Using Portable XRF for Elemental Analysis of Obsidian, Metals, Ceramics, and Other Archaeological Materials

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Mediterranean Sources, and Archaeological Sites with Obsidian Artifacts (Sardinian, Aegean, Carpathian sites not shown)
Typical neolithic obsidian tools
Most sites also have flakes and tools less formal
Monte Arci (Sardinia) Obsidian

Four main subsource groups: SA, SB1, SB2, SC
with further subgroups identifiable SB1a, SB1b, SB1c, SC1, SC2
Visual and Physical Differences

Density Measurements Useful
Electron Microprobe

Major and minor elements only

1-inch disks with 14-16 samples
Electron Microprobe Discrimination of Monte Arci Subsources

multivariate statistical analysis provides even clearer distinctions
Obsidian from Filiestru Cave (Sardinia) over 4 Neolithic Periods

published in *Journal of Mediterranean Archaeology* (1996)
Missouri University Research Reactor

Instrumental Neutron Activation Analysis (INAA)
Laser Ablation ICP-Mass Spectrometry
(with Michael Glascock & Jeff Speakman)

Laser ablation trace
200° wide

Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) at U Missouri

microscopic signature left
modern XRF instrument: needs liquid nitrogen to maintain vacuum and analyze lower Z elements

automated sample system

non-destructive, if sample fits in the sample holder
Comparison of Relative Standard Deviation
(based on the analysis of geological samples from a single source)
For a description of the data, visit physics.nist.gov/constants.
X-Ray Fluorescence

An electron in the K shell is ejected from the atom by an external primary excitation x-ray, creating a vacancy.

When a vacancy is created in the L shell, an electron from the M or N shell "jumps in" to occupy the vacancy. In this process, it emits a characteristic x-ray unique to this element.

An electron from the L or M shell "jumps in" to fill the vacancy, and emits a characteristic x-ray unique to this element.
Multiple X-rays are produced, with characteristic energies, for each element in the sample.

Overlaps are minimized by using filters, and different beam settings (voltage and current).
Portable XRF Systems

ElvaX

Niton

Bruker, with vacuum

Bruker, on tripod
Portable X-Ray Fluorescence Spectrometer (pXRF)

Advantages
- Non-destructive
- Any size sample
- Quantitative analysis
- Low Z elements (w/ vacuum)

Settings for pottery analysis
- no filter
- 40 kV, 1.5 μA, 180 seconds
- results calibrated against standards
Obsidian analyses by:

- Acquafredda & Muntoni, in press
- Ammerman et al. 1990
- Ammerman & Polglase 1997
- Barca et al., in press
- Berton et al. 2004
- Crisci et al. 1994
- Crummett & Warren 1985
- de Francesco & Crisci 2000
- Francaviglia & Piperno 1987
- Lugliè et al. 2007a; 2007b
- Mello 1983
- Michels et al. 1984
- Pessina & Radi 2006
- Petrassi & Zarattini 1997
- Tykot 1995...2009
Monte Arci Subsource Distribution

Early Neolithic Sites in Sardinia and Corsica

Sardinia C
Sardinia B
Sardinia A

Monte Arci Subsource Distribution

Early Neolithic Sites in Sardinia and Corsica

Sardinia C
Sardinia B
Sardinia A
Open-air, Late Neolithic site of Contraguda

Areas excavated at Contraguda (above); Structural feature A-B (left)
Comparison of subsources present in different areas of the Contraguda site (combined LA-ICP-MS and pXRF data)

Comparison of subsources present within Area 3 at Contraguda (combined LA-ICP-MS and pXRF data)
Sardinia (Italy)

Previous analytical studies mostly in northern (e.g. Filiestru Cave)

Obsidian from 15 sites in the Museo Pigorini collections tested here, plus from open-air site of Contraguda

Pigorini Collection
S. Bartolomeo & S. Elia cave artifacts acquired in 1880s by Francesco Orsoni; Oristano area surface finds collected in 1899 by T. Zanardelli
Examples of Obsidian Artifacts Tested from Museo Pigorini

Note some visual differences in transparency, luster, inclusions
## Archaeological Sites in Sardinia from Pigorini Museum collection

<table>
<thead>
<tr>
<th>Site Time</th>
<th>Time Period</th>
<th>VisualpXRF</th>
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<tbody>
<tr>
<td>Su Cuccuru de Is Arrius (Cabras)</td>
<td>Middle Neolithic</td>
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<td>Grotta San Bartolomeo (Cagliari)</td>
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<td>Grotta Sant'Elia (Cagliari)</td>
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<td>Simaxis</td>
<td>Neolithic</td>
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<td>Palas de Casteddu (Cabras)</td>
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<td>Mes'e Arrius (Cabras)</td>
<td>Late Neolithic</td>
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<td>Stazione La Gumarense (Santa Giusta)</td>
<td>Late Neolithic-Chalcolithic</td>
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<tr>
<td>Domus de janas di Triarzu (Paulilatino)</td>
<td>Neolithic-EBA</td>
<td>1010</td>
</tr>
<tr>
<td>Cantoniera Frumini (Sili)</td>
<td>Chalcolithic</td>
<td>1010</td>
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<td>Palmas Arborea (Oristano)</td>
<td>Chalcolithic</td>
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<td>Serra de Castius (Sili)</td>
<td>Chalcolithic</td>
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<td>Su Casteddu Becciu (Fordongianus)</td>
<td>Chalcolithic-EBA?</td>
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<td>Nuraghe Tiria (Villaurbana)</td>
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<td>Nuraghe Loddu (Fordongianus)</td>
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<td>Nuraghe Nieddu (Oristano)</td>
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<td><strong>Total</strong></td>
<td></td>
<td><strong>468178</strong></td>
</tr>
</tbody>
</table>
Using Rb, Sr, Y, Zr, Nb to identify obsidian sources

High Rb relative to low Sr

Roughly equal Rb and Sr
pXRF Discrimination of Monte Arci Subsources and Assignment of Artifacts

multivariate statistical analysis provides even clearer distinctions
Map of Sardinia shows obsidian source area (Monte Arci) and the area of Nuragic sites with obsidian tested.
Central Marghine Region in Sardinia

large cluster of Nuragic sites occupies about 40 sq km in Borore and adjacent comuni
Nuraghi in the Marghine Area
Excavations near Tower A at Duos Nuraghes

In the mid-1980s led by Penn State faculty Joseph Michels & Gary Webster
Excavations done first in the village area outside of the nuraghi...
...followed by excavations within the nuraghi
Distinctions visibly clearer using multiple elements
Nearly 300 artifacts tested for these 5 Marghine sites

Only about 90 artifacts tested in total for six other Nuragic sites
Over 200 tested from specific contexts within Duos Nuraghes
Other Nuragic Sites Tested

- Tiri
- Loddu
- Nieddu
- Duos Nuraghes
- Marghine
- Domu Beccia
- Ortu Comidu
- Antiguri

<table>
<thead>
<tr>
<th>Site</th>
<th>SA</th>
<th>SB</th>
<th>SC</th>
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<tr>
<td>Tiri</td>
<td>10</td>
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<td>9</td>
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<tr>
<td>Loddu</td>
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<td>Nieddu</td>
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<td>Duos Nuraghes</td>
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<tr>
<td>Domu Beccia</td>
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<tr>
<td>Ortu Comidu</td>
<td>100</td>
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<tr>
<td>Antiguri</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The Chaîne Opératoire

- Reduction
- Production
- Modification
- Use
- Re-use
- Deposition
- Acquisition (extraction)
- Transport
- Exchange
Greenstone and Copper Artifacts from Florida tested

Pure copper, consistent with native (natural) copper, rather than smelted from copper ore. From the Blueberry Site
Use in lab, field, museums…
…on stone, metals, ceramics, etc.
Orlando Museum of Art – South American Collections
More Examples of Testing at the Orlando Museum of Art
Tampa Museum of Art – Classical Period Metal Artifacts
More Examples of Metal Artifacts Tested at Tampa Museum of Art
Silver object in Tampa Museum of Art
Brass object in Tampa Museum of Art
Malta National Museum of Archaeology, Valletta

tested obsidian from residential site of Skorba and mortuary complex of Brocchtorff Circle
Tested wooden sculpture to see if there was gold paint on surface...  
Tested statue to see if modern or ancient gold alloy...  
...and there was!  
...and it appears to be truly ancient  

Malta National Museum of Archaeology, Valletta
Analysis of Copper-Based Artifacts from Morocco, at University of Siena, Italy

Specifically testing to see whether objects were brass (containing zinc), rather than pure copper or bronze (containing tin)
At USF - testing human bone samples to look at diet (differences between terrestrial plants/animals and seafood)

need to use vacuum to detect phosphorus (P) – important for comparison with calcium (Ca), strontium (Sr), and barium (Ba) values
Human bone sample from coastal site of Is Arrutas, Sardinia

note Sr peak
Human bone sample from inland site of Scab'e Arriu, Sardinia

note lower Sr peak

remember, this is just the visual concentration peaks; calibrated numeric values are what is significant
Yon Mound (Apalachicola, Florida)

excavations by Nancy White & Jeff DuVernay (USF)
For homogeneity, powder samples removed by drilling...

...while analyses of clean surfaces also shown to be consistent and reliable
pXRF of Yon Mound Ceramics
Florida Ceramics
(tested samples for Tom Pluckhahn)

Differences in ceramic composition for Sr, Zr
pXRF of inner surface of Yon Mound ceramics (2009)

note cluster of Lamar Complicated Ware samples, while probably multiple sources of Fort Walton and Marsh Island incised wares
Kolomoki (Georgia)
(excavations by Tom Pluckhahn)
Ceramic Samples from Kolomoki (Georgia)

Note: one or two central groups (local?), plus several outliers (from other sources?)
Many possible applications, but need to ...
... have specific purpose for the testing;
... know what elements should be tested;
... have other data to compare with
... remember that analysis is of surface (if sample not powdered)

Florida possibilities include:
... sourcing ceramics;
... sourcing recently found obsidian;
... identifying native vs. historic metals;
... composition of metal alloys (ancient and modern tools, jewelry);
... soil testing (ancient activities, modern contamination);
... seafood consumption (by testing bones)

Samples can be solid, powder, or liquid
Portable and precise... but not inexpensive!

And does require use by someone trained in X-ray analysis and data processing
If interested in collaborative research projects, I can be contacted at:

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or just google “Tykot”