation of titanium as anatase during the production of the iron sulfate used to make an ink is the proposed source of the anatase. The possibility of this has been demonstrated.<sup>10</sup> However, experiments to demonstrate that anatase of the size and crystallinity of the anatase in the Vinland Map can be produced in the laboratory would not be convincing evidence that this has in fact occurred in the production of medieval inks. Analysis of medieval inks containing titanium to see in what form the titanium is present is required. In the meantime, however, the Vinland Map cannot be assumed to be a forgery on the basis of the presence of anatase of a particular size and crystallite size in the ink.

The elemental composition of the ink of the Vinland Map as published by McCrone, is consistent with an iron gall ink made using components produced by a medieval process known as hydrometallurgy.<sup>10,11</sup> McCrone interpreted the appearance of the ink of the map to indicate that two inks had been used. Based on this, he presented his date as representing the compositions of two different inks, yellow ink and black ink. However, descriptions of deteriorated iron gall inks show the same appearance as the Vinland Map ink and are not the result of two inks but rather the result of the migrations of components of the ink as a consequence of aging.

The elements copper, aluminum, zinc, and gold are particularly interesting. All are present in the Vinland Map ink as reported by McCrone. The source of the iron found in the ink samples of the Vinland Map ink could be an iron sulfate known as green vitriol. It was green vitriol that was made using a process known as hydrometallurgy. It is important to recognize that the interpretation in earlier publications of the elemental composition of the ink of the map did not include consideration of historical knowledge of metallurgical processes used in the production of medieval ink components. This information is highly relevant in interpreting the analytical studies the ink.

In the hydrometallurgical process, sulfide ores were exposed to the weather for a long period of time, producing sulfuric acid. During that process, various sulfates used in the medieval period were produced. Among these are copper sulfate and aluminum sulfate. Copper sulfate was used in the production of copper, and aluminum sulfate was used as alum. Both copper and aluminum are present in the Vinland Map ink and could have been introduced as components of the impure sulfate minerals used in the production of the ink. Zinc is also present in the ink and is consistent with a green vitriol produced by the process of hydrometallurgy in the medieval period. The mineral melanterite would be a source of the zinc as it was part of the secondary enrichment zone that developed over the sulfide ores. Gold would be present, as well, in the sulfide ore itself. Although iron is not present in all of the areas of the ink of the Vinland Map, it is present. It is not unusual that the composition of the ink is not consistent throughout the map but varies as a consequence of the deterioration of the ink.12

Using Raman spectroscopy, Brown and Clark have again determined that the ink of the Vinland Map contains anatase.<sup>2</sup> They have also reported that it contains carbon. They have proposed that the ink of the Vinland Map is a carbon ink and not an iron gall ink and implied, therefore, that anatase could not be present as a consequence of the materials used to make a medieval iron gall ink. The presence of carbon in an ink is not evidence that the ink is a carbon ink. It could just as well have been iron gall ink to which carbon has been added as a colorant. Carbon was added to iron gall inks as a colorant in the medieval period as reported and as evidenced by its presence in the ink of the Tartar Relation.<sup>2,13</sup> The authors, Brown and Clark, stated "Had the VM been drawn in a medieval iron gallotannate ink, a vellowing at the borders of the ink such as that seen on the map might have been expected". However, they go on to say "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". This is curious proof that the Vinland Map is a forgery and more likely the yellowing should be taken as evidence that the ink of the map is medieval. The references given by the authors to "broad diffraction lines by XRD" for the anatase in Olin's simulated fifteenth century ink are not published in the McCrone references cited in their paper. Only an electron diffraction pattern for a vellow ink flake from the Vinland Map has been published.<sup>14</sup> The authors cited the absence of ilmenite as proof that the anatase was not a precipitated form from the fifteenth century. In his 1988

<sup>(9)</sup> Heslop, R.; Robinson, P. L. *Inorganic Chemistry*, 3rd ed.; Elsevier: Amsterdam, NY, 1967.

<sup>(10)</sup> Olin, J. S. Pre-Columbiana 2000, 2:1, 27-36.

<sup>(11)</sup> Koucky, F. G.; Steinberg, A. In *Early Pyrotechnology: The Evolution of the First Fire-Using Industries*, Wertime, T. A., Wertime, S. F., Eds.; Smithsonian Institution Press: Washington, DC, 1982; pp 149–180.

<sup>(12)</sup> Gerhard, B. In *Iron-gall Ink Corrosion*, Proceedings European Workshop on Iron-gall Ink Corrosion, June 16 and 17, 1997, Museum Boijmans van Beuningen, Rotterdam and Netherlands Institute for Cultural Heritage, Amsterday, 21–26.

<sup>(13)</sup> Carlo, J. In Postprints of the Iron Gall Ink Meeting, September 4-5, 2000. Conservation Department, University of Northumbria at Newcastle-up-Tyne.

<sup>(14)</sup> McCrone, W. C. Judgment Day for the Turin Shroud, McCrone Research Institute: Chicago, 1996; Section 6.1, pp 38–48.

paper, McCrone cited the presence of iron as causing the yellow of the anatase in the Vinland Map ink. He stated that during the first few years after 1917 the manufacturers were not able to effectively remove all of the iron. It is known that anatase today is made from ilmenite so that the presence of ilmenite in the Vinland Map ink would be equally easily given as an explanation of a forgery as evidence for authenticity. Its absence is not proof of forgery.

The presumption that anatase, which was available in the fifteenth century, would have to be the mineral anatase, which the Vinland Map ink is not, is invalid. Precipitated anatase could result from the process of hydrometallurgy and was present in the simulated fifteenth century ink as discussed earlier. Therefore, it is irrelevant to argue, as many have, that "it would be extremely difficult to grind the mineral anatase to such a uniformly small size range" as that found in the ink of the Vinland Map. The presence of anatase in a fifteenth century ink would not result from the use of a ground sample of the mineral anatase or from the presence of anatase in the impure mixture of sulfates used in the preparation of the ink.

#### CONSIDERATION OF THE OVERALL COMPOSITION OF THE VINLAND MAP INK

There is no discussion in the Brown and Clark paper, or in any other paper published previously on the ink of the map, of the significance of the other elements found in the ink. Heretofore, there has not been any effort to explain the presence of these elements, which are present in other medieval inks, nor to explain the overall composition of the ink and support or deny the concept of a modern ink. The evidence provided by the elemental composition of the Vinland Map ink has heretofore been ignored.

At no time in the discussions by various authors that the ink of the Vinland Map was prepared by a forger is there evidence of how the forger would have prepared the ink or what medium he would have used to suspend the anatase. McCrone carried out infrared spectroscopy on the ink of the map and identified the presence of gelatin.9 He did not attempt to explain how the forger would have made an ink containing gelatin nor how it could be used to draw the map. He did not address the possibility of gelatin being present as a result of hydrolysis of the collagen of the parchment by the acid present due to the deterioration of an iron gallotannate ink. In addition, no consideration was given to the gelatin being present as a proteinaceous binder for the suspension of the metal complexes of gall ink. The overall composition of the ink presents a significant comparison to a fifteenth century iron gall ink. Both McCrone and Brown and Clark have described the appearance of the ink as characteristic of the yellow stain that normally results from discoloration by ink components that migrate into the fibers. When carbon is present in medieval gall ink, the carbon remains on the surface as the iron gall component migrates into the surface.13 This is what is observed on the Vinland Map ink.

### CONCLUSION

It is sometimes possible on the basis of analytical studies to prove that an object is a forgery. It is very difficult to prove that an object is authentic. This paper is presented, therefore, as evidence that the Vinland Map is medieval. The elemental composition of the ink is consistent with a medieval ink.

Based on the radiocarbon date of the parchment of the Vinland Map and the elements present in the ink, there is evidence that supports the authenticity of the map. Important cartographic questions such as that regarding the depiction of Greenland as an island during the fifteenth century have already been addressed.<sup>3</sup> The analytical evidence has been given great credence in the question of authenticity of the Vinland Map, and the historical information important to the interpretation of that evidence should be given equal attention.

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