WDXRF Analysis of White Colour Pigments Used by Ancient Artistsin Central Tanzania Rock Paintings

ABSTRACT

In central Tanzania, there are large numbers of ancient rock paintings which have been drawn mostly on shelter rocks. Different colours were used in the paintings including white paint. The pigments and the material used by ancient artists in making these colours were not known. This studyaimed to determine the composition of the white colour and suggests the pigments and materials used in making the white colour. A technique namely WDXRF was used to determine the composition of white paint in order to suggest the pigment used while a CHN elemental analyser was used to determine the presence and amount of organic carbon in the samples. Theresults from the analysis of the rock sample were compared to the results of the analysis of the paint sample. White colour was found to be from chalk ($CaCO_3$) and gypsum ($CaSO_4X2H_2O$). Both pigments were found to contain some amount of organic carbon in different concentration. Organic carbon in the pigment is related to the use of organic binders during the preparation of the colour.

Keywords: shelter rocks, rock paintings, pigments, Organic carbon, WDXRF, CHN elemental analyser

INTRODUCTION

During prehistoric times people used to leave their marks for the purpose of marking either a territory or track indicating the source of food or water by means of scratching trees or rocks using stones. By doing so they discover some materials which can do better especially when mixed with some medium such as water (Barnett *et al.*2005). Painting started during this time and basically, colours were discovered during this time. In some known early civilized areas like Egypt, colours were used for spiritual purposes, healing and decoration (Haynes 1992). Nubians in Sudan, who had occupied the middle part of the river Nile valley since around 6000 BC used to paint and curve rocks in order to keep records of their way of life and their travel (Haynes 1992). Ancient artists used pigments which were dug directly from the earth. For example, one of the most known ancient works is that of Lascaux, believed to have been painted 15 millennia ago. The most common colours which can be obtained directly from the earth are white, black, red and yellow (Ball 2001). Charcoal from firewood and soot from burning animal fat were also the source of black colour. These colour pigments were mixed with different binders before they were applied. It is believed that wax, egg, water and tree resin were used by ancient artists from Egypt and Rome (Barnett *et al.* 2005).

Central Tanzania has a large number of ancient rock paintings spreading from the Singida region to Dodoma region. The colour used in the paintings from Kondoa-Irangi in Dodoma region are white (which constitutes 59%), red (which constitutes 32%), yellow (which constitutes 8%), black (which constitutes 2%) and Bichrome Images (which constitute only 0.1%) (Bwasiri and Smith 2015). Also, the same colours were used in Singida rock paintings but their quantity was not well documented. The materials used to make the rock paintings for all colours are not yet known; although for black colour charcoal is suggested (Bwasiri and Smith 2015). Kessy (2005) noted that the chemical constituents of the material used for white paintings in Kondoa-Irangi are not yet known. Similar paintings found in South Africa are said to have been made from silica, clay and gypsum (Hall *et al.* 2007). Several researchers have worked on these drawings, some explained the authorship of the drawings (Kessy 2011), some explained the meaning of these drawings and some even related the drawing with time (Massao 1976). However, the elemental composition of the pigments used by the ancient artists and the preparation of these colours is not well explained.

The paintings in Kondoa-Irangi are now considered as World Heritage but analysis of the composition of the pigments used and those of Singida in central Tanzania has not yet been done. Most of the archaeological researchers suggest the nature of the pigments basedon the remains excavated from the shelter rocks. Bwasiri and Smith (2015) have shown the presence of white kaolin around the rock painting sites so they suggest that white pigment is from kaolin but there is no direct evidence which links the white paints with kaolin. That means there is a need to scientifically determine the composition of the pigments in the white colour used in the ancient paintings of Singida and Kondoa-Irangi rock paintings. The results will show clearly the elemental composition of the white colour pigments used in Singida and Kondoa-Irangi rock paintings. Knowing the chemical composition of archaeological samples is important to make a suitable conservation study (Kaplan *et al.* 2014).

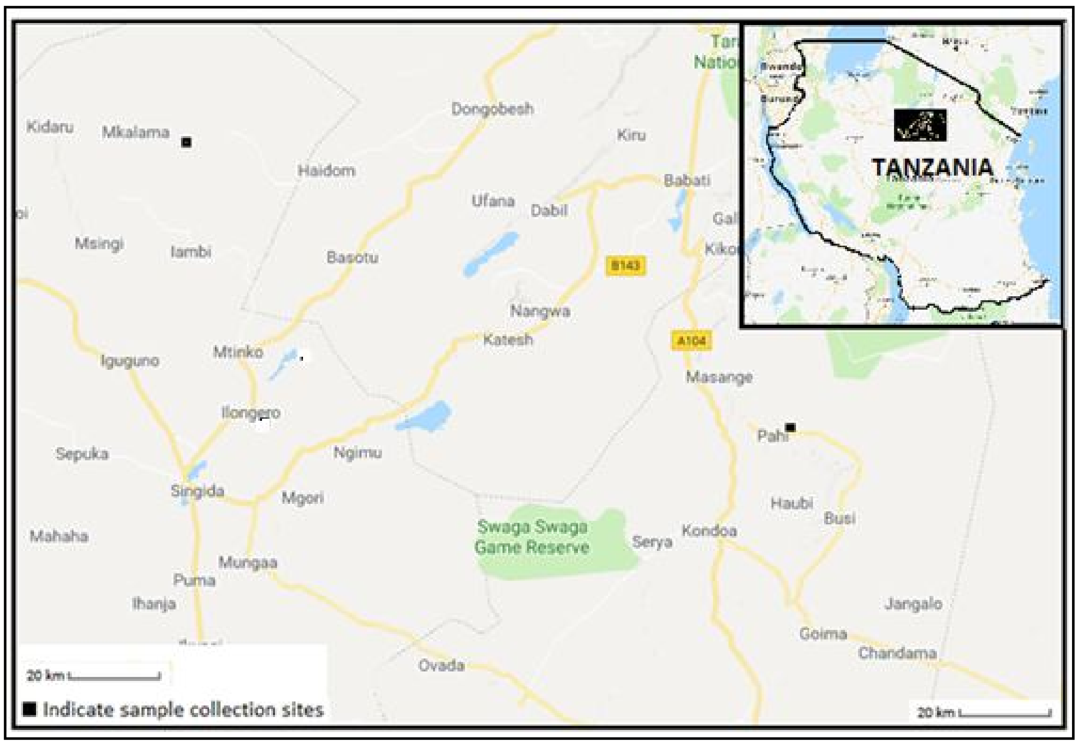
The information from this study can help in preservation and restoration if needed. The elemental composition of the paintings can be used as a guide to scientific dating since the method of dating depends on the elemental composition of a given sample. The chronology of most pigments used by the ancient artists is well known, so knowing the elemental composition of a colour used in a particular painting will lead to pigment characterization of major and minor constituents and allows provenance, age and authenticity of the artefact (Calza *et al.* 2005). San rock art in South Africa was dated following the identification of black pigment as carbon black (Bonneau *et al.* 2012). The results from this study will significantly support our history and depict the trend of our civilization

MATERIALS AND METHODS

Description of the Study Area

Dodoma and Singida are among the regions of central Tanzania in which most of Tanzania's rock paints can be found(Massao 1976).In this study rock art sites situated inMkalama district in the Singida Region and Kondoa district in Dodoma region were used in sample collection. In Singida region Mkalama district samples were collected from three sites namely Mnyeti, Kinyingogo and Isumbirira. These sites are located about 108 km from Singida town by using Singida - Iguguno - Gumanga - Mkalama road. Kondoa Irangi rock art sites are located 9 km east of Dodoma Babati highway and approximately 20 km from Kondoa town. The area of Dodoma region, Kondoa district, bounded by the latitude 4° 26′ 49″S and 4°43′28″S and longitude 35° 43′ 02″E and 35°50′02″E contain about 400 painted sites (Bwasiri and Smith 2015) from about 150 rock shelters which are nominee of the UNESCO and cover an area of about 2336 km^2.

Figure 1: Map showing sample collection sites



Sample Collection From the Site

Samples were collected from Singida region in Mkalama district and Dodoma region in Kondoa district. In Mkalama district three sites namely Mnyeti, Kinyingogo and Isumbirira were used. These sites were selected because the caves are really shelter caves and they are rich in drawings. In Kondoa district samples were collected from Kondoa Irangi rock art sites at Pahi Juu. Since the paintings in Kondoa Irangi are highly protected, the sites for sample collection were selected by the authority of that place.

A technique resemble that of Whitley and Dorn (1984), who used a steel blade to remove very small amount of sample from a painted rock at Great Basin rock art of North America and analyse those samples by using XRF and Scanning Electron Microscopy (SEM), was also applied in this study.After identification of the places where paint samples were going to be collected, the areas on the rocks containing the paints were cleaned to remove upper contaminants like cobwebs and other dirties. Then the steel blades were used to remove a small amount of paint, which was removed with parts of the rock and stored in a plastic container. The containers were then closed tightly, labelled and stored.A small portion of the rock where the paints were drawn but at a place where there are no paints was also collected and labelled as ground. All samples were labelled according to their place of collection.

Sample Preparation

The samples collected contained large particles which were not suitable for WDXRF analysis and so they required to be grounded to a very fine powder. In order to avoid contamination with the grinding instrument, a grinding stone was made from the rock like those rocks from where ancient paints were drawn, for grinding the sample to reduce the size of large particles. It was easy to use hand-held hummer to grind the sample particle to a small size but it was seen that a hummer can introduce some contaminants which are not originally from the sample and so alter the results.

After grinding the sample with the stone, a pestle and motor were used again to grind the sample to get more small particles and then the samples were taken to an electric tungsten grinder in order to get a very fine powder which can be used for analysis in WDXRF.

In order to analyse samples by using WDXRF, the samples have to be prepared in pellet form. A small amount of powdered sample was mixed with a verysmall amount of wax and homogenized. Then powdered boric acid of the same amount as the sample was measured and placed at the bottom of the pressing machine. The powdered boric acid acted as a sample plate and on top of the powdered boric acid the mixture of the sample and wax was placed. A semi-automatic pressing machine was then set for pressing. The machine was adjusted to press the sample with a force of 210 kN. After pressing, a small pellet was formed which was labelled and then taken to an oven to be dried. After drying, the pellets were taken to the WDXRF machine ready for measurements.

All the samples were ground again to a very fine powder, homogenised and dried. The inorganic carbon was removed from the sample by acidification; where 2 ml of hydrochloric acid was added to 1 to 1.7 g of the sample. After acidification, the sample was dried in an oven for overnight. The samples were folded on aluminium foil after being dried to avoid moisture and ready for CHN elemental analysis.

Measurements with WDXRF

The analysis of the paint sample together with the rock samples, which were collected from the rocks from which the paints were drawn, was performed by using a WDXRF spectrometer from the XRF laboratory of African Minerals and Geosciences Centre (AMGC) at Kunduchi Dar es Salaam. The machine was Bruker S8 tiger model which was operated at Rh anode tube voltage of range between 32 to 60 kV and a current of 0.5 to 170 mA. The machine was operated by MDI SRS 3000 software called quant software.

Measurements with CHN Elemental Analyzer

The system was set up for measurement, the oxidation column was installed, and the ash catcher, the cupper column, and the water trap were also installed and inspected.

The acidified samples were weighed in tin capsules. The tin capsule was pressed to remove the air and enclose the sample. The CHN analyzer was switched on. The gases were checked (helium and oxygen), and the instrument furnace and oven temperature were also checked. Then the samples were loaded in a sampler holder and the measurement was carried out.

Minimum Detection Limit

Minimum Detection Limit of WDXRF

The minimum detection limit of an element is the lowest concentration of that element which the machine can detect due to the ability of the quantitative tool to distinguish the peak intensity from the fluctuation of the background intensity. The WDXRF machine which is Bruker S8 tiger model is capable of detecting elements from Boron to Uranium but with different detection limits.

Table 1: The minimum detection limits of the elements for WDXRF used.

Element	MDL (ppm)	Element	MDL (ppm)	Element	MDL (ppm)
Al	138.3	Mn	1.26	S	1.12
Ba	7.12	Na	218.7	Sr	20
Ca	4.64	Ni	0.08	Ti	5.0
Cl	18.4	O	1.18	Zr	24
Cs	4.7	p	0.50	K	10.2
Fe	2.64	Rb	12.7	Si	134.4

Minimum Detection Limit of CHN Elemental Analyzer

The minimum detection limit for carbon for a sample which is about 2 to 3 mg is 0.02% which is equivalent to 0.6 µg/mg. The detection limit can be improved by increasing the amount of sample loaded in the machine.

In this study, white samples were collected from Pahi, Mnyeti, Isumbirira and Kinyingogo. The results of the paint sample and rock sample (ground) are shown below

RESULTS AND DISCUSSIONS

Results from WDXRF

The results of the white colour sample were compared with the rock sample and the elemental composition of white pigments.

The elemental compositions of different white pigments are listed in *Table 2*below.

Table 2: Elemental compositions of different white pigments (von Bohlen 2004)

White pigments			
Antimony white	Sb_2O_3	White lead	$2PbCO_3$ X $PbCrO_4$
Lithopone	$ZnO+BaSO_4$	Zinc white	ZnO
Kaolin	$Al_2Si_2O_5(OH)_4$	Chalk	$CaCO_3$
Permanent white	$BaSO_4$	Gypsum	$CaSO_4X2H_2O$
Titanium white	TiO_2		

Pahi Sample

Table 3: The concentration (in %) of elements in the Pahi white paint sample and ground (rock sample)

Element	Pahi White sample	Ground (rock sample)	Element	Pahi White sample	Ground (rock sample)
Al	4.53	4.96	O	45.3	45.37
Ba	0.08	0.31	P	0.19	0.32
Ca	6	1.76	Rb	0.09	0.11
Cl	0.21	BDL	Sc	0.07	0.03
Cs	0.11	0.09	Si	29.49	31.37
Cu	0.2	BDL	S	1.06	BDL
Fe	2.09	2.81	Sr	0.07	0.05
K	9.94	12.21	Ti	0.29	0.29
Mg	0.25	0.06	Zr	0.0084	0.01
Na	0.2	0.26			

When these results are compared with the elemental composition of white pigments, it can be observed that from the above elements in *Table 3*, Al, Ba, Ca, Ti and S can make white pigments as can be seen in *Table 2.*

Figure 2: Comparison of concentration of elements in white pigment and ground (rock sample) from Pahi site.

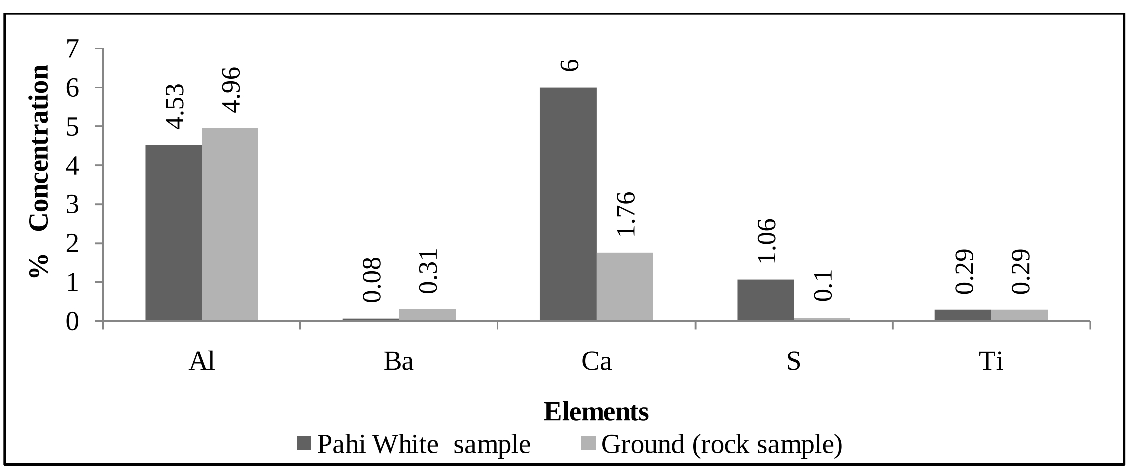


*Figure 2*compares the concentration of white pigment elements in the paint sample and rock sample. It can be seen that no significant increase in concentration in the paint sample for Al, Ba and Ti compared to their concentration in the rock sample. The concentrations of Calcium and Sulphur in the paint sample are greater than their concentration in the ground (rock sample). The increase in concentration suggests that the white paints were from the compounds $CaCO_3$ or $CaSO_4$. This means the pigments used were either Chalk or Gypsum.

Isumbirira Sample

Table 4: The concentration (in %) of elements in the Isumbirira white paint sample and ground (rock sample)

Element	White Isumbirira	Ground (Rock Sample)	Element	White Isumbirira	Ground (Rock Sample)
Al	4.4	2.29	Ni	0.01	0.02
Ba	0.12	0.31	O	46.4	46.75
Ca	2.9	1.94	P	0.12	0.08
Cs	0.15	0.15	Rb	0.06	0.06
Fe	2.54	2.56	Sc	0.06	0.02
K	9.44	9.49	Si	32.36	35.26
La	0.04	0.25	S	0.57	0.14
Mg	0.09	0.15	Sr	0.03	0.03
Mn	0.14	0.1	Ti	0.17	0.13
Na	0.36	0.23	Zr	0.04	0.04

From *Table 4*above, the elements Al, Ba, Ca, Ti and S can make white pigments as can be seen in *Table 2*.

Figure 3: Comparison of concentration of elements in white pigment and rock sample from the Isumbirira site.

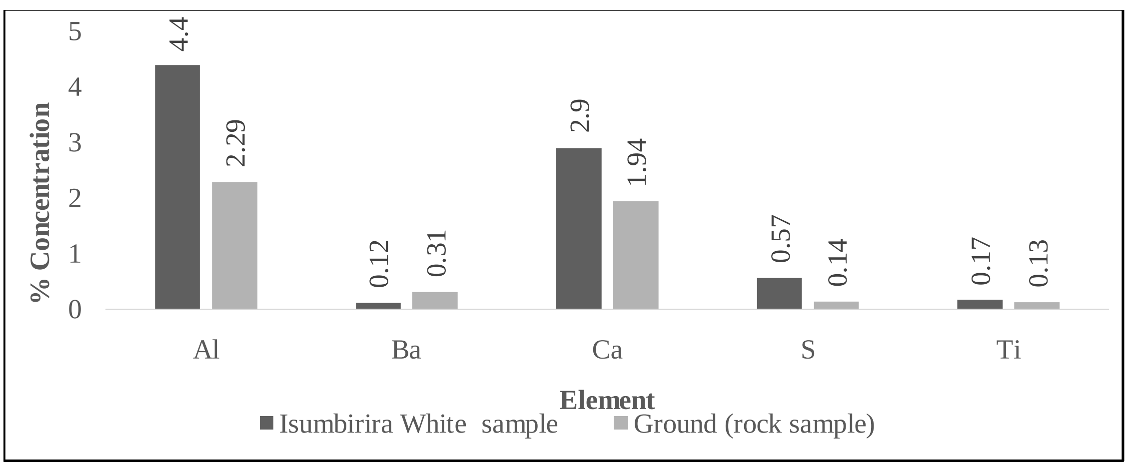


Figure 3 compares the concentration of white pigment elements in the white paint sample from Isumbirira and its rock sample. It can be seen that no significantincrease in concentration in the paint sample for Ba and Ti compared to the rock sample. The concentrations of Aluminium, Calcium and Sulphur in the paint sample are greater than their concentration in the ground (rock sample). The increase in concentration suggests that the

white paints were from the compounds $Al_2Si_2O_5(OH)_4$, $CaCO_3$ or $CaSO_4$. This means the pigments used were either kaolin, chalk or gypsum. Kaolin ($Al_2Si_2O_5(OH)_4$) and gypsum ($CaSO_4X2H_2O$) are the most probable.

MNYETI SAMPLE

Table 5: The concentration (%) of elements in the Mnyeti white paint sample and ground (rock sample)

Element	White Mnyeti	Ground (Rock Sample)	Element	White Mnyeti	Ground (Rock Sample)
Al	3.51	2.63	O	45.44	46
Ba	0.32	BDL	P	0.46	0.19
Ca	12.51	4.12	Rb	0.05	0.08
Cs	0.22	0.16	Sc	0.02	0.07
Fe	2.45	2.9	Si	23.1	31.43
K	6.03	10.11	S	5.23	1.5
Mg	0.1	0.11	Sr	0.16	0.06
Mn	0.12	0.07	Ti	BDL	0.18
Na	0.28	0.34	Zr	BDL	0.03
Ni	BDL	0.02			

From the above elementsin *Table 5*, Al, Ba, Ca, Ti and S can make white pigments. *Table 2* shows their chemical formula.

Figure 4: Comparison of concentration of elements in white pigment and ground (rock sample) from the Mnyeti site.

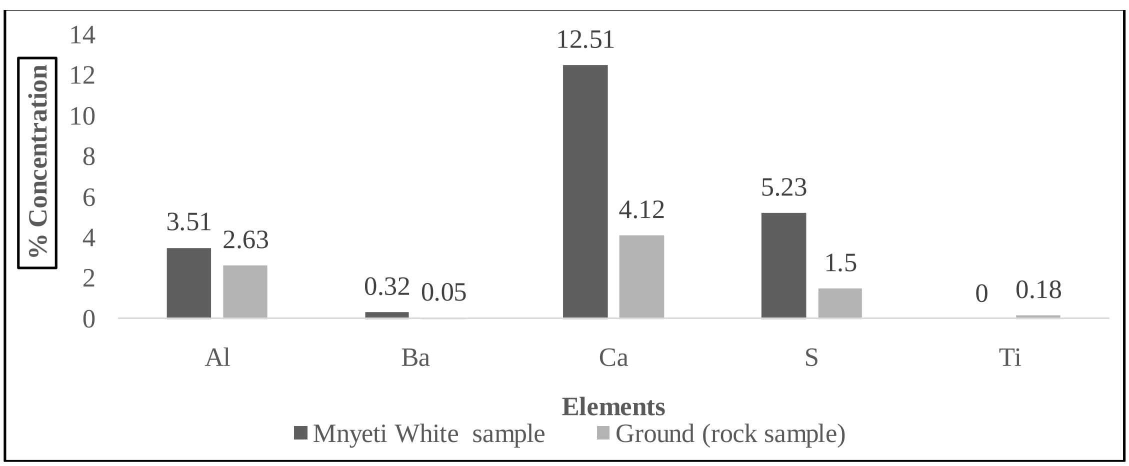


Figure 4 compares the concentration of white pigment elements in the paint sample from Mnyeti and its rock sample. It can be seen that no significant increase in concentration in Ti and Ba in the paint sample compared to their concentration in the rock sample. The concentrations of Aluminium, Calcium and Sulphur in the paint sample are greater than their concentration in the ground (rock sample). The increase in concentration suggests that the white paints were from the compounds $Al_2Si_2O_5(OH)_4$, $CaCO_3$ or $CaSO_4$. However the

increase in the concentration of calcium is very large. This means the pigments used were either chalk ($CaCO_3$) or gypsum ($CaSO_4X2H_2O$).

Kinyingogo Sample

Table 6: The concentration (in %) of elements in the Kinyingogo white paint sample and ground (rock sample)

Element	White Kinyingogo	Ground (rock sample)	Element	White Kinyingogo	Ground (rock sample)
Al	0.44	0.5	Na	0.98	0.94
Ba	0.39	0.28	Ni	BDL	0.08
Ca	25.93	16.89	O	31.74	33.53
Ce	0.1	0.21	P	0.61	0.07
Cl	BDL	0.02	Rb	0.18	BDL
Cs	0.32	0.48	Sc	0.23	BDL
Fe	11.64	13.85	Si	8.7	10.79
K	15.53	17.83	S	BDL	1.72
La	BDL	0.13	Sr	0.77	0.39
Mg	0.56	0.37	Ti	1.33	1.29
Mn	0.55	0.47			

From *Table 6*above, elements Al, Ba, Ca, Ti and S can make white pigments as their chemical formula is shownin *Table 2.*

Figure 5: Comparison of concentration of elements in white pigment and rock sample from Kinyingogo site.

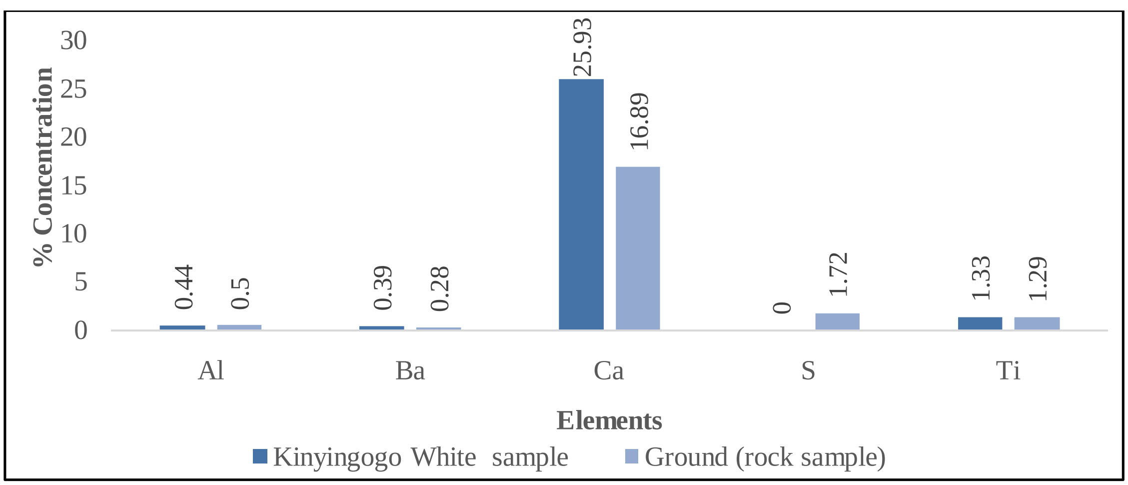


Figure 5 compares the concentration of white pigment elements in the paint sample from Kinyingogo and its rock sample. It can be seen that no significant increase inconcentration in

the paint sample for Al and Ti and a very small increase in Ba, but since S was not detected then Ba cannot make a white pigment. The concentration of Calcium in the sample is greater than its concentration in the ground. The increase in concentration suggests that the white paint was from the compound $CaCO_3$. This means the pigments used werechalk.

Comparison of the results with other researchers

Sugihara *et al.* (2001) used a portable XRF to analyze the pigment used in scroll paintings of a Japan national treasure known as “Tale of Genji” which is in possession of Tokugawa Art Museum and found that the main component in white colour is white lead, though there is trace amount of mercury detected also in the white colour together with white lead, and calcium. Calcium in white pigment is normally related to gypsum and chalk.

The study done by van Rijssen (1990) by X-Ray analysis (E D S) of various pigments used for Khoisan rock paintings shows that white pigments was obtained from clays, also the study suggested that the presence of sulphur and or phosphorus are probably organic in origin. In this study clay was detected only in one site, Isumbirira, and if sulphur is of organic in origin then Kaoline is the most probable pigment for that site.According to different studies done from the year 1987 to the year 2014 shows that pigment used in white paint consist of calcium carbonate or clays (van Rijssen 1987; Rudner 1989; van Rijssen 1990; Wilson et al. 1990; Peisach et al. 1991; Hughes and Solomon 2000; Williamson 2000; Escott et al. 2006; Prinsloo 2007; Prinsloo et al. 2008; Arocena et al. 2008;Tournié et al. 2011; Bonneau et al. 2012; Prinsloo et al. 2013;Bonneau et al.2014). These findings norrows the probability of gypsum being the source of white pigment.

Kessy (2005) reported that white chalks were among the materials found in rock shelter sediments during excavation and suggested that they were brought to the rock shelter for making paintings. Most of the white sample in this study shows the presence of white chalk as the pigment used.

Bwasiri and Smith (2015) have shown the presence of white kaolin around the rock painting sites so they suggest that white pigment is from kaolin, however the presence of kaolin was detected from the sample collected in only one shelter rock known as Kirumi Isumbirira. According to Massao (1976) white pigments are of letter traditions. Due to its structure the Kirumi Isumbirira rock shelter was used till recent years and so there is probability that Kaolin was among latest pigments.

According to Campbell (1994), Tsodilo Hills images were finger painted and made with pigments from hematite (for red), charcoal (for black) and calcrete (for white). Calcrete is calcium rich hard mineral crust formed near soil. In this study all samples contain considerable amount of calcium.

Results from CHN Elemental Analyzer

All samples from the Kondoa, Pahi site, contain some amount of organic carbon. Also, organic carbon was detected in all samples collected from Singida though very little amount of organic carbon was detected from the samples which were collected from Isumbirira rock. These results signify the assumption that there is a high probability that organic binders were used during the preparation of the colours. According to Campbell (1994) the pigments were possibly mixed with animal fat, blood, marrow, egg-white, honey, sap, or urine of which all are organic substance.Gum from aloes was also suggested to be used with white pigment (Hall *et al.*2007), where that has been used as a binder or whitener.

Table 7: The Concentration of carbon in paintings from different sites

Sample Name	% of Carbon in the paint sample
Pahi white sample	0.240
Isumbirira white sample	0.088
Mnyeti white sample	0.394
Kinyingogo white sample	0.396

CONCLUSIONS

This studysuccessfully usedthe nuclear technique in the identification of the pigments used by ancient artists in central Tanzania rock paintings.

Gypsum ($CaSO_4X2H_2O$) and chalk ($CaCO_3$) were identified as the most probable pigments used to make a white colour. Gypsum and chalk are the most probable and not Kaolin ($Al_2Si_2O_5(OH)_4$) as suggested by archaeological researchers though still there is probability that kaolin was used insome areas to make white colour. Detection of a higherconcentration of calcium and sulphur in the white sample than in the ground (rock sample) is the reason to consider gypsum as the most probable pigment used for white colour than any otherbut the presence sulphur can be of organic origin (van Rijssen 1990), and for that case then the most probable pigment will be chalk ($CaCO_3$).

RECOMMENDATIONS

The sample collected containsa large amount of rock so the results obtained could be affected by the composition of the geochemical background. The sulphur detected in the pigments can be from the pigments or from the binder/whitener mixed with pigment, this study recommend further analysis to establish evidence of the origin of sulphur. In situ analysis of the paints and a combination of different methods with the application of more sophisticated analytical instruments is recommended.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr. Ismael N. Makundi, Prof. Hamza M. Njozi, Prof. Najath K. Mohammed, Dr. Fatma K. Mohammed, Dr. O. Ilomo, Prof. Yusuf Koleleni, Dr. N. R. Mlyuka, Dr. F. Banzi, Dr. Eliwasa Maro, Kolo rock art site staff under site manager Zuberi Mabeo, village administrators of Kolo and Pahi in Kondoa, Kirumi and Ikhanoda in Singida and villagers of those place who helped me in showing painted shelter rock places and help me in carrying my instruments for sample collection. Also my siblings,Omari, Hassan, Habiba and Mwanaima, my wife and daughters who supported me throughout the work.

REFERENCES

Arocena JM Hall K and Meiklejohn KI 2008 Minerals provide tints and possible binder/extender in pigments in San rock paintings (South Africa), Geoarchaeology, 23(2), 293–304.

Ball P 2001 Bright Earth: The Invention of Colour; London, Pengium

Barnett JR, Miller S and Pearce E 2005 Colour and Art: A Brief History of Pigments, *Optics and Laser Technology* 38: 445-453.

Bonneau A, Pollard AM and Pearce DG 2012 A Multi-technique Characterization And Provenance Study of the Pigments Used in San Rock Art, South Africa. *Journal of Archaeological Science* 39: 287-294.

Bonneau A Hoerlé S Pearce D and Pollard AM 2014 A multi-technique characterization study of the pigmentsused in San rock art.*Paleo***Numéro spécial**, 57–9.

Bwasiri EJ and Smith BW 2015 The Rock Art of Kondoa District, Tanzania, *Azania:Archaeological Research in Africa*, 50(4): 437-459

Calza C, Anjos MJ, Mendonça deSouza SMF, Junior AB, Lopes RT 2005 X-Ray Microfluorescence Analysis of Pigments in Decorative Paintings from Sarcophagus Cartonage of an Egyptian Mummy INAC 2005, Santos, SP, Brazil.

Campbell, A. 1994. Tsodilo Management Plan Scheme of Implementation. Gaborone:Government Printer

Escott B Hughes JC and Schulze D 2006 An archaeometric study of Later Stone Age paintings from KwaZulu-Natal, South Africa, Paper presented at the 18th World Congress of Soil Science, 9–15 July 2006.

Hall K Meiklejohn I and Arocena J 2007 The thermal responses of rock art pigments: Implications for rock art weathering in southern Africa. *Geomorphology* **91**, 132–145.

Hall K Meiklejohn I Arocena J Prinsloo L Sumner P and Hall L 2007 Deterioration of San Rock Art: New Findings, New Challenges. *South African Journal of Science*103:361-362.

Haynes JL 1992 Nubia Ancient Kingdoms of Africa Museum of Fine Art, Boston.

Hughes JC and Solomon A 2000 A preliminary study of ochres and pigmentaceous materials from KwaZulu-Natal, South Africa: towards and understanding of San pigment and paint use, *Natal Museum Journal of Humanities*, **12**, 15–31.

Kaplan M Arican P Kalayci Y Senyurt SY Akcay A and Kamis Y 2014 Inorganic Paint Pigment Analysis in Ovaoren Ceramics by Micro XRF Spectrometry. *International Interdisciplinary Journal of Scientific Research*1(1): 157-164.

Kessy ET 2005 The Relationship Between the Later Stone Age (LSA) and Iron Age (IA) Cultures of Central Tanzania PhD Dissertation, Simon Fraser University.

Kessy ET 2011 Determining Rock Art Authorship from Excavated Remains of Kondoa, Central Tanzania *Anthropos***106:** 563–578

Massao FT 1976 The Letter Stone Age and the Rock Painting of Central Tanzania PhD. Thesis, Simon Fraser University.

Peisach M Pineda CA and Jacobson L 1991 Nuclear analytical study of rock paintings, *Journal of Radioanalytical and Nuclear Chemistry Articles*, **151**(1), 221–7.

Prinsloo LC 2007 Rock hyraces: a cause of San rock art deterioration? *Journal of Raman Spectroscopy***38**, 496–503.

Prinsloo LC Barnard W Meiklejohn I and Hall K 2008 The first Raman spectroscopic study of San rock art in the Ukhahlamba Drakensberg Park, South Africa, *Journal of Raman Spectroscopy***39**(5), 646–54.

Prinsloo LC Tournié A Colomban P Paris C and Bassett ST 2013 In search of the optimum Raman/IR signatures of potential ingredients used in San/Bushman rock art paint, *Journal of Archaeological Science***40**, 2981–90.

Rudner I 1989 The conservation of rock art in South Africa, National Monuments Council, Cape Town.

Sugihara K Tamura K Satoh M Hayakawa Y Hirao Y Miura S Yotsutsuji H Tokugawa Y Analysis of pigments used in scroll paintings of a national treasure "Tale of Genji" using a portable x-ray fluorescence spectrometer. *Adv X-ray Anal.* 2001; 44:432–41.

Tournié A Prinsloo LC Paris C Colomban P and Smith BW 2011 The first in situ Raman spectroscopic study of San rock art in South Africa: procedures and preliminary results, *Journal of Raman Spectroscopy***42**, 399–406.

van Rijssen JJ 1987 Paintings in peril, South African *Archaeological Bulletin***42**, 5–9.

van Rijssen WJ 1990 Analysis of South African rock art pigments by X-ray fluorescence spectroscopy (EDS), *South African Archaeological Bulletin* 45, 58–9.

von Bohlen A 2004 Total Reflection X-ray Fluorescence Spectrometry – A Versatile Tool for Ultra-micro Analysis of Objects of Cultural Heritage. *e-Presarvation Science***1**:23-34.

Williamson BS 2000 Direct testing of rock painting pigments for traces of haemoglobin at Rose Cottage Cave, South Africa, *Journal of Archaeological Science***27**, 755–62.

Wilson ML van Rijssen, W JJ and Gerneke DA 1990 An investigation of the Coldstream Stone, *Annals of the South African Museum***99**(6), 187–213.

Whitley DS and Dorn RI 1984 Chemical and Micromorphological Analysis of Rock Art Pigments From the Western Great Basin *Journal of New World Archaeology***6**(3): 48-51.