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Elemental Identification of Pigments used in Traditional Bark Paintings in the Northern Territory of Australia

ABSTRACT

This paper discusses a major study undertaken by Harvard Art Museums into traditional bark paintings from locations in the Northern Territory of Australia. The study focuses on the pigments used by Aboriginal Artists and is the first major analytical survey of traditional bark paintings from the late 19th to 20th century. These naturally occurring pigments contain a wide range of elements in varying amounts, characteristic of pigments types such as ochres, clays and mineral blacks. The pigments have been analyzed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP MS) alongside complimentary techniques, including scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Raman and Fourier transform infra red (FTIR) spectroscopy. The samples in this study include natural deposits of pigments, obtained from recorded historical expeditions and collected directly by a member of the project team in consultation with local artists, as well as approximately 200 samples from 50 bark paintings collected from galleries and museums in Canberra, Sydney and Melbourne. The opportunity to compare samples from paintings with samples of natural raw materials provides a unique opportunity to trace the geographical origin of the pigments and may shed new light on the movements of raw materials through trade and add information to an informal atlas of Australian ochres. The study is ongoing and will be included in the catalogue for an upcoming exhibition at Harvard Art Museums opening in January 2016.

1. INTRODUCTION

The art of bark painting has long played an integral part of aboriginal life and culture and it still performed today (Tworek-Matuszkiewicz 2007). The process of bark painting begins with sourcing the bark. A eucalyptus tree, known generally as ‘stringy bark’, is carefully chosen ensuring that the tree is tall and knot free to provide a good painting surface. The bark is prised from the tree and placed into a fire to drive out the moisture, making it pliable. The bark is then weighed down to flatten it. Finally, the outer layer of the bark is removed and the inner surface sanded (Tworek-Matuszkiewicz 2007). Before painting, the surface can be primed by rubbing with juices from plants, such as orchids, as demonstrated by Yirrkala artist Mulkun Wirrpanda in Figure 1. Orchid juice may also be uses as a paint binder along with other plant gums and resins, wax, honey, egg, animal fat and saliva (Tworek-Matuszkiewicz 2007, Reeves, Popelka-Filcoff, and Lenehan 2013, Ellersdorfer, Sloggett, and Wanambi 2012).

Figure 1. Preparation and use of orchid juice demonstrated by Mulkun Wirrpanda

The paint is prepared by grinding rocks of natural pigment on a stone or on a breeze block with water and/or the addition of binder, as illustrated in Figure 2 by Yirrkala artist Nyapanyapa Unupingu who uses poly(vinyl acetate) (PVA) as a binder. Traditionally the paint is applied using special brushes made from animal or plant derived materials such as bark fibers, feathers and hair. Commercial brushes are often used nowadays where they are available (Tworek-Matuszkiewicz 2007).

Figure 2. Preparation and use of ochre paint by Nyapanyapa Unupingu

Paintings may depict everyday scenes such as hunting or camping, while others relate to the legendary time of creation known as Dreamtime. The palette is usually limited to four colors, red, yellow, white and black. Mixing of colors is rare, although black and white may be added to obtain lighter or darker shades (Tworek-Matuszkiewicz 2007). Colors often have symbolic meaning; red may represent blood, yellow fat, black aboriginal skin and white bone. Red and yellow pigments are generally ochres comprising iron oxide. Black pigments are carbon based or manganese oxides. White pigments vary a little more and may include kaolin (aluminium silicate), gypsum (calcium sulfate), quartz (silicon dioxide), chalk (calcium carbonate) and huntite (magnesium calcium carbonate).

Techniques used to identify the composition of the natural pigments include infra-red spectroscopy (Popelka-Filcoff et al. 2014, Bikiaris et al. 2000), Raman spectroscopy (Clark and Curri 1998, Smith, Bouchard, and Lorblanchet 1999, Košařová et al. 2013, Bikiaris et al. 2000, Ospitali, Smith, and Lorblanchet 2006, Froment, Tournié, and Colomban 2008), X-ray fluorescence (XRF) (Popelka-Filcoff et al. 2007, Kingery-Schwartz et al. 2013, Montalto 2010, Jercher et al. 1998), X-Ray diffraction (XRD) (Jercher et al. 1998, Kingery-Schwartz et al. 2013, Montalto 2010, Nel et al. 2010, Bernatchez 2008, Ford, MacLeod, and Haydock 1994), particle induced X-ray emission (PIXE) (Nel et al. 2010, Bernatchez 2008), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) (Montalto 2010, Ford, MacLeod, and Haydock 1994), inductively coupled plasma mass spectrometry (ICP MS) (Green and Watling 2007, Zipkin et al. 2014, Smith and Fankhauser 2009), (instrumental) neutron activation analysis (NAA) (Popelka-Filcoff, Lenehan, Glascock, et al. 2012, Popelka-Filcoff, Lenehan, Walshe, et al. 2012, Popelka-Filcoff et al. 2007, Kingery-Schwartz et al. 2013), polarized light microscopy (PLM) (Montalto 2010) and mineral magnetic analysis (Mooney 2002).

Characterization of the natural pigments, in particular the trace elemental composition, from both natural sources and bark paintings may allow differentiation between geological sources and provide an insight into the use and trade of ochre between different communities and across the continent. Of particular interest for this work was the laser ablation inductively coupled plasma mass spectrometry (LA-ICP MS) study published by Green and Watling (2007). Using LA-ICP MS the authors were able to establish the provenance of Australian ochres through regional variation in their trace elemental composition. The authors analyzed paint

samples composed of ground natural ochre and PVA, and small paint samples taken from indigenous artworks.

2. SAMPLE COLLECTION AND PREPARATION

Working in collaboration with the Macleay Museum Sydney University, the Australian Museum, Art Galley New South Wales, National Gallery of Australia, National Gallery of Victoria, Melbourne University and Museum Victoria, samples were collected from bark paintings known to have originated in the Northern Territory. The paintings chosen for study date from the late 19^{th} through the early 20^{th} century and used traditional materials and methods. For each painting one sample of each color present was taken. Examples of bark paintings that were involved in this study are shown in Figure 3.

Natural pigment samples were collected from geological sources across the Northern Territory (NT) and close to the Western Australia/Northern Territory Border (WA/NT) during pigment collecting expeditions (Figure 4). Sources of pigment are significant to the artist due to it's connection with Dreamtime and its qualities as a pigment (Popelka-Filcoff, Lenehan, Walshe, et al. 2012). In total there are 25 samples of natural pigment to use for this study. In particular there is a large reference set of pigments from Yirrkala, highlighted on the map in Figure 5. Figure 5 marks with a red star where paintings that have been sampled originated and a yellow star marks the location of where samples of natural pigment were collected.

Figure 3. Examples of bark paintings sampled as part of this study; a) Mawalan Marika, Djang'kawu story, 1959, natural pigments on bark, 35.9 x 17.5 cm, Gift of Dr Stuart Scougall 1959, Art Gallery New South Wales IA53.1959; b) Australian Museum E47839, c) Narritjin Maymaru, Cluds at Wayawpuy, c.1965, natural earth pigments of eucalyptus bark, 110.5 x 56.5 cm, National Gallery of Australia, Canberra 90.1084, Gift of Lady Gorton, © the estate of the artist/Buku-Larrnggay Mulka; d) Bununggu Yunupingu, Hunting Scene with diamond stingray, 1959, natural pigments on bark, 79.4 x 59.1 cm, Gift of Dr Stuart Scougall 1959, Art Gallery of New South Wales IA57.1959

Figure 4. Geological sources where natural pigment is harvested; a) Bathurst Island, Northern Territory b) Waringarri, Western Australia and c) Yirrkala, Northern Territory

The raw pigment was prepared in three forms for analysis. This enabled comparisons between the results for different preparations of the same material. Pellets of pigment were prepared by grinding the rock into a fine powder using a mortar and pestle before being compressed into a mould. Paints were prepared by grinding the rock on or between glass, depending on the hardness of the rock, with water. Small chips of the rock were also taken from the original pigment rock. PVA was used as the binder and added to the dried pigment which was then painted onto a Mylar sheet. The process is illustrated in Figure 6. Paints incorporating 2 or 3 pigments were prepared following a traditional aboriginal method. Layered samples were also prepared from the paints. These additional paint samples were produced so that the effect on the elemental composition could be studied when more than one pigment is being analyzed simultaneously.

Figure 5. Sample site locations for the natural pigments (yellow star) in the reference pigment collection and location of origin for bark paintings (red star)

Figure 6. Preparation of paint from natural ochre

3. ANALYTICAL METHODS

During this study a combination of analytical techniques are being utilized to analyze the natural pigment collection and bark painting samples. Optical microscopy is being used to identify contributing pigments that may be present in a sample. FTIR and Raman spectroscopy are being used to identify the minerals present in the samples and SEM-EDS to study the basic elemental composition. Trace elemental composition of the pigments is being determined by LA-ICP MS. This technique was used in previous research into aboriginal ochres (Green and Watling 2007) and is the main focus of this paper.

Inductively coupled plasma mass spectrometry is capable of detecting metals and non metals in trace amounts (Watling, F. Lynch, and Herring 1997). The use of a laser to ablate the samples removes the need for extensive sample preparation. It is a destructive technique as the

laser burns a crater approximately 250 μm wide into the sample during the analysis. Sample size is an issue when using this technique for samples taken from bark paintings as they are often so small that they are completely destroyed by the laser. Another problem encountered is related to the ablation volume, defined as the amount of material that is ablated by the laser. An ideal sample would be thick with a flat surface so that a uniform amount of material is ablated as the laser scans across the surface. Samples taken from bark paintings are very thin and have an uneven surface which prevents a uniform amount of sample being ablated. An additional issue encountered with thin samples is that the laser can penetrate through the sample completely, hitting the mount underneath. Carbon pads and aluminum stubs were used as the mounts for the samples and contamination of the results by associated mount elements can be seen in the data. Due to the issue of ablation volume it was not possible to correct samples for these elements as the amount of material that has been ablated cannot be determined. As a result elements including aluminum, nickel, copper, zinc and lead have been disregarded from the data.

Additional complications include bark paintings often containing multiple layers of paint, contamination from other pigments found both in the rock itself, and as a result of preparing the paint, and finally sample staken from a bark painting are still often on the bark support (Figure 7). All of these factors have been taken into account during the LA-ICP MS analysis and data interpretation.

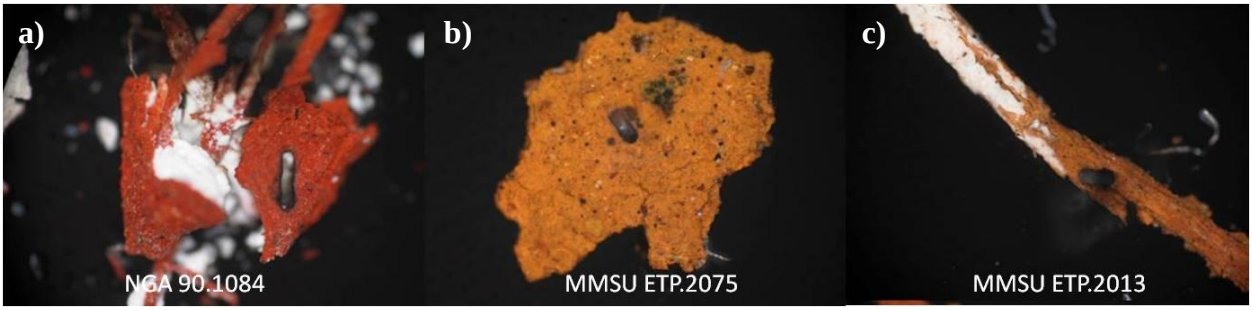

Figure 7. Samples taken from bark paintings after LA-ICP MS analysis that illustrate the difficulties encountered; a) layers of paint, b) contamination by other pigments and c) paint still on the bark support

4. RESULTS AND DISCUSSION

Comparisons between the three different preparations (rock, paint and pellet) of natural pigment were first completed using LA-ICP MS analysis. Figure 8 show the minor elements observed for ochre 8, a yellow ochre collected from Gathalala, located just south of Yirrkala. The three preparation forms displayed the same major and minor elements with small variations in the observed counts. The high Ca value observed in the paint sample is attributed to the use of PVA as a binder. A sample of PVA was analyzed by LA-ICP MS so that the samples could be corrected for the PVA contribution. For the best comparison, samples taken directly from bark paintings will be compared to reference paints prepared from the pigment rocks.

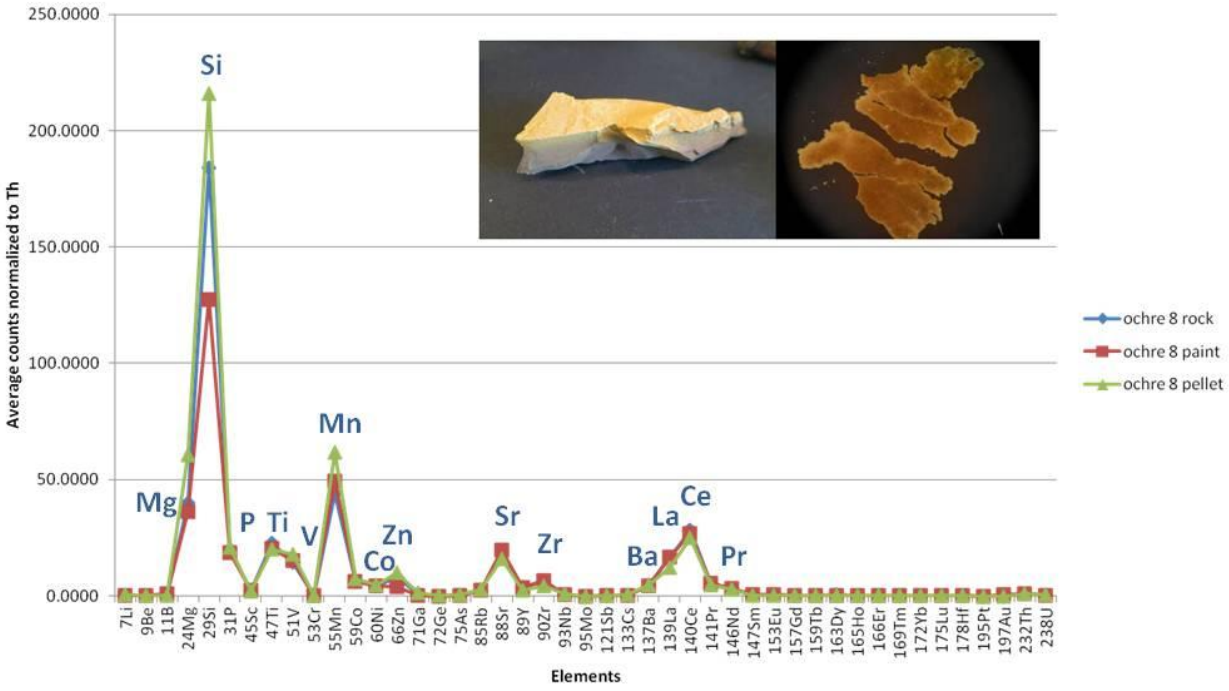

Figure 8. Minor elements found in the rock, paint and pellet preparations of ochre 8

As mentioned in the introduction, there are four color groups: red, yellow, black and white. The focus of this study thus far has been the white and black pigments. Images of the natural white pigments in the reference collection are shown in Figure 9. Samples 1-3 are from Bathurst Island, samples 5, 21 and 22 are from Yirrkala, samples 14 is from the Western Australia/Northern Territory (WA/NT) border, sample 19 is from the Kimberley region in

Western Australia (WA) and sample 25 is a sample of Huntite, a carbonate material containing Magnesium ($Mg_3Ca(CO_3)_4$), sourced from inside Arnhem Land.

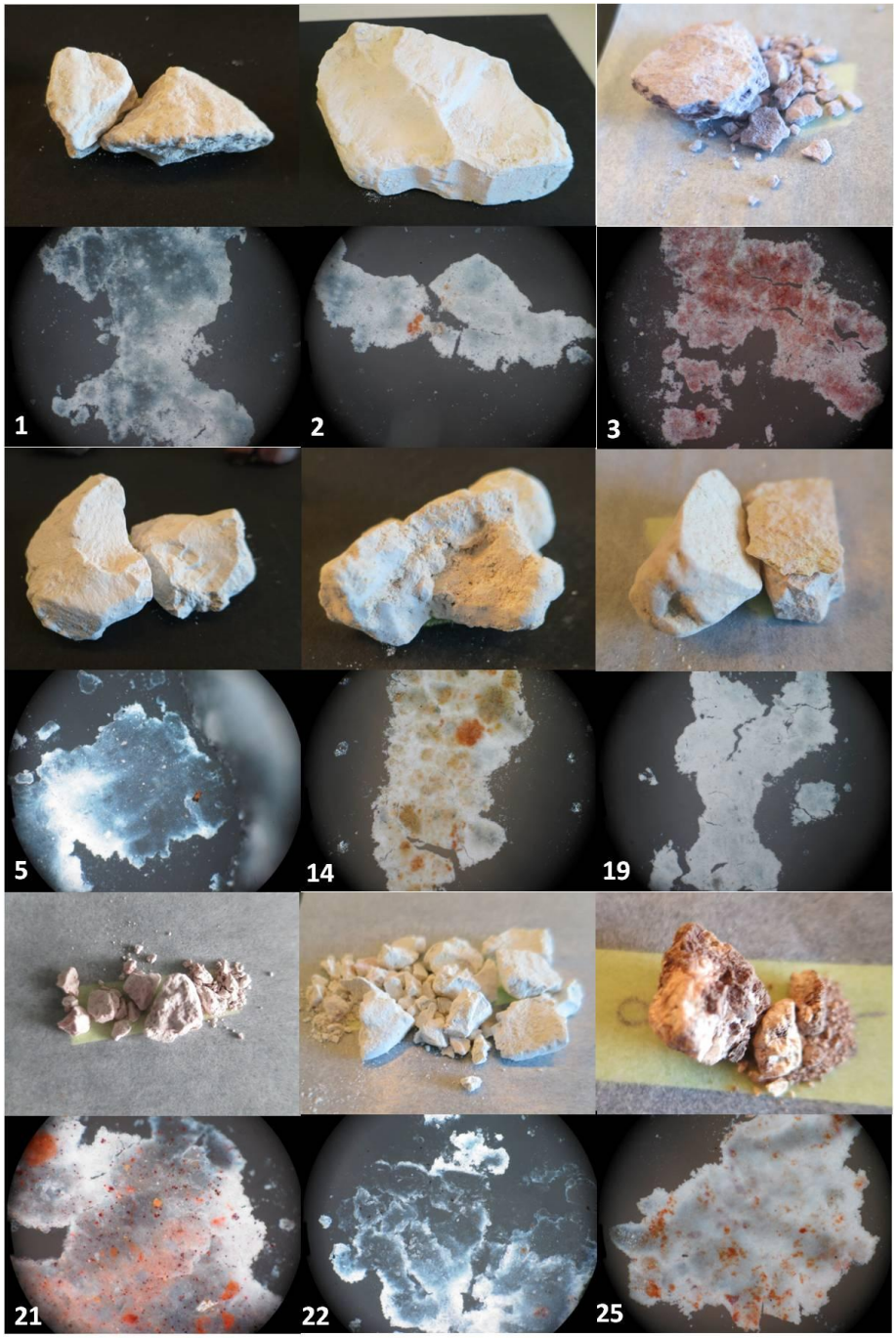

Figure 9. White pigments in the reference collection. Pigment contamination observed in the samples is shown underneath the images of the pigment rock.

Ternary plots are being used to look at the relationship between three elements in a sample, and depending on the elements chosen we aim to separate samples by region. In a plot of Na, Mg and Si, three samples sit apart from the group of white pigments, sample 14, 19 and 25. One is the sample of Huntite (sample 25), known for its Mg contribution and the two samples from the WA/NT border and WA. Sample 14 from the WA/NT border also shows a high Mg contribution. Upon changing the elements of interest to Ba, La and Ce, the three aforementioned samples continue to sit apart from all the white pigments, but samples from Yirrkala (samples 5, 21 and 22) and Bathurst Island (samples 1-3) separate in to groups (Figure 10). These groupings continue when comparing other elements and demonstrate that it is possible to group the white pigments based on their elemental composition and location.

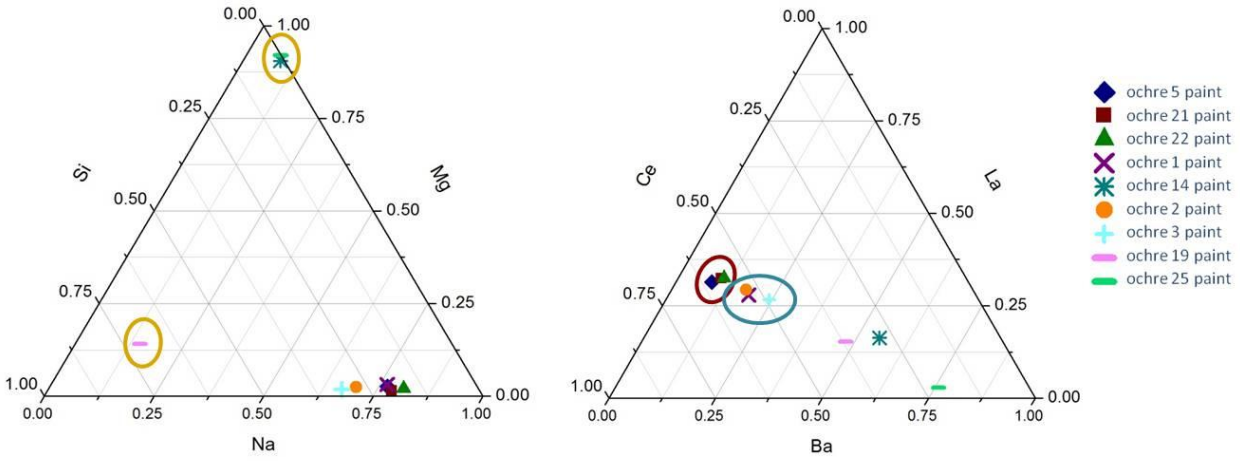

Figure 10. Ternary diagrams for the natural white pigments in our reference collection

Black pigments present a more complicated picture. In the reference pigment collection there are four mineral blacks from Yirrkala (samples 10, 12, 13 and 23) and one (sample 15), a charred bark, from the WA/NT border (Figure 11). Sample 15 from the WA/NT border sits apart from the Yirrkala mineral blacks when plotting ternary diagrams (Figure 12), as would be expected based on the difference in materials. However, we also see a good degree of variation in the Yirrkala samples as well. Depending on the elements chosen for the ternary diagram it is possible to observe samples 13 and 23 group together, however, this is not always the case,

indicating that there are some similarities between the two pigments but they are not the same material.

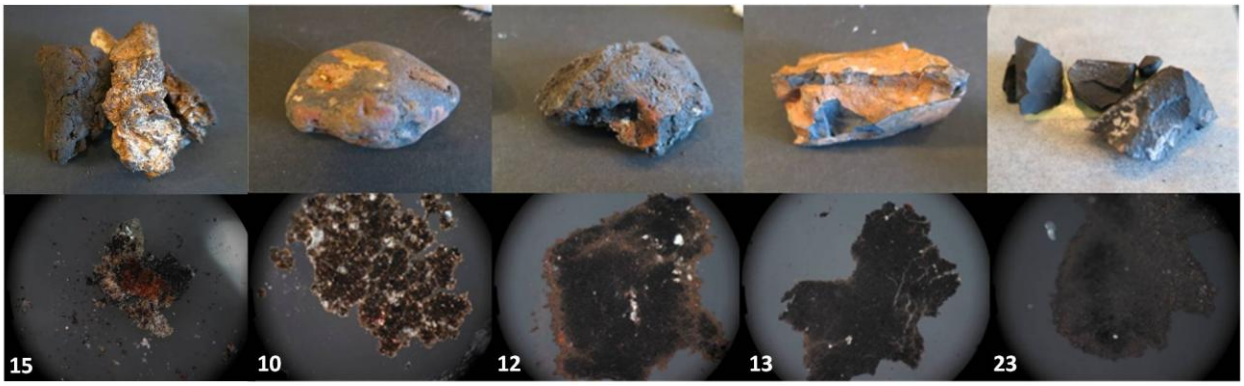

Figure 11. Black pigments in the reference collection. Pigment contamination observed in the samples is shown underneath the images of the pigment rock.

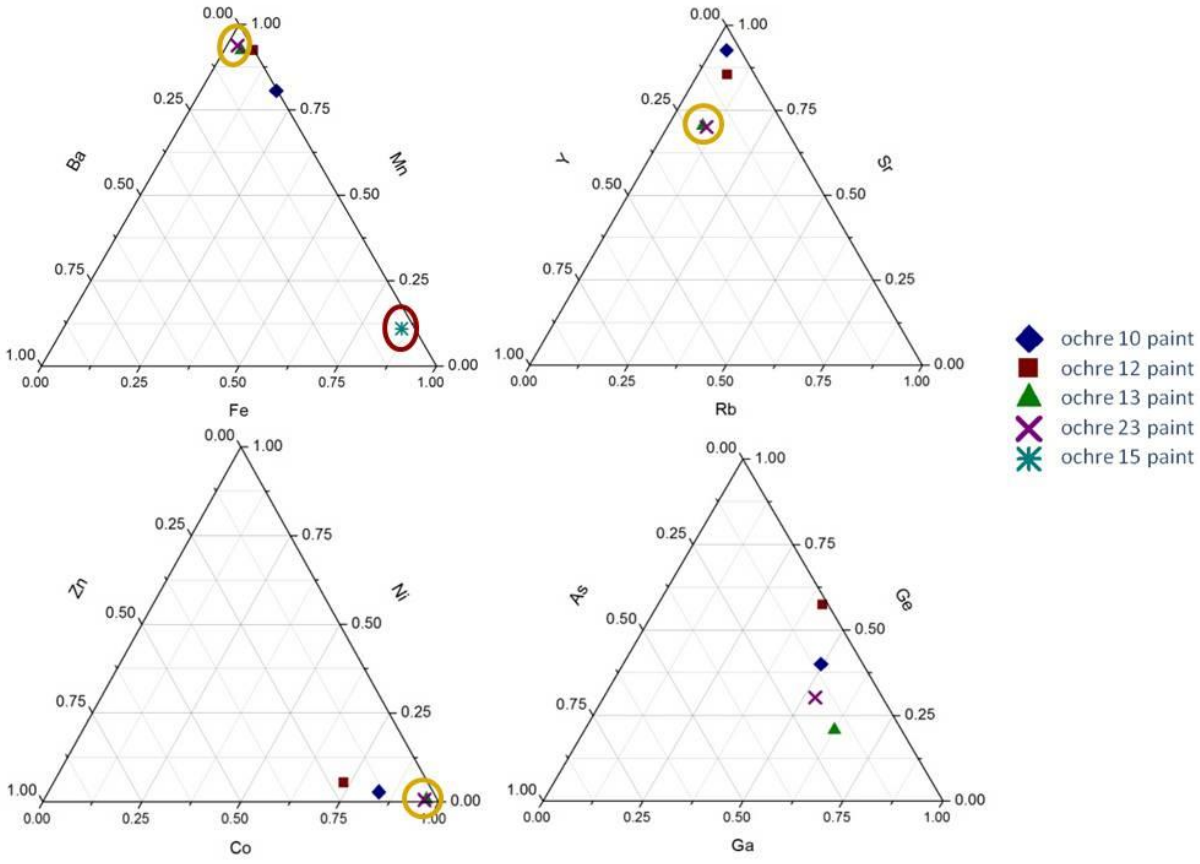

Figure 12. Ternary diagrams for the black pigments in the reference collection

5. CONCLUSIONS

Variation between different preparations of a pigment is apparent for the major and minor elements. For the purposes of data interpretation, paint made from the natural pigment collection will be used for comparison with the samples of interest; chips of paint from bark paintings.

Difficulties experienced when using LA-ICP MS on the small samples limits the number of elements available, making data interpretation difficult and reducing the effectiveness of the technique for the ultimate goal of determining the provenance of pigment. Additional complications within the samples, most notably contamination by other pigments, resulted in a large amount of variation in elemental composition being seen within a sample. This problem may be addressed by multiple analysis of the same pigment with multiple spots across a rock.

Despite complications, it was possible to determine trends that enable white pigments to be grouped together based on their geological origin. Work will continue by comparing the red and yellow ochres in the natural pigment collection and then expand to incorporate samples taken from bark paintings to see if there is a correlation between the natural pigments in the reference collection and the pigments used in a bark painting from the same geological area.

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