On the formation and distribution of ochreous minerals in northern Malawi

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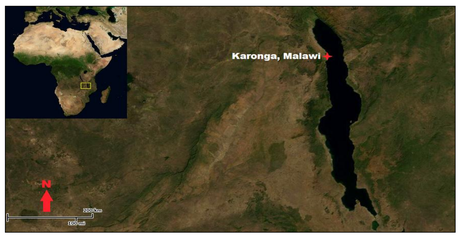
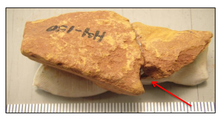
INTRODUCTION

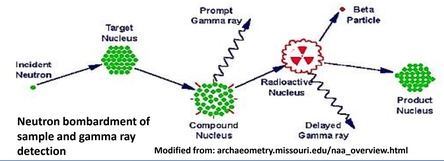
- The Chaminade 1A (CH-1A) Middle Stone Age (MSA) site, located west of Karonga, Malawi, was excavated by J. Desmond Clark and colleagues in 1965.
- > 2 kg of ochre artefacts were recovered from the site and are now curated at the Stone Age Institute. Several artefacts exhibit macroscopic evidence of abrading and incising (below right) consistent with pigment production.
- In 2011 the Malawi Earlier-Middle Stone Age Project opened new excavations near the CH-1A site and began sampling geological sources of ochre in the region west and south of Karonga through collaboration with local guides.
- Conducting a provenance study of ochre artefacts will facilitate the study of procurement preferences, transport patterns, and early material symbolism.
- Rather than forming *in situ* from local weathering of iron-rich rocks, Malawian sources identified thus far are challenging-to-characterize sedimentary deposits with minerals transported from multiple parent rocks.
- **Research Questions**
  - **What is the most effective method of distinguishing between ochre from different geological sources?**
  - **What parent rocks weathered to form the extant sources of ochre in northern Malawi?**





MATERIALS AND METHODS

Three Approaches to Ochre Provenance Geochemistry

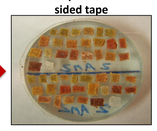


Instrumental Neutron Activation Analysis of Bulk Ochre

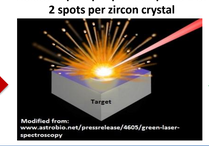
Mix ground ochre with neutral pH glue

Dry for 24 hours, then extract 1x1 mm "paint chips"

Mount two chips from each sample on double-sided tape



Ablate 5 spots per paint chip and 1 or 2 spots per zircon crystal



Laser Ablation - Inductively Coupled Plasma Mass Spectrometry : Bulk Ochre "Paint Chips"

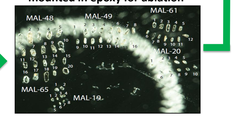
Wash out clay-sized sediment and water soluble iron oxides

20% HCl added to silt-sized sediment

≥ 500, 250, and 63 micron sieves

Separation of heavy minerals in bromoform

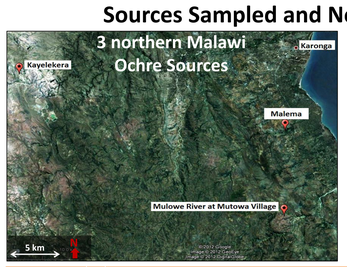
Manually picked zircon crystals mounted in epoxy for ablation



LA-ICPMS: Zircon Crystal Ablation

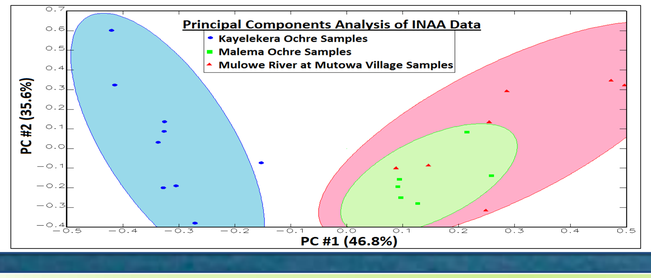
RESULTS

Sources Sampled and Neutron Activation Analysis Results

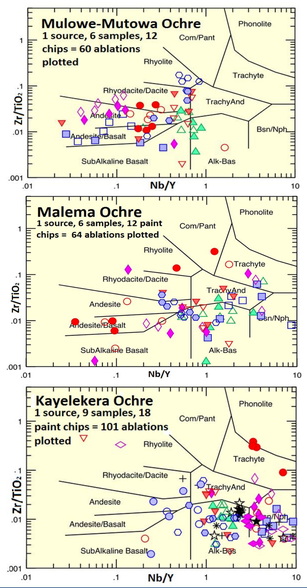


Source	n	Description
Kayelekera	9	Unlithified ochreous clay in open-air pit
Mulowe	7	Ochreous mudstone clasts in conglomerate
Malema	6	Band of ochreous clay exposed by river cut

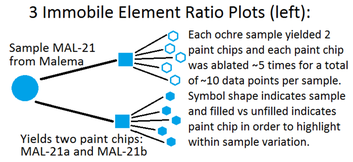
- 1 bulk analysis of homogenized ochre per sample for 22 analyses total
- Long count INAA element concentrations used in Principal Components Analysis (PCA) below
- 33 elements detected by INAA, 30 used in PCA, data normalize to ratio with Fe-content, then log10 transformed
  - 90% confidence ellipse for each group
  - Intra-source variation in the Mulowe group is too great to separate it from the Malema source group.



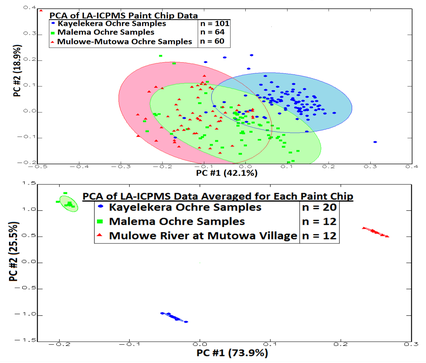
LA-ICPMS Paint Chip Results



3 Immobile Element Ratio Plots (left):

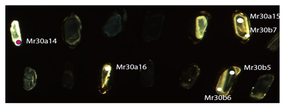


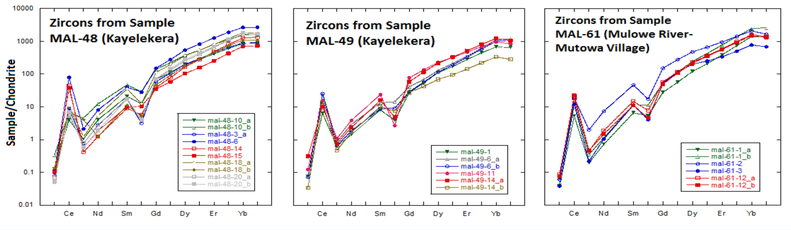
Principal Components Analysis (below): 40 elements detected, normalized to Fe-content, log10 transformed



LA-ICPMS Zircon Crystal Results

- 6 ochre samples, 2 per source, were processed to determine if zircon crystals were present.
- Heavy minerals separated by bromoform were primarily composed of iron oxides and zircon.
- Heavy weathering (left) and the heterogeneity amongst zircons from a single ochre sample under cathodoluminescence (below left) suggest that the grains were transported from the rocks in which they crystallized and that multiple parent rocks contributed to a single ochre deposit.
- Log-normal chondrite-normalized REE plots (below) for zircons from the 3 samples containing the most crystals viable for ablation indicate that all contain typical igneous zircon.





CONCLUSIONS

- INAA is not precise enough nor does it detect enough elements to distinguish between multiple sources of ochre in which each source has a substantial detrital mineral component. The Kayelekera source may be especially distinct because it overlies Chambo Gneisses while the other two sources are located above Karroo and Post-Karroo sedimentary rocks.
- Plots of immobile element ratios derived from LA-ICPMS of Paint Chips indicate that the Malema source is the most heterogeneous, reflecting diverse parent rocks and variability in each paint chip. The Kayelekera and Mulowe groups are more homogeneous and indicate strongly alkaline and subalkaline parents, respectively.
- Paint Chip LA-ICPMS generated a 225 point dataset that was initially less effective than the INAA data in separating the 3 ochres sources. However, by reducing the ~5 ablations per chip to an average for each chip and running a PCA on the means, 3 very distinct and constrained groups appeared and ~99.4% of variation in the data set was explained by PC1 and PC2.
- Data processing rather than the data collection technique may be the key to characterizing heterogeneous ochres. Technique development should focus on reducing sample size to facilitate analysis of artefacts.
- For the first time, refractory mineral grains (zircon) have been isolated from an ochre sample and analyzed for Heavy Rare Earth Element composition. LA-ICPMS targeted at zircon crystals may not be applicable to artefact sourcing due to the large sample mass of ochre required (0.5 – 1.0 kg). However, this technique may eventually facilitate the distinguishing of ochre sources from one another on the basis of the age of crystallization for zircons found in each source.

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REFERENCES

A list of references is available in hard copy below or by e-mail upon request. Please send inquiries to amzipkin@gwmail.gwu.edu