HH-XRF analyses of geological, archaeological, and experimental materials at Meroe, Sudan

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Introduction

Meroe, Sudan was a royal capital of the Kingdom of Kush from the 3rd Century BC to the 4th Century AD, and a major Kushite production centre for much longer. The site is noted amongst archaeometallurgists for its extensive remains of iron production. UCL Qatar's Sudan Project (2012-present) includes investigations of these remains in order to model the iron technology and its impact on the social, political, economic and natural environments. As a part of this research, a series of iron smelting experiments was conducted in January 2015. One goal of these experiments was to evaluate the character and performance of local geological resources, especially potential ores.

Ironstones, clays, and sand were prospected from the region immediately surrounding the site in November of 2014. Ironstones, in particular, were collected from the hills east of Meroe and from a road cut approximately 40 km north. Collected specimens were then subjected to chemical characterization by handheld X-ray Fluorescence (HH-XRF) in order to estimate iron richness of potential ores (Fe_2O_3 and SiO_2 concentrations). Clay and sand samples were analysed for chemical comparison to ironstones and a potential estimation of refractory properties (i.e. Al_2O_3 and SiO_2 contents). Additional site finds of slag, furnace lining, and unidentified materials were also submitted for analysis, as were products of a few ad hoc experimental smelts.

Despite hopes of high performance, it was apparent after the first few analyses that data for Fe_2O_3, Al_2O_3 and SiO_2 generated by the HH-XRF could not be trusted in terms of accuracy. Nonetheless, data continued to be collected on the basis that they would, in aggregate, produce good estimates of major oxide measures on an ordinal scale.

Materials and methods

Ironstone batches were prospected and collected from designated areas in the hills east of Meroe. Upon return to the project dig house, specimens were grouped by colour and texture. Primary groups include: Crimson/Purple; Ochre, and Dolin (from the northern roadcut). Samples from each group were then analysed by HH-XRF and then sub-grouped based on analytical results.

An Innov-X Systems Delta, Model DP-4000 HH-XRF equipped with a Au anode and silicon drift detector was used for all analyses. With one exception, all analyses were conducted in the Mining Plus mode with factory-installed calibration settings and data rendered as oxide weight %. A single analysis of an experimental iron bloom was conducted with the instrument set to Alloy Plus mode, data being rendered as element weight %. Mining Plus is a two beam method, beam 1 operating at 40 kV for analysis of heavier elements and beam 2 operating at 10 kV to detect lighter elements. XRF is incapable of measuring oxygen or concentrations of molecules. Geological materials are, however, assumed to exist as oxides. Oxide concentrations are, therefore, calculated by stoichiometry.

The majority of ironstone measurements were made on three spots of each specimen and the arithmetic mean calculated. Lack of material consistency on any given specimen (sometimes comprising 2 or more layers of stratigraphy) meant that individual analyses were sometimes more suitable for comparison than a measure of central tendency. Efforts were made to find the flattest possible areas of the specimen in which to engage the beam in order to maximize measurement standardization and detection sensitivity. Matrix effects were assumed to be constant for ironstone analyses, though grainsize effects were uncontrollable.

Because HH-XRF instruments are sensitive to high temperatures and fluctuations, all analyses were undertaken in a well-ventilated office during the cooler mornings and evenings. Calibration checks were also run at start of sessions and approximately once an hour hours thereafter to monitor analytical stability using the 316 stainless steel alloy coupon provided with the instrument.

As noted above, results were not expected to be either accurate or precise and no attempt was made to better calibrate the instrument with certified or standard reference materials. Rather it was assumed that HH-XRF device yields semi-quantitative (ratio scale, but not accurate or correctable) values for most major oxide constituents. Measures of Fe_2O_3 are further complicated by the fact that the internal calibration curve of Mining Plus mode is quadratic. As true Fe concentrations increase beyond the linear range of the calibration curve, the intensity of their fluorescence becomes almost constant. This results in the systematic underestimation of the Fe_2O_3 content by the instrument and clustering of measures containing higher concentrations (between 30 and 40 weight %).

Data usage

All data are provided in the accompanying *.txt* and *.xlsx*, and *.Rdata* files named *hhxrf data_Meroe*. The column labelled **data.type** specifies whether the specimen chemistry represents a *mean*, one of several *measure*s from one object, or a *single* measurement from one object. Data are presented in the form generated by the instrument—unit free atomic symbols—though it is emphasized that Mining Plus mode renders concentrations for major and minor elements as oxide weight %. Limitations of accuracy and precision prohibit usage of this data for most purposes beyond basic material sorting. Similarly, elements with atomic numbers of ≤ 12 are not well measured by the instrument in open air. Though provided for the sake of completeness and the potential information they contain, light element data should not be trusted at any level of measurement.

The usage of this data within the context of the Meroe smelting experiments was restricted to examining the ratio Fe_2O_3 and SiO_2 between individual measures. The ratios were used as ordinal scale measures or ore richness. Archaeological slag from Meroe was analysed in the same way to serve as a crude anchor for ore acceptability. The results indicate a wide range of chemical variability across all ore types, with the purple (and related species) and Dolin ores being the richest. The Dolin ores, in particular, seemed to be both the richest and most consistent of the ores tested.

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