

HANDHELD X-RAY FLUORESCENCE ANALYSIS (HH-XRF): A NON-DESTRUCTIVE TOOL FOR DISTINGUISHING SANDSTONES IN HISTORIC STRUCTURES

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Abstract

Determining the provenance of building stone can be important when researching the history of historic structures or identifying suitable substitute stone to use in building repairs. Commonly, however, there is no written record of stone source, and a visual examination alone is inconclusive. In many such situations stone provenance can only be constrained with confidence if the stone has a distinctive property or character that allows it to be distinguished from, or matched with, other stones. A small proportion of stones have one or more genuinely distinctive visual characteristics that uniquely confirm their provenance, but for most stones such distinctive properties, if they exist at all, are cryptic and usually revealed only by microscope examination or bulk chemical analysis. However, collecting and analysing representative hand samples for this purpose can be difficult, time-consuming and damaging to historic structures. Handheld X-Ray Fluorescence analysis offers the potential to provide bulk composition data without the need to collect physical samples. HH-XRF instruments are lightweight, wireless and portable, and they provide a rapid, non-destructive means of analysing most materials in a wide range of settings. This study has examined the benefits and limitations of the instrument when applied to sandstone building stones from the UK. A programme of laboratory tests has been used to: develop a robust methodology for gathering, managing, displaying and interpreting data; determining the extent to which sample surface condition affects the analytical results; and assessing the degree to which different sandstones can be distinguished on the basis of their bulk composition. The results are promising: the data can be used to compare, distinguish and match visually indistinguishable sandstones (and potentially a wide range of other geological and man-made materials) quickly and easily, and as such the method should find widespread application in disciplines such as building conservation and archaeology.

Keywords: sandstone, composition, non-destructive, analysis, HH-XRF, provenance

1 Introduction

A means of gathering and comparing sandstone composition data from buildings and other stone structures without causing damage to the masonry would be of considerable benefit; for example, it may help to distinguish similar-looking sandstones, which may be of use in understanding the construction and repair history of buildings, and it could help to identify (or constrain) stone provenance which might be helpful when selecting stone to use in building repairs.

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Handheld X-Ray Fluorescence (HH-XRF) analysis is a non-destructive means of obtaining bulk composition data, which potentially offers the means to differentiate geological (and other) materials, and in some cases could help to constrain or confirm their provenance.

HH-XRF analysis has been applied successfully in several studies of the provenance of archaeological artefacts, for which non-destructive analytical methods are essential; the analysed materials have included obsidian (Dyrdahl & Speakman 2013; Cecil et al. 2007) and pottery (Morgenstein & Redmount 2005) artefacts. Most HH-XRF instruments are designed by the manufacturers to provide optimised analytical sensitivity for elements of economic importance and/or potentially harmful elements, (e.g. Pb, Zn, Cu) because the mineral exploration industry and contaminated land sectors are the main customers. HH-XRF analysis has been applied to chemostratigraphy in borehole cores (oil and gas industry), rapid prospectivity analysis (mineral exploration industry; e.g. Fisher et al. 2014) and contaminated land assessments. A brief literature review has revealed only one example of HH-XRF being used to analyse building stone (Historic Scotland 2012); however, the details and outcomes of that work have not been published.

This paper summarises the key findings of a study to develop a methodology for applying HH-XRF analysis to *in situ* testing of sandstone building stones, and to establish how the method can be used to distinguish or match sandstones using the results. The study is documented in more detail in Everett (2016).

2 The instrument

HH-XRF analyses were obtained using a Thermo Niton XLt 700 Series Environmental Analyser. The instrument is simply pressed against the sample surface and ‘fired’ using a trigger. The analysed volume corresponds to an area approximately 8mm wide and up to 5mm deep. An X-ray beam fired into the sample produces a spectrum of secondary X-rays, reflecting the bulk chemical composition of the analysed volume, that are measured by the detector inside the instrument. A calibration routine, which is built-in to the CPU of the instrument, was run before each analysis session. The routine measures the X-ray spectra and adjusts the internal electronics and sensors according to pre-loaded factory settings. This means that results should be internally consistent but may not be comparable to data produced using a different instrument.

The instrument can measure the concentration (in parts per million (ppm)) of 22 elements; Sb, Sn, Cd, Ag, Sr, Rb, Pb, Se, As, Hg, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, Sc, Ca, and K.

However, the concentration of any of these elements is only reported by the instrument if it exceeds the Lower Limit of Detection (LLD), which is determined by the instrument for each individual analysis but is not recorded (i.e. the instrument reports the concentration of an element, or that it is below LLD, but does not record what the LLD value is). Broadly speaking, LLD values tend to be lower for elements with higher atomic numbers than for elements with lower atomic numbers.

3 Sample details

Sandstone building stones typically are comprised predominantly of detrital sand, primarily grains of quartz, feldspar and rock fragments in varying proportions. A range of other

minerals, including mica, Fe (-Ti) oxide, apatite, tourmaline and zircon, are usually present in minor to trace proportions. Secondary (authigenic) minerals, including calcite, dolomite, iron oxide (or oxyhydroxide), clay and quartz, are also commonly present in minor to trace proportions. Most building stone sandstones are porous (up to 25% pore volume). Quartz (SiO₂), which is usually the dominant constituent, will not produce a response from the HH-XRF instrument as neither Si nor O are measureable elements. This means that the compositional maturity of a sandstone (i.e. the proportion of quartz relative to other detrital components) has the potential to strongly influence the analytical results.

The programme of laboratory analysis was conducted on a suite of 26 hand samples of sandstone from 11 quarries in the UK. The samples were selected to represent much of the range of colour and mineral composition range displayed by UK sandstones, and some of the most important lithostratigraphic and chronostratigraphic associations. All the samples were obtained from the BGS Collection of UK Building Stones, and all consisted of fresh (unweathered) sandstone. Most of the samples are mineralogically and texturally uniform (not obviously bedded or laminated) when viewed at the hand specimen scale. The maximum grain-size in any sample is around 1.5 mm; this is much smaller than the volume of stone included in each analysis (section 2), so it is assumed that variations in grain size do not affect results significantly. For the sake of brevity only a subset of samples, all of which are uniform, are referred to in this paper (Table 1). The modal composition of each sample was estimated by visual assessment of thin sections under the microscope, and using this information each sample was classified according to its compositional maturity.

Table 1: Summary details of sandstones referred to in this paper

Quarry name	Location	Compositional maturity *	Colour	Lithostratigraphic and chronostratigraphic association
Craighleith	Edinburgh (Scotland)	very mature	white	Gullane Sandstone Formation, Strathclyde Group; Carboniferous
Cullalo	Burntisland, (Scotland)	very mature	white	Strathclyde Group; Carboniferous
Blaxter	Otterburn (England)	mature	buff	Tyne Limestone Formation; Carboniferous
Peakmoor	Matlock (England)	mature	buff	Ashover Grit, Millstone Grit Group; Carboniferous
Stanton Moor	Matlock (England)	mature	buff	Ashover Grit, Millstone Grit Group; Carboniferous
Crossland Hill	Huddersfield (England)	moderately mature	buff	Rossendale Formation, Carboniferous
Corsehill	Annan, (Scotland)	moderately mature	orange	St Bees Sandstone Formation; Triassic
St Bees	Ravensworth (England)	moderately mature	orange	St Bees Sandstone Formation; Triassic
Swinton	Kelso (Scotland)	moderately mature	buff	Ballagan Formation, Inverclyde Group; Carboniferous
Pennant	Forest of Dean (Wales)	immature	purplish grey	Pennant Sandstone Formation; Carboniferous

* Based on the proportion of thin section area occupied by quartz, where *very mature* = >70%, *mature* = 50-70%, *moderately mature* = 40-50% and *immature* = <40%.

4 The test programme

4.1 Plotting parameters

A key objective was to develop a means of gathering, assessing and interpreting analytical results quickly but with sufficient rigour to ensure they are meaningful. This is important because the method is likely to be useful only if it is quick and easy to use, without the need for the rigorous statistical evaluation that commonly is associated with other methods using bulk composition data. Ideally, a single set of elements or element ratios would be used to represent sandstone compositions, and the data would be evaluated using a simple, empirical method. With this in mind, the first test involved analysing each sample 10 times (on 10 different sites) to identify which elements are present in sufficient concentration to be useful.

Only Fe, Ti, Sr, Rb and K were consistently above the Lower Limit of Detection (LLD) in most (22) of the samples. Based on this result, plots of Fe/Ti vs Sr/Rb were identified as the optimum means of presenting data; in most sandstones these element ratios will be controlled mainly by Fe(-Ti) oxides and feldspar, respectively, though other minerals (notably carbonate minerals, mica and clay) will play a role. Mean values and coefficient of variance (CV) values for these elements are presented in Table 2.

Table 2: Average values and CV for elements measured in selected samples

Sample	Sr		Rb		Fe		Ti		K	
	Mean	CV	Mean	CV	Mean	CV	Mean	CV	Mean	CV
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
Craigleith A	*	*	*	*	417.5	18.3	307.5	14.2	1702.8	14.8
Cullalo A	64.1	8.9	*	*	282.3	15.9	499.1	22.7	2009.2	14.9
Blaxter A	125.0	6.4	14.9	26.9	3807.9	5.5	1630.4	4.5	5719.1	6.4
Blaxter B	48.5	14.9	15.2	20.5	3063.8	3.4	668.4	5.7	6943.9	4.9
Blaxter C	31.5	13.5	22.1	24.0	5290.2	5.1	1927.0	4.3	7754.8	6.6
Peakmoor A	78.8	7.6	33.1	19.2	5706.3	5.6	2856.6	6.0	16076.6	8.1
Peakmoor B	91.5	6.9	33.6	15.4	4572.2	4.0	2419.6	3.7	17061.0	2.9
Peakmoor C	79.1	9.0	39.9	10.5	7431.8	5.5	2577.6	2.6	17222.6	3.0
S. Moor A	79.4	7.2	29.1	14.8	4073.8	6.3	2210.7	6.3	15685.9	2.8
C. Hill A	54.8	10.9	30.1	17.4	5504.3	3.7	1483.6	4.3	15320.9	3.2
C. Hill B	49.7	11.3	25.6	12.6	5097.9	3.5	1380.4	3.5	14301.2	5.2
Corsehill A	54.8	3.8	42.5	10.7	4175.5	5.9	1065.0	5.9	19556.7	2.3
St Bees A	65.4	8.2	82.1	10.6	8014.5	8.2	1931.9	11.6	28210.7	2.9
St Bees B	52.2	6.5	76.2	9.3	5639.5	3.0	1126.7	4.5	25578.3	2.1
St Bees C	62.9	6.5	84.8	8.5	8023.0	3.7	1137.5	5.4	29869.8	2.3
Swinton A	109.0	7.0	70.2	8.7	10787.2	4.1	2592.2	5.2	34044.3	3.0
Swinton B	100.7	9.3	63.0	9.7	4621.0	6.0	1847.3	3.3	30590.4	2.6
Swinton C	107.7	10.5	71.9	10.2	13514.4	4.4	2999.0	3.9	36958.6	1.9
Pennant A	43.2	15.2	53.1	11.8	13289.2	4.8	2428.4	6.0	21433.4	5.6

* indicates value below LLD. Coefficient of variation (CV) is a measure of the variation within a group of analyses; in this case it is the standard deviation of 10 analyses divided by their mean, expressed as a percentage.

Not surprisingly, the mean concentrations of these elements generally increase, and CV values correspondingly decrease, as compositional maturity decreases (Table 2). In samples

of *very mature* sandstone only K, Fe and Ti were measured in concentrations above the LLD, and a different means of discriminating these sandstones will be required.

4.2 Comparison of sandstones

HH-XRF data for several sandstones that come from different geological formations and can readily be distinguished by eye in hand specimen, are plotted on Figure 1. In each case, 3 samples from the same quarry (denoted -A, B, C) were used to represent each sandstone, and 10 analyses from different positions on the surface of each sample were obtained to represent the composition range of the stone at hand specimen scale. The following observations can be made.

- The data for two samples of Blaxter sandstone (A and B) display a much bigger range of Sr/Rb values than other samples and consequently do not form tight clusters. Blaxter sandstone is compositionally mature, and the Sr and Rb data have the highest CV values of any sandstone analysed in this study; this means that much of the range in Sr/Rb values is probably due to poor analytical reproducibility (due to low element concentrations) rather than natural compositional variation. The data for Blaxter sandstone therefore are considered unreliable. This result highlights the importance of taking CV values into account at an early stage, particularly for compositionally mature sandstones that don't produce tight clusters on scatterplots. Data displaying a significant degree of scatter but a low CV value are more likely to be a product of natural compositional variation on the scale of the analysed sample.

For the three remaining sandstones (Peakmoor, St Bees and Swinton):

- The data for individual samples typically form tight clusters, demonstrating that the instrument is capable of producing results which can be used to characterise and distinguish sandstones on an empirical basis.
- Data clusters for different samples of the same sandstone sometimes overlap on the scatterplot and sometimes do not; this probably reflects differences in the degree to which sandstones display real compositional variation on the bed or quarry scale.
- The data for all samples of each sandstone define a well constrained and largely distinct field; each field represents a compositional 'fingerprint' for the sandstone.

HH-XRF data for some sandstones that cannot be distinguished by eye are presented in Figure 2 (Sr/Rb axis expanded to clarify cluster distributions). Two samples of orange sandstones come from different quarries in the same geological formation, while two buff sandstones (each represented by two samples from the same quarry) come from different geological formations. Each orange sandstone and each buff sandstone produces a distinct cluster on the plot, confirming that the method is able to distinguish sandstones that cannot be distinguished by eye.

4.3 Optimising analytical procedure

4.3.1 Number of analyses per sample

A test was carried out to determine how many analyses of a sample of uniform sandstone are typically required to define its compositional character. Two samples, one a compositionally mature sandstone (Peakmoor) and the other an immature sandstone

(Pennant), were analysed 4, 10 and 20 times and the resulting data clusters were examined to determine the minimum number of analyses needed to adequately represent the sandstone composition. Both samples produced similar results: the 'spread' of the cluster on the X-Y plot expands up to 10 analyses, but thereafter does not change significantly (Figure 3). On this basis it is concluded that a minimum of 10 repeat analyses is required to represent the composition of a typical sample.

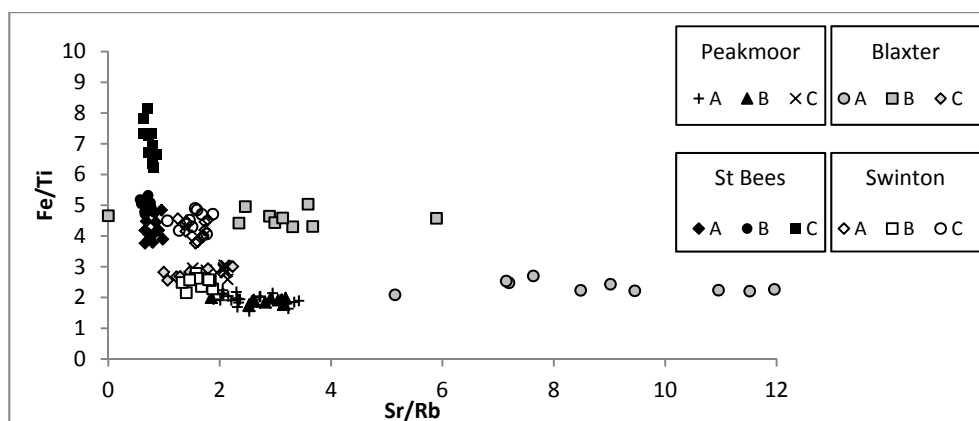


Figure 1. HH-XRF data for sandstones that can be distinguished by eye

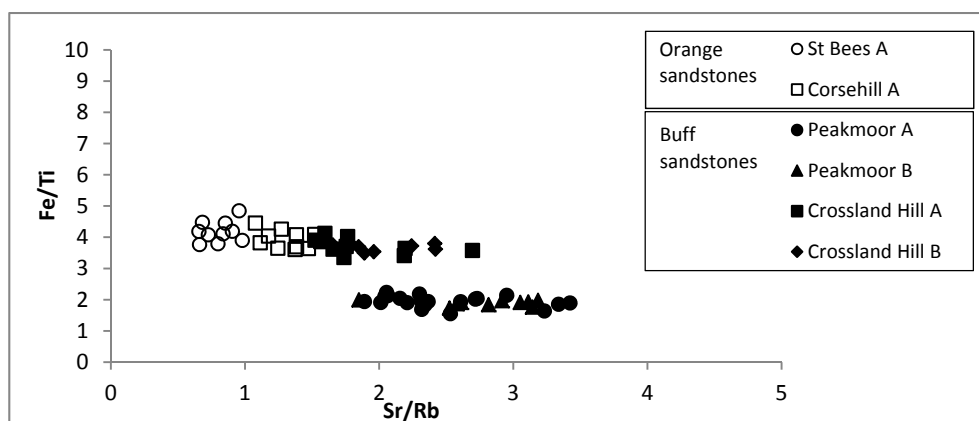


Figure 2. HH-XRF data for sandstones that cannot be distinguished by eye

4.3.2 Sample surface condition

Stone surfaces might be analysed in a range of settings, including in the laboratory, on exposed building facades, and in quarries, so two tests were conducted to compare the effects of different sample surface conditions.

Results from smooth (sawn²) and rough (freshly broken) surfaces of the same samples generally are closely similar (Figure 4); slight differences can be attributed to small sample-

² Surfaces were cleaned to ensure pores were not blocked by rock powder produced by sawing.

scale natural variations in bulk composition. An essentially similar pattern of results for moist and dry surfaces suggests variations in surface moistness also do not significantly affect results. However, to maximise the consistency of results it would be sensible in real-world applications to test samples of similar surface character (ideally smooth, dry surfaces) wherever possible.

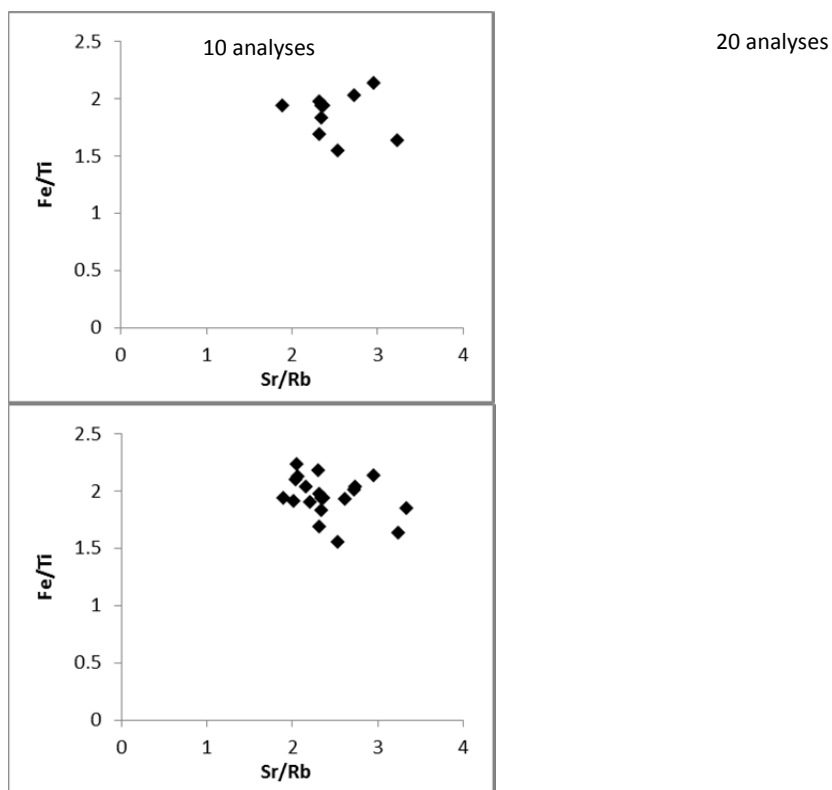


Figure 3. Comparison of results for 10 and 20 repeat analyses of Peakmoor sandstone

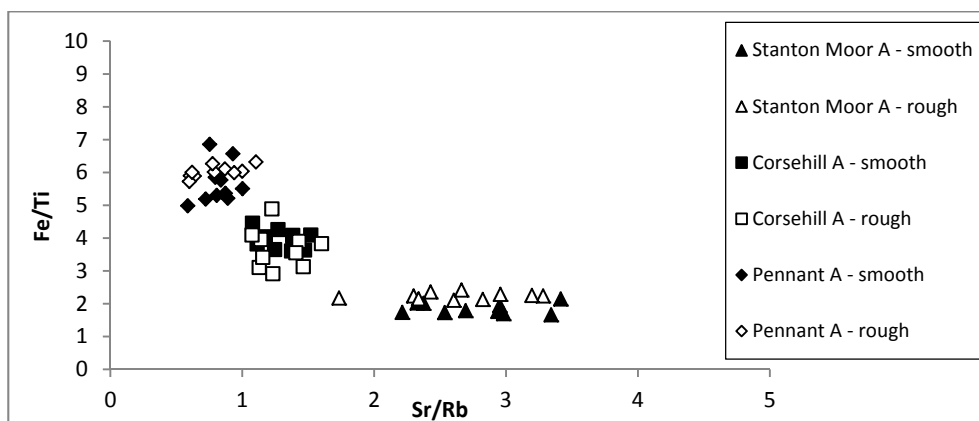


Figure 4. Comparison of results for smooth and rough sample surfaces

5 Conclusions

This study has shown that HH-XRF analysis, and evaluation of results on Fe/Ti vs Sr/Rb plots, can be used to distinguish building stone sandstones, including sandstones which are difficult to distinguish visually, quickly and easily, and without damaging the sample. Ideally, at least 10 analyses of visually uniform sandstone should be obtained to produce a robust cluster of data which could be considered to be a ‘compositional fingerprint’ for the stone. Surface moisture and roughness appear to have little effect on results; however, it would be sensible wherever possible to analyse dry, smooth surfaces.

The method clearly also has potential to help constrain the provenance of sandstone used in buildings, but this would require a reference dataset of values for sandstones from known sources. Combining the HH-XRF ‘fingerprint’ for a sandstone with one or more other discriminatory features (e.g. a distinctive mineral or textural property) could significantly increase the capacity of the method to constrain the provenance of sandstones.

Sandstones which are compositionally ‘very mature’, (and some that are classed here as ‘mature’) contain insufficient concentrations of key elements to produce reliable data; however, this problem is likely to diminish as manufacturers produce more sensitive instruments.

This study has concentrated on sandstones which are visually uniform on the hand sample scale. However, sandstones can be heterogeneous at a range of scales (e.g. due to lamination, bedding and facies variations) and further work will be needed to understand how best to deal with this. Further work will also be needed to evaluate the effect of weathering before the instrument is used in the field.

The accuracy of the instrument when testing sandstones could be better understood by comparing HH-XRF results from a sandstone sample, with high-precision laboratory-based XRF results from the same sample. In time, introducing a calibration routine that involves one or more suitable reference materials could lead to more consistent results, and a situation where results from different projects can be compared.

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