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X-ray Fluorescence and Neutron Activation Analysis of Obsidian from the Red Sea Coast of Eritrea

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Introduction

The strategic location of Eritrea along the Red Sea coast and the Horn of Africa makes it an important place to study human prehistory over a long span of time. However, recurrent political instability and the environmental adversity in the region have hindered comprehensive archaeological investigation. Paleolithic research in Eritrea began after the country obtained independence from Ethiopia in 1991. Geological survey in the Abdur area, along the Gulf of Zula coast (Figure 1), identified Paleolithic artifacts embedded in reef limestone dating to ~ 125 Ka BP (Walter et al., 2000). Based on this evidence, human coastal adaptation during the Late Pleistocene has been proposed.

To explore the archaeological potential of the region, surveys and excavations were recently initiated along the Gulf of Zula and Buri Peninsula portions of the Red Sea coast. The survey documented a series of prehistoric sites from coastal and inland contexts featuring Acheulian, Middle Stone Age (MSA) and Later Stone Age (LSA) artifacts (Beyin and Shea, 2007). The Acheulian and MSA Lithic assemblages include highly deflated surface scatters of handaxes, prepared core products and retouched points made on locally available materials such as basalt, shale, and rhyolite. These assemblages however, lack secured stratigraphic contexts and obtaining radiometric dating is problematical.

Excavations at three sites, Asfet, Misse East and Gelalo NW (Figure 1) in 2006 produced archaeological deposits of LSA affinity with mollusk shell association. A large quantity of debitage, blades, bladelets, backed tools and microliths characterize the lithic artifacts. A few of the artifacts are shown in Figure 2. The LSA bearing archaeological strata have been dated to the Early Holocene by 14C (AMS).

Raw Material Exploitation

Obsidian is the dominant lithic material at a majority of the LSA sites along the Red Sea coast, but few sources comparable to its availability in the assemblages are known. This could be due to the limited time invested in searching for source areas and the lack of detailed geological maps to guide surveyors. It is also possible that the source areas could have collapsed or may have been buried. Obsidian generally occurs in the form of cobbles and pebbles along streams and in gravel piles as well as in lava flows eroding out of tuffaceous bedrock. Those found in the eroding surfaces are usually smaller in size and unconsolidated.

For this study, source samples were collected from a single rich obsidian source area called Kusrale Basin. Kusrale is a wide multi-tributary river basin along the southeastern margin of the Gulf of Zula. During rainy times, sediments and obsidian cobbles and pebbles are transported into the basin from a steep mountain on the eastern side. The approximate distances from the Kusrale Basin to Asfet, Misse and Gelalo NW are 20 km, 15 km and 30 km, respectively. A collection of 93 obsidian artifacts from the three sites and three raw material samples from the Kusrale Basin were submitted to the Archaeometry Lab at the University of Missouri (MURR) for chemical analysis.

Analytical Procedures

The artifacts and source materials were analyzed by X-ray fluorescence (XRF) and neutron activation analysis (NAA) using well established procedures which we will describe here very briefly. All of the samples were initially analyzed by an ElvaX desktop energy-dispersive-XRF spectrometer. The instrument consists of an X-ray generator, X-ray detector, and a multi-channel analyzer (MCA). The detector is a solid-state Si-pin-diode with an area of 30 mm2 and a resolution of 180 eV at 5.9 keV (at a count rate of 1000 counts per second). The X-ray tube is an air-cooled, tungsten anode with a 140 micron beryllium end-window.

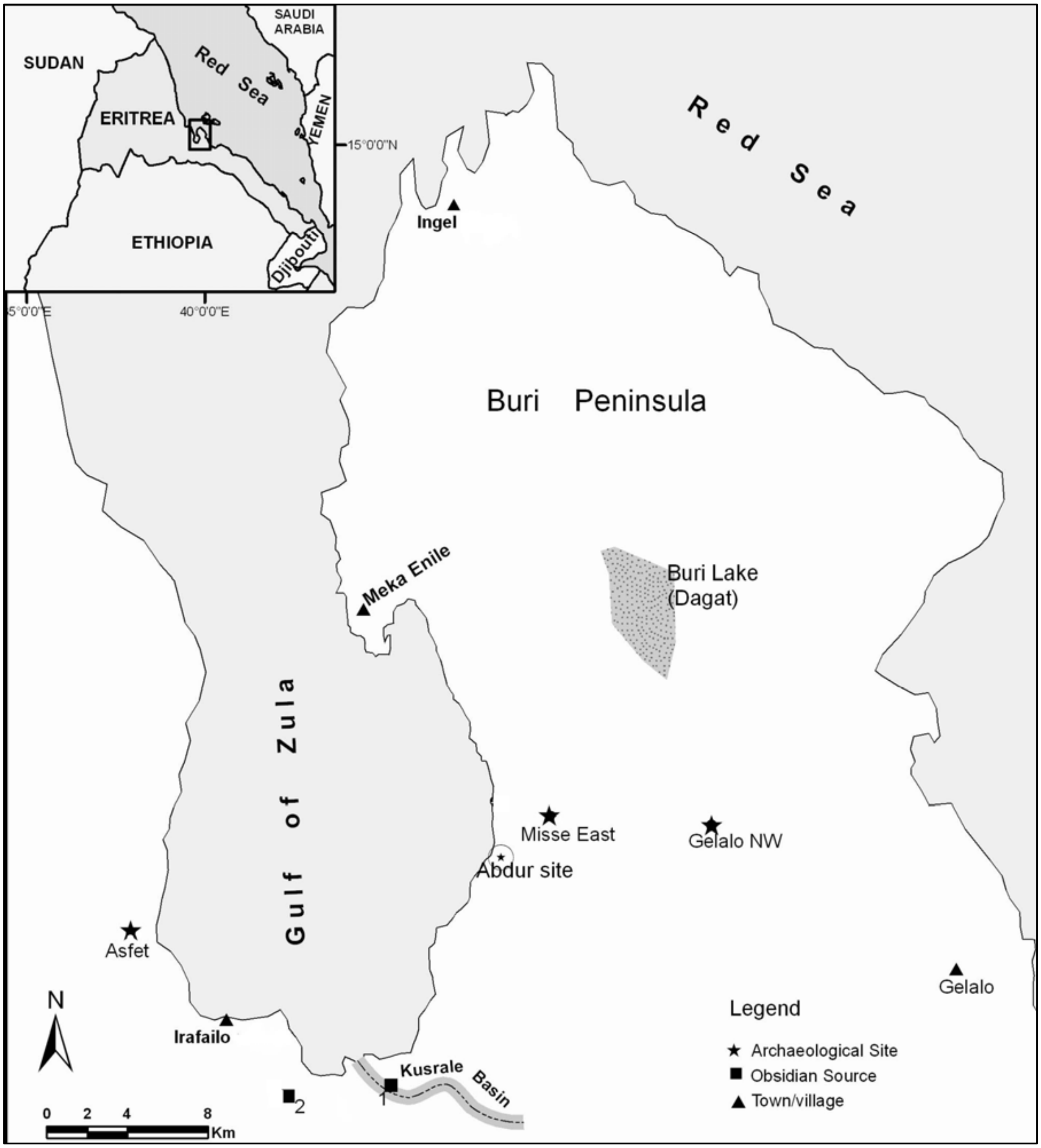

Fig. 1. Map showing the location of the excavated LSA sites and source area, Kusrale.

Fig. 2. Selected artifacts from Misse East: Backed blades and geometric tools

The XRF analyses were conducted at 35 kV using a tube current of 45 microamps and an operating time of 400 seconds. Concentrations were calculated in parts per million by the ElvaX Regression program based on use of a quadratic regression model for a series of obsidian reference samples previously characterized by both XRF and NAA. The XRF analysis permits quantification of the following elements in obsidian: K, Ti, Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr, and Nb.

After completing the analysis by XRF, a subset of the artifacts and the three Kusrale Basin samples were analyzed by NAA to obtain higher resolution data. Due to the destructive nature of sample preparation by NAA, only twenty artifacts were available for analysis. The procedures employed were described in Glascock et al (1999). Two irradiations and three measurements were used to determine the maximum number of elements possible by NAA. The elements measured were (1) six short-lived elements: Al, Cl, Dy, K, Mn, and Na; (2) seven medium-lived elements: Ba, La, Lu, Nd, Sm, U, and Yb; and (3) 15 long-lived elements: Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr.

Results

The XRF results obtained for the entire collection of artifacts and raw material samples in this study are illustrated in Figure 3 using the elements Fe and Rb. Although the artifacts cover a broad range of concentrations for Fe from 1.5 to 3.4%, the Kusrale Basin source samples are tightly grouped around an Fe concentration of about 2.0%. The figure suggests that subgroups might exist within the data. To search for possible differences in source exploitation, the artifacts were plotted with different symbols according to their archaeological site. Careful examination of the plot suggests a possible difference for the artifacts from Gelalo NW versus those from Asfet, but the Misse E artifacts cover the entire range of Fe. Although the data are sparse, it appears that the Kusrale Basin samples are associated with Gelalo or Misse E, but not with Asfet.

The higher resolution NAA data were also examined to search for the possibility of chemical subgroups as suggested by the XRF results. A plot of Fe versus Th indicates that a majority of the artifacts can be assigned to one of three groups, with a significant number of outliers (25%) not

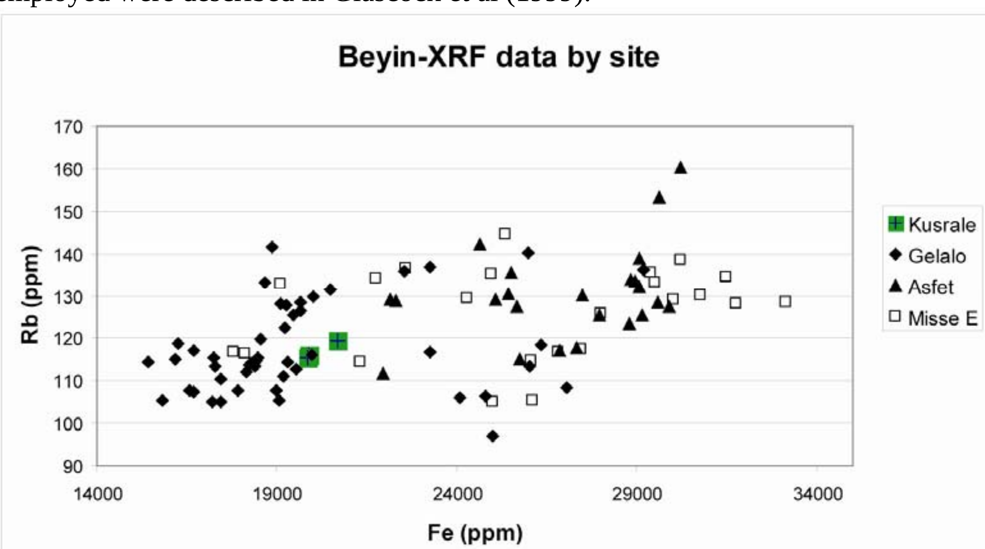

Fig. 3. Bivariate plot of Fe and Rb showing the XRF data obtained for three Kusrale Basin source samples and 93 obsidian artifacts from three sites along the Red Sea Coast of Eritrea. Note that Fe can be converted from ppm to percent by dividing by 10,000

belonging to any of the groups as shown in Figure 4. Group 1 has the highest Fe concentration of 2.7% and it has Ba concentrations below detection by NAA (less than 50 ppm). It consists of nine artifacts with no particular association to a specific archaeological site. Group 2 is made up of five samples (two artifacts and the three Kusrale Basin samples) with an intermediate concentration for Fe of about 2.2% and it also has Ba concentrations below detection. Group 3 consists of four artifacts with an average Fe concentration of 1.9% and a relatively high average Ba concentration of about 900 ppm. Although the outlier samples are unclear, it is quite possible that other chemical groups may be present. Until we are able to analyze more artifacts and obtain a representative collection of source samples, we are left with the results obtained to date.

Conclusions

In reviewing the results of site survey and excavations on the Red Sea Coast, there is a clear contrast in raw material use between the Acheulian and MSA assemblages on one hand and the LSA and Neolithic assemblages on the other. The LSA sites are dominated by obsidian and (to a lesser extent) quartz, whereas the Acheulian and the MSA assemblages display higher diversity of raw materials with more emphasis on locally available rocks, such as shale, basalt and rhyolite. The LSA humans had different mode of adaptation and they selectively utilized obsidian over other local lithic raw materials. One possible explanation for this is due to the variation in the nature of resources exploited by the two groups and the duration of settlement. It suggests that the LSA groups had a better information network to

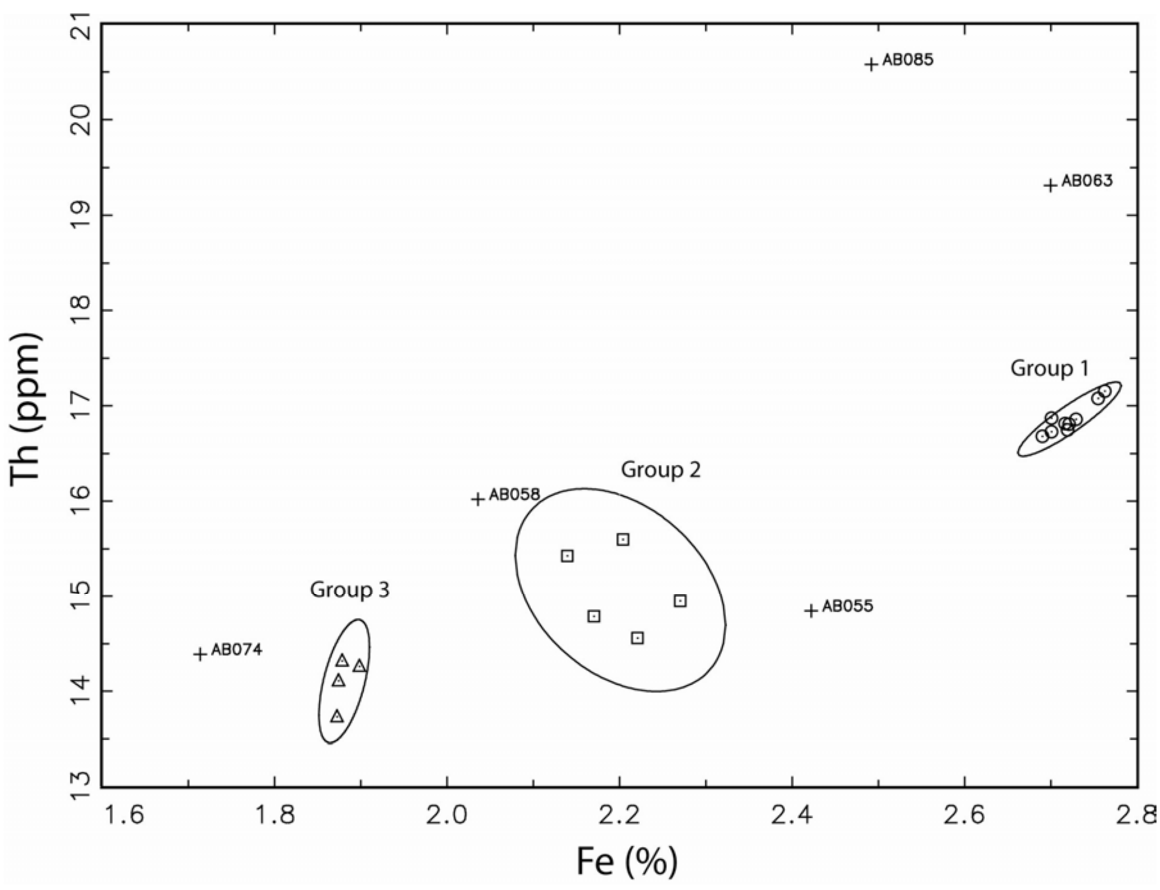

Fig. 4. Bivariate plot of Fe and Th showing the NAA data obtained for three Kusrale Basin source samples and 20 obsidian artifacts from three sites along the Red Sea Coast of Eritrea. Ellipses around the subgroups are plotted at the 95% confidence level. The Kusrale Basin samples are members of Group 2.

explore for high-quality raw material sources, such as obsidian. Obsidian seems to have been transported more than 15 km to the LSA sites. Whether this implies higher mobility associated with resource scarcity or "provisioning place" model of technological organization (Kuhn, 1995) awaits further scrutiny from the overall dataset that one of the authors (Beyin) hopes to generate in the near future as part of his dissertation.

The results reported here show that obsidian was widely used along the Red Sea coast of Eritrea and indicate that the obsidian can be grouped into at least three chemical fingerprints (i.e., different sources). Unfortunately, at this time we have no information concerning the primary deposits of obsidian in the region. And, we do not know to what extent the obsidian from primary deposits may have been eroded to create secondary deposits in the Kusrale Basin. It is clear that much more can be learned after chemical analysis by XRF and NAA of a more systematic collection of raw material from potential source areas is performed.

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DELPHI, GREECE, OBSIDIAN CONFERENCE
The Dating and Provenance of Natural and Manufactured Glasses

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The intensive investigation of archaeological problems and technological advancements in instrumentation requires the frequent updating of an interdisciplinary science such as archaeology. It is the goal of the workshop organizers to bring together examples of recent investigations in obsidian provenance and dating that reflect successful applications of well developed technologies to cultural problems as well as new developments in the field. The scope of the workshop also includes ancient glasses since many of the problems and applications in the obsidian studies field are directly related to research on natural glasses. The first readings of the contributions will be conducted at the European Cultural Center of Delphi, Greece on January 11-14, 2008. Please see the workshop web page for a listing of the topics and presenters (http://www.rhodes.aegean.gr/tms/delphiobsidian2008/index.htm). The workshop has been generously supported by a contribution from the IAOS.