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An innovative method for nondestructive analysis of cast iron artifacts at Hopewell Furnace National Historic Site, Pennsylvania

By Ronald A. Sloto and Martin F. Helmke

Figure 1. The cast house encloses the furnace at Hopewell Furnace National Historic Site. The stone stack of the furnace is visible on the left side of the cast house. In the foreground, part of the furnace slag pile is exposed and makes up the left bank of French Creek.

THE U.S. GEOLOGICAL SURVEY (USGS) IS CONDUCTING research at Hopewell Furnace National Historic Site (fig. 1; see sidebar, page 53) in southeastern Pennsylvania to determine the fate of trace metals, such as arsenic, cobalt, and lead, released into the environment during the iron-smelting process. Arsenic is a carcinogen, cobalt is a suspected carcinogen, and lead can cause severe health problems.

Iron ore containing elevated quantities of trace metals was smelted at Hopewell Furnace during its 113 years of operation (1771–1883). The ore used at Hopewell Furnace was obtained from local mines, mainly the Jones and Hopewell mines, which were within 5 miles (8 km) of the furnace. The iron ore deposits were formed during the early Jurassic period about 200 million years ago. The deposits are mineralogically similar and contain abundant magnetite, the chief iron mineral, and accessory minerals enriched in arsenic, cobalt, copper, and other metals.

The study

For this study, we sampled iron ore, cast iron furnace products, slag, soil, groundwater, streamflow, and streambed sediment. It was important for us to determine which trace metals from the smelted ore were incorporated into the cast iron in order to provide a complete picture of the fate of those metals. It was the only missing piece of information after all other media were sampled. Standard techniques were used to sample and analyze all media except cast iron. Standard techniques require collecting samples in the field, shipping them to a laboratory, and performing a destructive analysis. We needed a nonstandard approach for analysis of the cast iron artifacts.

Sampling cast iron produced by the furnace posed two problems. First, verification that the iron was actually cast at Hopewell Furnace was necessary, as some iron objects found at Hopewell may not have originated there. This was accomplished by using artifacts on display at the Hopewell visitor center (fig. 2). All artifacts on display have been positively attributed to the furnace, and

Abstract

Iron ore containing elevated concentrations of trace metals was smelted at Hopewell Furnace during its 113 years of operation (1771–1883). For this study, we sampled iron ore, cast iron furnace products, slag, soil, groundwater, streamflow, and streambed sediment to determine the fate of trace metals released into the environment during the iron-smelting process. Standard techniques were used to sample and analyze all media except cast iron. We analyzed the trace-metal content of the cast iron using a portable X-ray fluorescence spectrometer, which provided rapid, on-site, nondestructive analyses for 23 elements. The artifacts analyzed included eight cast iron stoves, a footed pot, and a kettle in the Hopewell Furnace museum. We measured elevated concentrations of arsenic, copper, lead, and zinc in the cast iron. Lead concentrations as great as 3,150 parts per million were measured in the stoves. Cobalt was detectable but not quantifiable because of interference with iron. Our study found that arsenic, cobalt, and lead were not released to soil or slag, which could pose a significant health risk to visitors and employees. Instead, our study demonstrates these heavy metals remained with the cast iron and were removed from the site.

Key words: arsenic, cobalt, lead, trace metals, iron smelting, cast iron, X-ray fluorescence

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Figure 2. Stoves cast at Hopewell Furnace are on display in the Hopewell Furnace National Historic Site visitor center. These stoves were analyzed for trace metal content. This style of stove was cast in the 1820s and 1830s.

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Figure 3. Martin Helmke analyzes the trace metal content of a cast iron stove using a portable X-ray fluorescence spectrometer. This stove was cast at Hopewell Furnace in 1772 and is the finest known example of a rococo sand casting.

stoves produced by the furnace are easily recognized by the name "Hopewell" cast into them. The second problem was the analysis of the trace metal content of the cast iron, because it was not possible to break off part of a historically important artifact and send it to a laboratory for analysis. This problem was solved when the USGS collaborated with West Chester University, which owns a portable X-ray fluorescence (XRF) spectrometer.

Methods

We analyzed the trace metal content of cast iron produced by Hopewell Furnace using a portable XRF spectrometer (Innov-X Systems Avenger™). This was an ideal tool because it could perform on-site, nondestructive, real-time analysis. This instrument employs a silver-anode, 10–40 keV (kilo-electron volt), 5–50 mA (milliampere) X-ray tube as an excitation source and a silicon PIN diode detector. It is a handheld instrument (fig. 3) that provides analytical results for 23 elements in less than one minute. Data are displayed on a screen on the instrument as well as stored for later uploading to a computer.

The portable XRF spectrometer contains a miniature X-ray tube that emits high-energy primary X-rays, which strike the sample. The X-ray photons have enough energy to knock electrons out of an atom's inner orbital shells. When this occurs, the atoms become ions, which are unstable. The atom regains stability when an electron from an outer orbital shell moves into the newly vacant space in the inner orbital. As it does so, it emits an energy known as a secondary X-ray photon or fluorescent X-ray. The X-ray emission wavelength or energy of the fluorescent X-ray is characteristic of a specific element, and the amount of the element present is determined by the intensity of the emission.

Table 1. Range and mean concentrations of elements measured in cast iron products from Hopewell Furnace by X-ray fluorescence spectroscopy

Element Analyzed	Stoves		Footed Pot		Kettle	
	Range	Median	Range	Median	Range	Median
Antimony	ND	ND	ND	ND	ND	ND
Arsenic	ND–1,330	438	607–1,440	988	ND	ND
Barium	ND	ND	ND	ND	ND	ND
Bromine	89–429	299	142–396	237	353–373	357
Cadmium	ND	ND	ND–5	ND[1]	ND	ND
Chromium	ND	ND	ND	ND	ND	ND
Cobalt	ND–17,720	11,300	ND–7,640	ND[1]	ND	ND
Copper	ND–4,790	1,860	ND	ND	ND	ND
Gold	81–400	265	178–385	298	259–323	264
Iron	>900,000	>900,000	>900,000	>900,000	>900,000	>900,000
Lead	ND–3,150	319[2]	469–6,270	2,720	401–540	536
Manganese	ND–7,000	ND[3]	ND	ND	5,240–6,120	5,480
Mercury	ND	ND	ND	ND	ND	ND
Molybdenum	37–112	76	69–108	92	41–70	50
Nickel	ND	ND	ND	ND	ND	ND
Rubidium	ND–258	ND[4]	ND	ND	ND	ND
Selenium	ND–9	ND	ND	ND	ND	ND
Silver	ND	ND	ND	ND	ND	ND
Strontium	30–233	64	23 E–41	31	ND–45	33
Tin	ND	ND	ND	ND	ND	ND
Titanium	ND	ND	ND	ND	ND	ND
Zinc	ND–8,220	834	348–2,450	964	376–1,270	785
Zirconium	ND–47	25[5]	ND–44	ND[6]	ND	ND

Notes: ND, value below detection limit; >, greater than.
[1]One detection in 6 samples.
[2]Twenty-seven detections in 48 samples.
[3]Seven detections in 48 samples.
[4]Three detections in 48 samples.
[5]Twenty-six detections in 48 samples.
[6]Two detections in 6 samples.

The Hopewell Furnace artifacts analyzed included eight cast iron stoves, a footed pot, and a kettle. One stove was cast in 1772 and the others were cast between 1820 and 1840. In addition, we sampled a stove cast at the Rock Furnace in Lancaster County, Pennsylvania, which was on display. Each stove was sampled three times on the ash lip and three times on the top. The pot was sampled three times on the inside and three times on the outside, and the kettle was sampled three times on the outside.

Discussion

The range and median concentrations of the 23 elements analyzed by XRF spectroscopy are summarized in table 1. The median arsenic concentration for stoves cast at Hopewell Furnace was 438 parts per million (ppm), and the median concentration measured for the pot was 988 ppm. Arsenic was not detected in the kettle. Lead concentrations as great as 3,150 ppm were measured in the stoves. Median lead concentrations were 319 ppm for the stoves, 2,720 ppm for the pot, and 536 ppm for the kettle. The implications of arsenic and lead in cooking utensils cast at Hopewell Furnace may warrant further study. Elevated cobalt concentration likely was caused by interference with high iron concentrations. Cobalt was detectable but not quantifiable in all stoves sampled. Cobalt was detected in only one of six samples from the pot and was not detected in the kettle.

We measured two other elements, copper and zinc, in elevated concentrations in cast iron. The median copper concentration for the stoves was 1,860 ppm. The stove cast at Rock Furnace did not have detectable levels of copper. Iron ore from the Jones mine is particularly rich in copper. Copper was not detected in samples from the pot and kettle. Median zinc concentrations were 834 ppm for the stoves, 964 ppm for the pot, and 785 ppm for the kettle.

An interesting finding from this study was the presence of gold in the cast iron. Median gold concentrations were 265 ppm for the stoves, 298 ppm for the pot, and 264 ppm for the kettle. Each stove may contain up to an ounce of gold. Gold was not analyzed in other media; however, gold concentrations up to 3.25 ppm were reported in ore samples from iron mines in southeastern Pennsylvania by Smith et al. (1988: 330).

Antimony, barium, chromium, mercury, nickel, silver, tin, and titanium were not detected in any sample of cast iron. Cadmium, manganese, rubidium, and selenium were rarely detected. When zirconium was detected, concentrations were low. Concentrations of bromine, molybdenum, and strontium were low.

Variability in trace metal concentration in the cast iron is caused, in part, by use of ore from different mines and by the percentage of sulfide minerals included with the magnetite. However, because the iron deposits had a similar origin, they have similar trace metal concentrations. The stove that was cast in 1772 had about the same concentration of trace metals as those cast between 1820 and 1840.

Conclusions

We found the portable XRF spectrometer to be a valuable tool in determining the fate of trace metals in iron ore smelted at Hopewell Furnace. The spectrometer provided rapid, on-site, nondestructive analyses for 23 elements in cast iron artifacts in the Hopewell Furnace museum. There was no other practical way these data could be obtained. Using this instrument, we filled a data gap and provided key information in understanding the fate of trace metals at Hopewell Furnace National Historic Site.

Our study found that arsenic, cobalt, and lead were not released to soil or slag, which could pose a significant health risk to visitors and employees. Instead, our study demonstrates that these heavy metals remained with the cast iron and were removed from the site or are now safely housed in the visitor center museum.

Acknowledgments

The cooperation of Hopewell Furnace National Historic Site personnel is greatly appreciated in granting access and providing assistance. Rebecca Ross, the park cultural resource manager, was especially helpful by providing assistance and the history of Hopewell Furnace artifacts.

Literature cited

Kurjack, D. C. 1954. Hopewell Village National Historic Site, Pennsylvania (now Hopewell Furnace). Historical Handbook Series No. 8. National Park Service, Washington, D.C., USA.

Smith, R. C., II, S. W. Berkheiser, Jr., and D. T. Hoff. 1988. Locations and analyses of selected early Mesozoic copper occurrences in Pennsylvania. Bulletin 1776, pp. 320–330. U.S. Geological Survey, Reston, Virginia, USA.

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