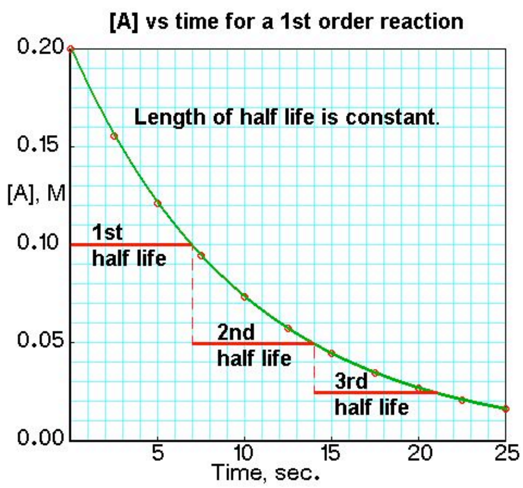
Summary of Rate Laws and Graphical Method

Reaction Order	Integrated Rate Law	Characteristic Kinetic Plot	Slope of Kinetic Plot	Units of Rate Constant
Zero	$[R]_0 - [R]_t = kt$	[R] vs. t	-k	mole L^{-1} sec^{-1}
First	$[R]_t = [R]_0e^{-kt}$ $\ln([R]_t/[R]_0) = -kt$	ln[R] vs. t	-k	sec^{-1}
Second	$1/[R]_t - 1/[R]_0 = kt$	1/[R] vs. t	k	L $mole^{-1}$ sec^{-1}

Half Life



Radioactive Decay

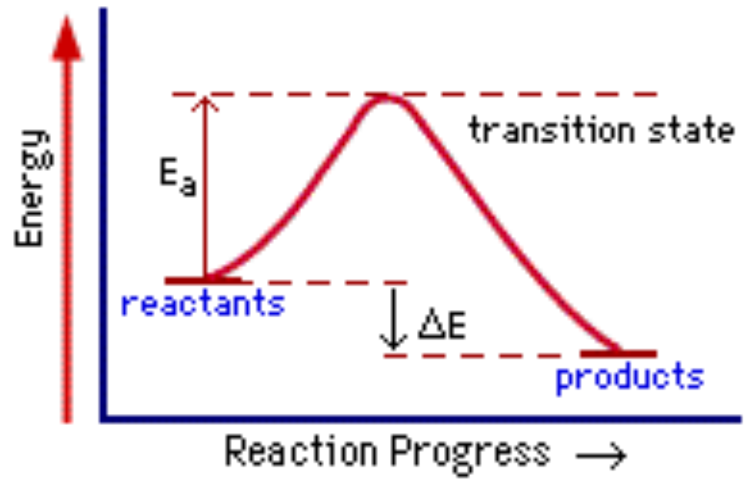
$$\ln\frac{N_t}{N_o} = -kt \qquad N_t = N_o e^{-kt}$$

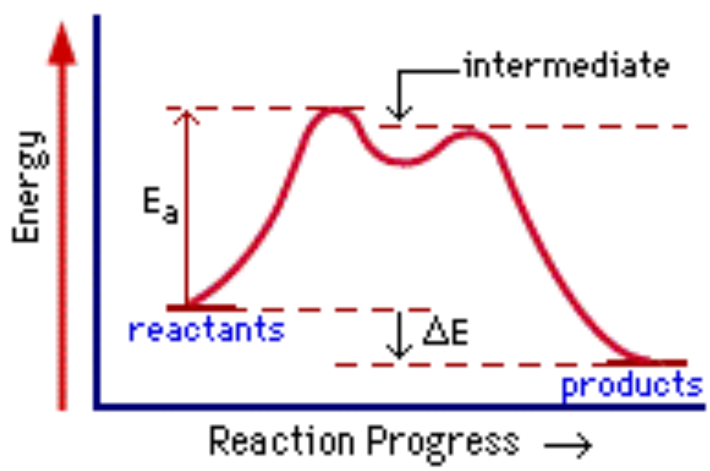
Radioactive gold-198 is used in the diagnosis of liver problems. The half-life of this isotope is 2.7 days. If you begin with a 5.6-mg sample of the isotope, how much of this sample remains after 1.0 day?

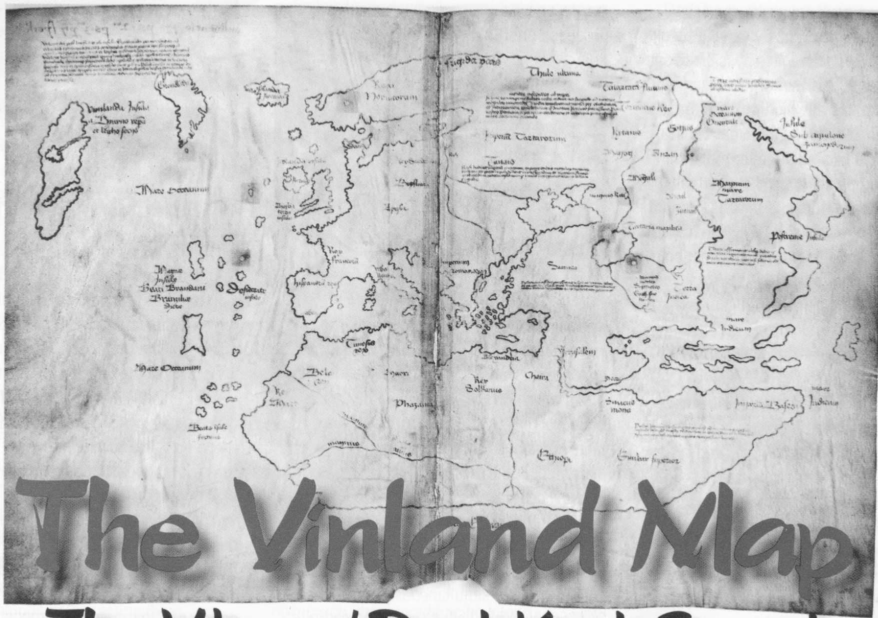
The Carbon-14 activity of an artifact in a burial site is found to be 8.6 counts per minute per gram. Living material has an activity of 12.3 counts per minute per gram. How long ago did the artifact die?

$t_{1/2}$ = 5730 years

Reaction Coordinate Diagrams






BEINECKE RARE BOOK AND MANUSCRIPT LIBRARY, YALE UNIVERSITY

The Vinland Map

The Vikings' Best Kept Secret

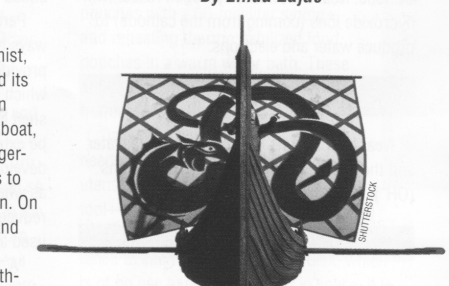
By Linda Zajac

Square sails billowed in the mist, as a great Viking ship carved its way past icebergs and ocean swells. In the open wooden boat, the Vikings ventured farther across dangerous uncharted waters, risking their lives to discover what lay beyond the setting sun. On the horizon, a new land of barren rock and glaciers rose from the sea.

The Vikings reached shore at the northern tip of Newfoundland, now part of Canada. On shore, they were chilled by an ocean breeze that swept through tall thick grasses on knobby green hilltops. On this lush green cove by the bay, the Vikings made their home.

But over time, the location of this historic Viking landing was lost. **In 1953,** Norwegian explorer Helge Ingstad visited a Viking settlement site in Greenland, sparking a burning desire to find a landing site in North America. He scoured the northeastern coast of Newfoundland, searching for possible sites.

Finally, **in 1960,** he spotted ridges in the grass, the remains of an ancient colony. He was unsure whether the site had been settled by Eskimos, American Indians, or Vikings. From 1961 to 1968, Ingstad led seven expeditions to unearth the ruins of a Viking settlement at L'Anse aux Meadows in Newfoundland. Archaeologists uncovered cooking pits and charcoal kilns, houses, and hearths. Later, scientists and scholars bitterly debated whether these brave explorers left a map of their voyage.


SHUTTERSTOCK

In 1957, a faded world map was discovered in Europe. It appeared to be drawn by the Vikings and cast doubt about whether Columbus knew of its existence. If authentic, it was proof the Vikings were the first to set sail for the New World. Scrutinized and disputed for nearly half a century since its discovery, that map is now locked safely in a vault at Yale University's Beinecke Library, New Haven, Conn.

One man's treasure changes history

The map first surfaced in Geneva, Switzerland, when Laurence Witten, an antique book dealer from New Haven, browsed through soiled and water-stained books that an Italian book dealer, named Enzo Ferrajoli, had offered him.

Witten spent hours examining the *Tartar Relation,* an account by Italian traveler and Franciscan monk Friar John de Plano Carpini of his mission to the empire of the Mongols (or Tartars) in Central Asia from 1245 to 1247. Although the slim volume, which contained a crude map, had been carelessly patched and rebound with a modern binding, Witten fell under its spell.

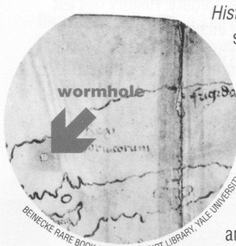
Other customers interested in purchasing the *Tartar Relation* had doubts about whether the map belonged with the manuscript. There was no record indicating where the book came from. Worms had chewed through the manuscript and map, but the holes didn't align. Despite the uncertainty, Witten paid $3,500 for the book.

On thin crisp folded parchment, in fine Latin script, the map detailed the voyage of the Vikings who sailed from Greenland to Vinland, a fertile land with vines. Vinland is thought to represent the Baffin Islands, Labrador, or Newfoundland, all parts of Canada. The Vinland Map is the only known map of a Viking voyage. In 1957, it was a sensational find.

The following year, at his home in Connecticut, Witten leafed through the dilapidated binding of another medieval manuscript. The *Speculum Historiale*, a Mirror of History, was like an encyclopedia for the Middle Ages. It contained portions of French Dominican Friar Vincent of Beauvais' history of the world from creation to the time it was written in the 15th century.

Witten noticed striking similarities to the *Tartar Relation*. Both manuscripts were written in two columns of Gothic cursive. He recognized a watermark he had seen in the *Tartar Relation*, a bull's head wearing eyeglasses. "My heart began to pound," Witten wrote.

With a ruler, he carefully measured where worms had chewed through the map and manuscripts. The wormholes in the *Tartar Relation* were in the same spots as the holes at the end of the *Speculum Historiale*. When Witten compared the wormholes in the map to those at the front of the *Speculum Historiale,* he was shocked—they perfectly aligned. Like a puzzle snapping into place, Witten realized that, at one time, the manuscripts and the map were bound together as one. He concluded that the *Speculum Historiale* was sandwiched between the Vinland Map and the *Tartar Relation* and that the map was drawn to illustrate a portion of the *Speculum Historiale.* In a stroke of good fortune, Witten had stumbled upon the missing manuscript. Now, he was certain the Viking Map was real.

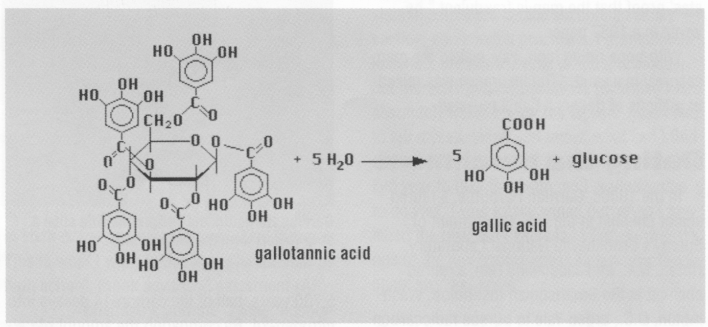


He immediately contacted the curator at Yale University's library. Yale assembled a team of scholars who painstakingly researched the map's authenticity. **In 1965,** Yale stunned the nation by announcing that the Vinland Map was the only map of America produced prior to the voyage of Columbus. Some scholars wondered whether Columbus knew of the map before setting sail.

A close look at the ink

The authenticity of the manuscripts was not questioned, but some scholars and scientists had concerns about the map. Greenland was drawn with striking accuracy. On all other medieval maps, Greenland is shown as a peninsula, but on the Vinland Map, it is an island.

In 1967, the ripple-edged map was flown to the British Museum for an exhibition. While it was there, A. D. Baynes-Cope, a scientific officer at the museum, examined it under a microscope. Under ultraviolet light, the inks in the manuscripts were black against a glowing fluorescent background. This is typical of inks made by crushing larval growths, or galls, on oak trees to create gallotannic acid which is used to make medieval iron-gall ink. But the ink in the map behaved differently. "The ink was unlike any other ink we had encountered in authentic medieval documents, and no explanation could be found for this," Baynes-Cope wrote.



gallic acid + ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) + H_2O → iron-gall ink

In the Midlle Ages, iron-gall ink was made by converting gallotannic acid into gallic acid (first chemical reaction), and then by combining gallic acid with ferrous sulfate heptahydrate and water (second chemical reaction).

In 1972, McCrone Associates, Inc., in Chicago, Ill., analyzed the map using new scientific techniques. With a tiny drop of rubber cement at the end of a fine-tipped needle, Anna Teetsov, a senior research microscopist from McCrone Associates, delicately plucked 29 ink samples from the map and viewed them under a microscope. Teetsov reasoned that the map was "double inked"—drawn first in yellow, then in black. After hundreds of years, the ink in medieval documents leaches into the parchment fibers to produce a yellow stain. She assumed that the map was drawn first in yellow ink, redrawn with black ink, and then most of the black ink was chipped away.

In the yellow ink, Teetsov, along with Walter McCrone, a chemical microscopist and founder of McCrone Associates, expected to find titanium dioxide (TiO_2), a brilliant white paint pigment that naturally occurs in three mineral forms: rutile, brookite, and anatase. With a transmission electron microscope, which uses a beam of electrons instead of light, they noticed small rounded crystals.

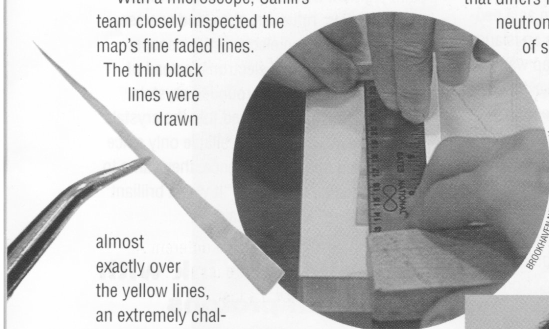
The scientists determined that the crystals were anatase, which was available only since 1917. Based upon the evidence, they came to an unfortunate conclusion. "It was a brilliant job of forgery," McCrone said.

Retesting the ink with a blast of protons

But the debate was far from over. **In 1985,** the map and manuscripts were tested at the Crocker Nuclear Laboratory at the University of California, Davis. Using a new method, Thomas Cahill, professor emeritus of physics and atmospheric sciences, and his colleagues retested the ink. They used a technique, called Proton Induced X-ray Emission (PIXE), in which a massive machine called a cyclotron is used to accelerate charged particles called protons. As a beam of high-energy protons is fired at a sample—in this case, the Vinland Map—the protons collide with atoms in the sample, and X-rays are recorded. X-rays of the elements in the map appeared as sharp peaks and valleys on one graph.

Although Cahill's team found titanium in several spots on the map, roughly one-third of the inked lines that they tested showed no titanium above a minimum detectable limit. They concluded that titanium dioxide was present only in trace amounts in the ink and that it could not be the basis of the yellow ink.

With a microscope, Cahill's team closely inspected the map's fine faded lines. The thin black lines were drawn almost exactly over the yellow lines, an extremely challenging feat. "The McCrone 'double inking' hypothesis was impossible," Cahill said. "Our work argues strongly against the specific McCrone Associates' proof that the map is fraudulent," he wrote in a 1987 paper.

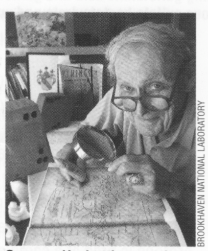


With hope riding high, Yale locked the map securely in a vault. "The insurance was raised to millions of dollars," Cahill revealed.

Dating the parchment

In the 1980s, Garman Harbottle, a retired senior chemist at the U.S. Department of Energy's Brookhaven National Laboratory, Upton, N.Y., and Jacqueline Olin, a retired chemist at the Smithsonian Institution, Washington, D.C., urged Yale to pursue radiocarbon dating to determine the age of the parchment. But this technique destroys the sample.

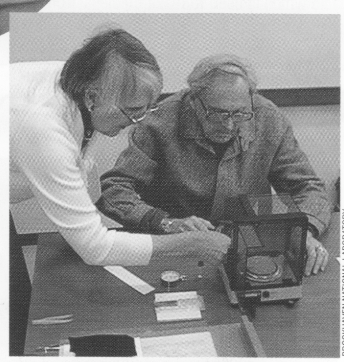
"We wrote two or three proposals to Yale University to allow the sampling," Harbottle said. "All were shot down." When Harbottle and Olin recruited a radiocarbon expert, Yale finally agreed.



Garman Harbottle examines the Vinland Map.

Radiocarbon dating is a method to estimate the age of an organic material. The parchment is a wafer-thin material made from the skin of sheep, goats, or calves. As living organisms breathe and eat, they consume carbon from the atmosphere. Most of the carbon consumed is carbon-12, an abundant isotope of carbon that contains six protons and six neutrons and does not change over time. Much rarer is carbon-14, a radioisotope of carbon that differs from carbon-12 in the number of neutrons that it contains (eight instead of six).

When a living organism dies, the ratio of carbon-12 to carbon-14 is the same as in the surrounding atmosphere. Over time, carbon-14 decays, that is, it transforms into another element, namely nitrogen-14, which contains seven neutrons and seven protons. After about 5,730 years, half of the carbon-14 decays into nitrogen-14. By comparing the amount of carbon-14 and carbon-12 in an organic material, scientists can determine a radiocarbon date.



Garman Harbottle and Jacqueline Olin slice a strip (inset) from the Vinland Map.

At Beinecke, **in 1995,** Olin sliced a strip from the bottom-right corner. Then, at the University of Arizona, Tucson, the sliver of parchment was snipped into six pieces. Each piece was first soaked to remove contaminants and then burned. Using a special machine, the carbon dioxide gas that was produced was converted to graphite.

Finally, a huge machine called an accelerator mass spectrometer counted all of the carbon-12 and carbon-14 atoms in the graphite sample. Radiocarbon dates for the parchment pieces fell between 1411 and 1468— stunning proof that the Vinland Map parchment was ancient.

Real or fake?

Despite numerous tests on ink and parchment, the controversy continues. One undisputed piece of evidence could be the key to solving the Viking mystery. For Ingstad, a critical piece of evidence linking the Vikings to the settlement site at L'Anse aux Meadows came on the final day of the last expedition.

Kneeling in the ruins of a four-room house and scraping the soil at the edge of a cooking pit, archaeologist Sigrid Kaland suddenly shouted, "I found bronze!" Carefully, Kaland brushed away the dirt. She stared in disbelief at a corroded pin the length of a twist-tie, green and bronze. Clearly, it was a Viking pin used to fasten a cloak. "The best find of all was in truth the final clue," wrote Anne Stine Ingstad, archaeologist and wife of Helge Instad. "We practically exploded in our excitement!"

Ingstad's remarkable discovery of Viking ruins left no doubt that the Vikings were the first to discover the New World. But did they leave a map of their voyage? Like a ring-headed pin lost among the ruins, the identity of the scribe is a key piece of evidence, buried in the past.

More than half a century has passed since the Vinland Map first surfaced. Scientists and scholars still debate whether the map is authentic or a clever forgery. History has left an incredible secret etched in the fine faded lines of this ancient parchment. ▲

SELECTED REFERENCES

Ingstad, H., Ingstad, A. S. *The Viking Discovery of America: The Excavation of a Norse Settlement in L'Anse Aux Meadows, Newfoundland*; Checkmark Books/Facts on File: New York, NY, 2001.

Seaver, K. A. *Maps, Myths, and Men*; Stanford University Press: Stanford, CA, 2004.

Dent, J. NOVA: *The Viking Deception: The Truth Behind the Vinland Map*. Providence Pictures, 2005.

Skelton, R. A., Marston, T. E., Painter, G. O. *The Vinland Map and the Tartar Relation*, Yale University Press: New Haven, CT, 1995.

YouTube Video; Lawrence Berkeley National Laboratory, Berkeley, Calif.: http://www.youtube.com/watch?v=M_jIcDOkTAY

Linda Zajac is a science writer in Vernon, Conn. Her most recent article, "Glowing Proteins with Promising Biological and Medical Applications," appeared in the December 2008 issue of *ChemMatters*.