Application of XRF to the Correlation of Colonial Bricks to a Local Clay Deposit in Southwestern New Hampshire

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INTRODUCTION

Colonial bricks were typically made from local clay sources deposited in glacial lakes (Garvin 1994). Numerous handmade "three fingered" bricks (Figure 1) were found eroding from the banks of the Cold River in Acworth, NH. Two possible clay sources for these are glacial lake clays found along the Cold River Valley and downstream along the Connecticut River Valley (Figure 2), both of which were occupied by glacial lakes. Through geochemical analyses, this study attempts to determine whether the bricks can be linked to either of these local clay deposits. The most likely prospect is the varved clay deposit along the Cold River, approximately 150 meters upstream from where the bricks were found, rather than the Glacial Lake Hitchcock deposits 14 km to the west along the Connecticut River.

Figure 1. One of many colonial bricks found along the Cold River in Acworth, NH. This brick retains the finger impressions of its colonial maker.

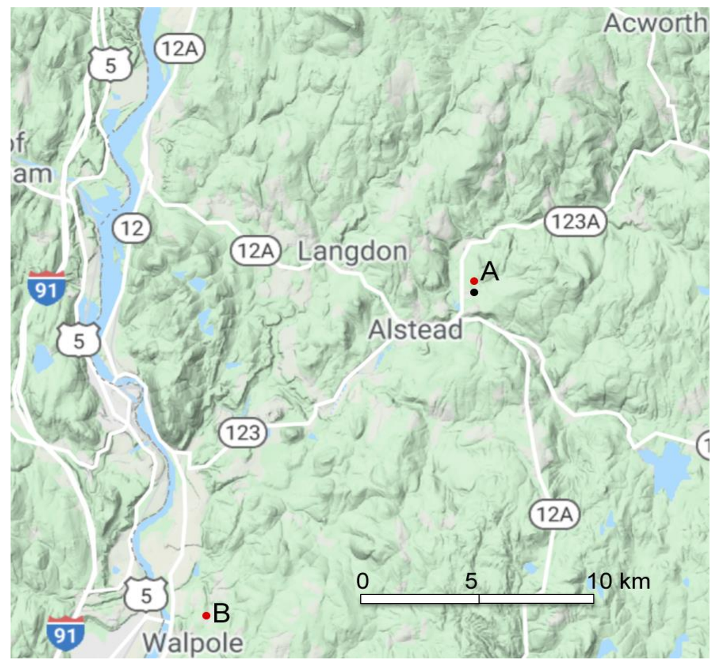


Figure 2. Location where colonial bricks (black dot) are eroding from the Cold River, and locations of clay deposits (red dots).
Site A is along the Cold River. Site B is the location of clays sampled along the Connecticut River. The Cold River is a tributary of the Connecticut River.

METHODOLOGY

Samples of the bricks and clay deposits were collected and prepared for X-Ray Fluorescence (XRF) Spectroscopy using a gun and bench XRF analyzer. Thin sections of one of the bricks were made in an attempt to identify its mineral composition.

Field Methods:

- Collect samples of clays and bricks
- Crush and powder brick
- Oven-dry clay samples to remove excess water
- Pack each sample into cups for XRF Spectroscopy
- Send out billets for thin sectioning

Analytical Methods:

- Analyze both clay and brick samples using XRF spectroscopy
- Using Excel, calculate the % change in elemental composition, and apply dehydration and decarbonation equations to find % of mass lost.
- Plot raw data for each clay sample with the brick and compare the results

Modeling Methods:

- Compare elemental ratios between the two varved clay deposits with the brick

RESULTS

- Dehydration and decarbonation equations (Table 1) found a mass loss of 11% to 28%.
- Twelve heavy metal ratios showed correlation between the brick and the Cold River clay (Figure 4).
- Three heavy metal ratios showed correlation between the brick and the Glacial Lake Hitchcock clay (Figure 4).
- One heavy metal ratio showed correlation between the brick and both clays (Figure 4).
- 17 elements fall into or possibly fall into the 11%-28% predicted range in the Cold River clay (Figure 3).
- 12 elements fall into or possibly fall into the 11%-28% predicted range in the Glacial Lake Hitchcock clay (Figure 3).
- The brick is 35% lithic clasts and 65% matrix (Figure 5).
- The brick's matrix likely contains quartz, potassium feldspar, and mica (Figure 5).

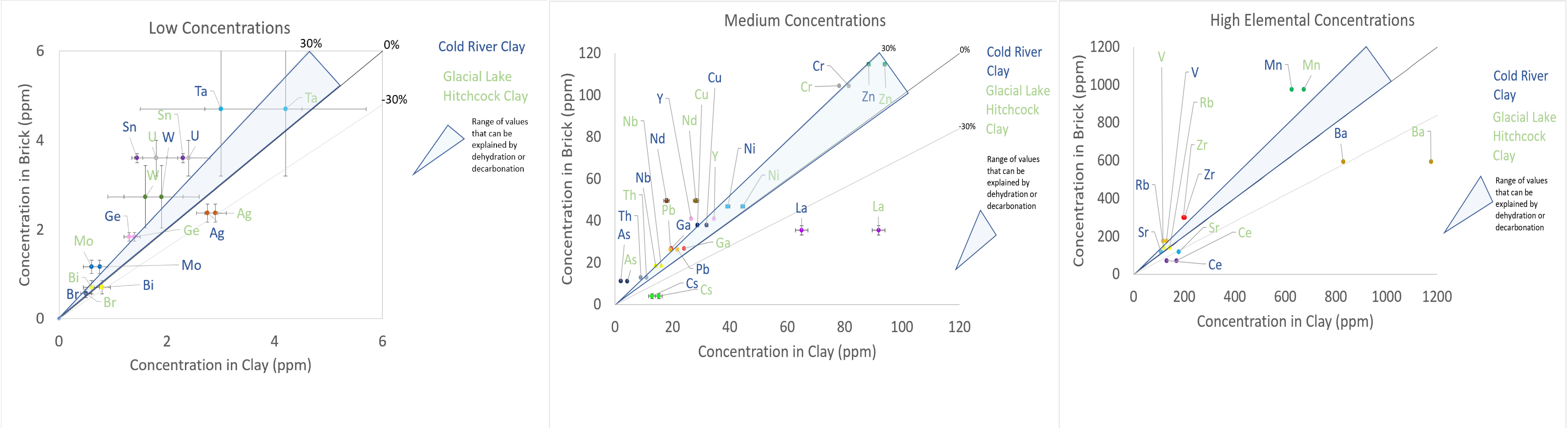
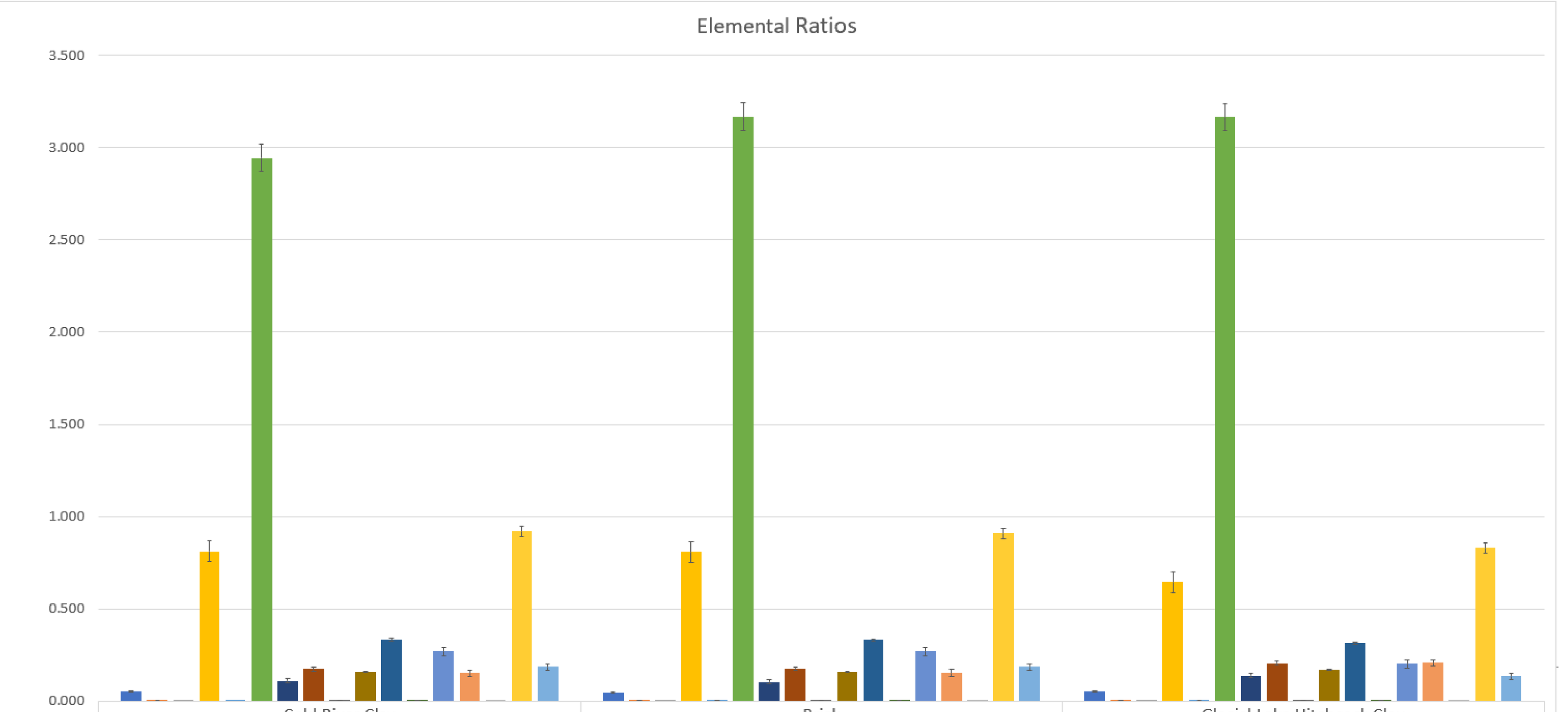


Figure 3. Equations in Table 1 provided a range of mass that would be lost during the firing process (through either decarbonation or dehydration). The range found was 11%-28%. In the graphs above, the blue highlighted area is the predicted range. Several elements were plotted for the Cold River clay (in blue) and the Glacial Lake Hitchcock clay (in green). Strontium, rubidium, vanadium, bromine, bismuth, molybdenum, tungsten, germanium, tantalum, lead, niobium, nickel, copper, chromium, zinc, gallium, and thorium either fall into or possibly fall into the predicted range in the Cold River clay. Niobium, thorium, gallium, copper, yttrium, zinc, lead, chromium, germanium, bromine, tungsten, and tantalum either fall into or possibly fall into the predicted range in the Glacial Lake Hitchcock clay. Some elements, such as tin or lanthanum, do not fall into the predicted range in either clay sample. This could be due to the mobility of the element during combustion, or the bedrock geology drained by the Cold River or the Connecticut River.



	Cold River Clay	Brick	Glacial Lake Hitchcock Clay
Zr/Ti	0.053	0.047	0.053
Zn/Fe	0.0018	0.0020	0.0021
Cu/Fe	0.00065	0.00066	0.00065
Ni/Cu	0.81	0.81	0.64
Cr/Fe	0.0016	0.0018	0.0018
Y/Th	2.9	3.2	3.2
Nb/V	0.11	0.10	0.14
Nb/Cr	0.17	0.18	0.21
Br/Sr	0.0046	0.0047	0.0028
Nb/Zn	0.16	0.16	0.17
Ni/Rb	0.33	0.33	0.31
Ta/Mn	0.0048	0.0048	0.0062
Cu/Rb	0.27	0.27	0.20
Ga/V	0.15	0.15	0.21
Mo/Mn	0.0012	0.0012	0.00089
Cr/Zn	0.92	0.91	0.83
Pb/Rb	0.18	0.19	0.14

Figure 4. Twenty heavy metals were evaluated for correlation between the clay samples and the brick. Twelve ratios correlated the brick to the Cold River clay. Three ratios correlated the brick to the Glacial Lake Hitchcock clay. One ratio correlated the brick to both clay samples. Correlation was shown when the ratios between two heavy metals, such as Cr/Fe, were the same value when evaluated for a clay sample and the brick. This established that, even though the values are different, the concentrations increased the same amount between both the clay sample and the brick.

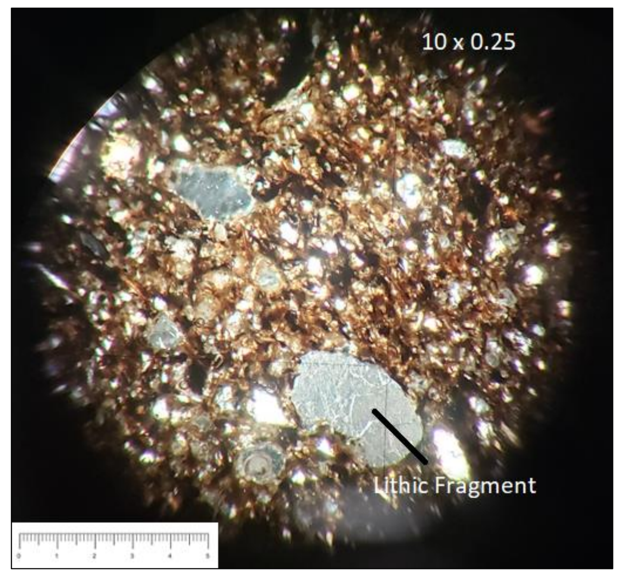


Figure 5. Thin section of the brick matrix and lithic clasts. Most crystals within the matrix are too small to be identified using a polarizing light microscope. The matrix most likely includes quartz, feldspars, and some micas, which are in keeping with phases found in bricks fired at these temperatures (El Ouahabi et al. 2015, Trindade et al. 2009). The brick's composition is heterogeneous, containing some sand and pebble clasts. This is consistent with the clays along the Cold River. No lithic clasts were observed in the clays of Glacial Lake Hitchcock.

Reaction	% Mass Lost
Calcite + Quartz = Wollastonite + CO_2	27.48%
Illite + 0.25 Quartz + 0.85 Calcite = H_2O + 0.60 k-spar + 0.25 Enstatite + 0.85 Anorthite + 0.85 CO_2	11.45%
4 $Fe(OH)_2$ + O_2 = 2 Hematite + 4 H_2O	18.40%
2 $Fe(OH)_3$ = 3 H_2O + Hematite	25.28%

Table 1. Dehydration and decarbonation reactions run using Excel to determine how much carbon and water could be lost. Results ranged from 11% to 28%. Elemental concentration increases ranged from 11% to 70%. This indicated that the source de-posit more heterogeneous than first assumed. The illite formula used is $(K_{0.6}Mg_{0.25}Al_{1.8})Al_{0.5}Si_{3.5}O_{10}(OH)_2$

CONCLUSION

The varved clay deposits along the Cold River are the likely source for the bricks based on similar elemental heavy metal ratios, the presence of lithic clasts in both the clay and the brick, and the amount of elements that fall into the 11%-28% range.

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