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Geochemical characterisation of archaeological sites in Mapungubwe National Park, South Africa

Authors:
Bongumenzi S. Nxumalo[1,2]
Federica Sulas[3]
Innocent Pikirayi[1]

Affiliations:
[1]Department of Anthropology, Archaeology and Development Studies, Faculty of Humanities, University of Pretoria, Pretoria, South Africa

[2]Department of History, Faculty of History, Northwestern University, Evanston, United States of America

[3]Department of Historical Studies, University of Gothenburg, Göteborg, Sweden

Corresponding author:
Bongumenzi Nxumalo,
bongumenzi.nxumalo@up.ac.za

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Research projects in the Shashe-Limpopo Basin have witnessed significant developments in the use of conceptual frameworks and multidisciplinary approaches such as electrochemical and geochemical sequencing. Accordingly, there is now data to question the widely accepted model for the evolution of Mapungubwe State (AD 1200–1300) which argues that favourable and unfavourable regional climatic weather conditions (wet and dry) lead to the rise and decline of the State. Floodplain agropastoral activities in the middle Limpopo Valley are a widely assumed hypothesis, despite the general absence of relevant chemical signatures and archaeobotanical data. This article discusses soil sequences and chemical analyses (Inductively Coupled Plasma Atomic Emission Spectroscopy and Redox Potential) to provide a palaeoenvironmental record of water regimes in relation to Mapungubwe. Findings confirm that geochemical techniques can be used to model or predict aquifer behaviour and the occurrence of groundwater. And, as such, highlighting the need for conservation planners to carefully consider integrative scientific tools to improve conservation practices of archaeological heritage and overexploitation of groundwater resources. Although more data is required, the results obtained allows researchers to begin reframing questions concerned with the links between changing water regimes and social changes, in this case relating to the decline of Mapungubwe. The understanding is important for the management and conservation of the Mapungubwe World Heritage site and surrounding landscape.

Keywords: Shashe-Limpopo Basin; middle Limpopo Valley; geochemistry; electrochemistry; Inductively Coupled Plasma Atomic Emission Spectroscopy.

Introduction

Agropastoral activities constitute most of Africa's livelihoods. Due to increasing population density, many societies generally occupy low lying valley plains, including borderline regions, to sustain themselves through crop production and animal husbandry. Mapungubwe (AD 1237–1697) is one such locality where socio-political and cultural developments are thought to have been established by a farming community near the confluence of Shashe-Limpopo Rivers (Huffman 1996, 2007; Manyanga 2000; Meyer 2000; Nxumalo 2019, 2021). Mapungubwe is regarded, among many farming sites in southern Africa, as among the most prominent and significant pre-colonial farming sites (Huffman 1996, 2000; Maggs & O'Connor 2000; Meyer 2000; Nxumalo 2019; Sadr 2008).

At about AD 1000–1250, when the Medieval Warm Epoch commenced, the dry Shashe-Limpopo Basin became wetter (Maggs & O'cconor 2000; Manyanga, Pikirayi & Ndoro 2000; Smith 2005; Smith, Lee-Thorp & Hall 2007). This was the period during which early Zhizo farming communities moved into the Shashe-Limpopo Basin and engaged in smelting iron, cultivating crops and exploiting long-distance trade which bolstered a bureaucratic government system (Huffman 1996, 2007; Manyanga 2006; Wood 2000). Huffman (1996, 2000) has argued that these developments were enabled by a wetter climate. In turn, the decline of Mapungubwe State has been linked to climate changes associated with the Little Ice Age (long-term drying) and large-scale migration out of the middle Limpopo Valley to more favourable regions in Zimbabwe (Huffman 1996, 2007; Smith et al. 2007). This, it has been suggested, gave rise to the Zimbabwean culture around the 13th century AD (Huffman 2000). However, the climate hypothesis does not explain the archaeological and historical data, which suggests that some communities may have remained in the middle Limpopo Valley even after the environment deteriorated (Manyanga 2003, 2007; O'Connor & Kiker 2004; Smith 1970). The reasons for Mapungubwe's decline are still debated, but a number of researchers (e.g. Huffman 2007; Scoones 1996; Smith et al. 2007) emphasise the role played by climate change leading to the subsequent abandonment of the middle Limpopo Valley.

Note: Special Collection: Celebrating Cultural Heritage within National Parks.

Research trends (e.g. Bradfield & Antonites 2017; Ekblom et al. 2012) have been conducted at Mapungubwe National Park to reconstruct palaeoenvironments and show ways in which humans may have interacted with their landscapes and responded to environmental change. For example, Ekblom et al. (2012) examined palaeoenvironmental proxies (fossil pollen, spores and diatoms) across the savannah vegetation biome and riparian settings to reconstruct moisture changes in the Kruger National Park (KNP) in South Africa and Limpopo National Park (PNL) in Mozambique. Accordingly, the analysis of diatom assemblages showed that planktonic taxa were preferred over benthic taxa, a pattern linked to weakened water attenuation and by inference, meaning improved moisture contents (Ekblom et al. 2012). This was while the palaeoecological analysis of savanna grassland vegetation cover shows that it was generally resilient against changing environmental conditions (Gillson & Ekblom 2009).

Together, these results showed that the middle Limpopo River Valley may have been episodically drier and wetter during AD 900–1300, than has been commonly accepted in the climatic hypothesis. Supporting evidence from stalagmite series T7/T8, calibrated using alpha dating series and high-resolution isotopic (δ18O) signatures, indicate that the Medieval Warm Epoch was characterised by unpredictable warming and high precipitation records (Holmgren et al. 2003; Huffman 2000; Tyson & Lindsey 1992). According to Bradfield and Antonites (2017), use of ware analysis from bone (i.e. bovine scapulae and long bone) suggests that Iron Age farmers in the middle Limpopo River Valley may have used bone hoe technology interchangeably with iron tools on the landscape. However, this technology remains poorly understood and speculative due to the lack of experimental studies in the region. As such, it is vital to examine new data on environmental change, linked with a discussion of possible strategies in response to environmental changes.

The detailed analysis of environmental proxies and water data in the literature of state-based societies in southern Africa is lacking (Pikirayi 2006, 2018; Pikirayi et al. 2016, 2022). The lack of suitable environmental proxies for reconstructing palaeodrainage systems has made it very difficult to test previously adopted models of climate-induced cultural transformations occurring in the Mapungubwe landscape. Geoarchaeological investigations (e.g. geochemistry) make it possible to begin the re-evaluation of cultural transformations in relation to climate variability. The study discussed in this article sought to identify and test viable techniques and approaches to examine cultural transformation in the middle Limpopo Valley.

Research methods and design

Regional setting

The middle Limpopo Valley region represents an important strand of research showing relevant developments of socio-political institutions about the emergence of metallurgy and agropastoralism in southern Africa (Nxumalo 2019, 2021; Sulas et al. 2013). Such developments over time are best illustrated by the Mapungubwe Hill, located about 3.5 km away from the Shashe-Limpopo confluence and its floodplains between Botswana, South Africa, and Zimbabwe (see Figure 1).

The present Mapungubwe landscape opens up to a series of geomorphic landforms such as valley plains, hills, low mountains, and gently sloping foothills. Topography changes subtly with altitude (600 m). The ecotype is semi-arid, and Mopani veld vegetation is found on the low-lying sandstone ridges. Rainfall seasons are between November and March of each year (Nxumalo 2016, 2019, 2021). Climate variability in the middle Limpopo Valley is induced by the Inter Tropical Convergence Zone (ITCZ), the Subtropical Eastern Continental Moist Maritime system (linked to regular occurrence of cyclones), the dry continental tropical, and west Mediterranean air masses responsible for winter rains (see Food and Agriculture Organization [FAO] 2004; Pomposi et al. 2017; Tyson & Preston Whyte 2000). These air masses shape a north to south rainfall gradient towards the Limpopo River. The four rainfall stations (Musina, Polokwane, Louis Trichardt and Beitbridge) show that the Shashe-Limpopo Basin receives an average mean rainfall circulation that ranges from 350 mm to 600 mm of precipitation annually (Nxumalo 2016, 2021). This precipitation occurs with occasional erratic rainfall peaks and droughts (FAO 2004; Nxumalo 2016, 2019, 2021; Venter, Scholes & Eckhardt 2003).

Researchers such as Zhu and Ringler (2010) and Holland (2011) have shown that rains in the Shashe-Limpopo Basin are influenced by the movement of low-pressure cells across oceanic currents (both Atlantic and Indian Ocean), the El Niño–Southern Oscillation (ENSO), and the displacement of the ITCZ. Accordingly, the Shashe-Limpopo Basin catchment is subject to occasional appearance of tropical cyclones which results in increasing inundation of tributary streams and sandstone ridges associated with occasional flooding of the Shashe and Limpopo Rivers (see Nxumalo 2016, 2019).

The geomorphological sequence and geological supergroup across the valley stem from Precambrian crust surfaces as well as Bushveld Igneous Complexes (De Wit & Roering 1990; Holland 2011; Nxumalo 2019, 2021). These geological complexes have a bearing on regional topography and hydrological corridors which are characteristic of sandstone ridges and igneous rock outcrops (De Wit & Roering 1990; Holland 2011; Nxumalo 2019, 2021). Moreover, the landforms and soil types are defined as red weathering Karoo sandstones, clay stones, shales and coal deposits. The main soil types in the middle Limpopo valley are broadly divided into two main groups: older soil (from weathered parent material) and younger soil (from erosional activities) types (Chinoda et al. 2009; Holland 2011; Nxumalo 2016, 2019, 2021; Roering et al. 1992). Overall, soil types change from a dark brown to dark reddish clay loams, also known as black basalt, and these are important for growing crops (Anderson et al. 1993; Blenkinsop 2011; Holland 2011). In turn, the

Source: Nxumalo, B.S., 2019, 'Integrating geoarchaeological approaches and rainfall modelling as a proxy for hydrological changes in the Shashe–Limpopo Basin, South Africa', *South African Archaeological Bulletin* 74(211), 67–77

Note: The red and yellow polygon in inset A represents the middle Limpopo Valley archaeological sites discussed in this article (Samaria, Schroda, Mapungubwe Hill, K2 Valley and Leokwe Rest Camp).

FIGURE 1: Map showing archaeological sites in the Shashe-Limpopo Basin (inset A and B).

chemical composition (Ferralsols and Acrisols) of these soils makes them attractive for private game farms especially where soil fertility is improved by access to water (Chinoda et al. 2009; FAO 2004; Huffman 2007).

Conceptual framework

This article takes on a landscape archaeology approach to understand the relationship between people and their environments. Landscape is here seen as a medium allowing to capture the ways in which people and the natural world interact and influence each other. This methodological approach has improved the understanding of microscale components of archaeological sites that were not observable using traditional archaeological excavation methods such as settlement patterns and spatial attributes (Bender 2002; Bruno & Thomas 2008; Crumley 2007). For example, the chemical and physical properties of buried soil sediments are valuable proxies for determining climatic conditions, cultural activities, and resource-use across archaeological sites. In turn, soil sediments may retain atmospheric deposition of chemical elements and from anthropogenic activities due to material inputs, either intentional or unintentional domestic factors and soil formation processes (Davidson et al. 2006; Fleisher & Sulas 2015; Murray, Rogers & Kaufman 2004; Norton 2007; Nxumalo 2019, 2021; Wilson, Davidson & Cresser 2009).

Investigations focusing on geochemical patterning across abandoned archaeological sites of Engaruka, in Tanzania have revealed that there is a significant uniformity in the concentrations of elements and patterning (see Fleisher & Sulas 2015; Sulas & Madella 2012; Sulas et al. 2019). The wide range availability of phosphorus (P) concentrations can be associated with cattle kraals and middens, while the increased concentrations of elements such as lead (Pb) were associated with hearth floors on abandoned archaeological sites (Fleisher & Sulas 2015; Sulas & Madella 2012; Sulas et al. 2019). It is from this relational context that geochemical characterisation in the form of soil element concentrations and their analysis have been mapped out in this article to evaluate the spatial patterns across archaeological sites in the middle Limpopo Valley. Like the Tanzanian studies, this article makes use of chemical and physical properties of buried soils to provide indications of cultural activities and resource-use over time. These methodological approaches enable researchers to understand the significance of soil in determining the distribution pattern of past societies in the middle Limpopo Valley.

This article reports on electrochemical or Redox potential from buried soil surfaces to provide proxies for evidence of the water content. The Redox potential characterises the measure or the capacity to either release or accept electrons from chemical reactions within a chemical substance (De Beer, Seither & Vorenhout 2016; Maharana, Srivastava & Tripathi 2018; Mausbach & Richardson 1994; Schaetzl & Anderson 2005; Shoemaker, Ervin & Di Orio 2017; Verpraskas 1999). It is measured in millivolts (mV) to capture the frequency of chemical substances either to reduce or oxidise other substances (De Beer et al. 2016; Schaetzl & Anderson 2005). For example, the Redox potential characterises the degree of reduction and predicting stability of various compounds that control nutrients and metal availability in sediment profiles (Maharana et al. 2018; Pansu & Gautheyrou 2006). As illustrated in Table 1, the Redox potential of soil is separated into four phases. Phases 1–2 represent the degree of oxidation conditions, where water is drained out of soil surface environments and leads to the restoration of aerobic conditions. Phases 3–4 characterise reducing conditions where water contents gradually percolate across soil surfaces such that oxygen is fully depleted and pore spaces are replenished with damp conditions.

TABLE 1: List of samples and types of analysis done from Samaria, Leokwe Rest Camp (LKC), and K2 Valley.

Number	Site name	Depth (cm)	Analysis
1	Denstaat	30–40	ICP-AES & Redox Potential
2	Leokwe Rest Camp (LKC) 1/1	10–35	ICP-AES & Redox Potential
3	K2/1.1	20–32	ICP-AES & Redox Potential
4	Samaria GA1/1	0–10	ICP-AES & Redox Potential
5	Samaria GA2/1	0–8	ICP-AES & Redox Potential
6	Samaria GA/2/2	8–28	ICP-AES & Redox Potential
7	Samaria GA4/1	0–12	ICP-AES & Redox Potential
8	Samaria GA4/2	12–17	ICP-AES & Redox Potential
9	Samaria GA4/3	35–54	ICP-AES & Redox Potential
10	Samaria GA5/1	0–10	ICP-AES & Redox Potential
11	Samaria GA5/2	10–42	ICP-AES & Redox Potential
12	Samaria GA5/3	45–57	ICP-AES & Redox Potential
13	Samaria GA6/1	0–8	ICP-AES & Redox Potential
14	Samaria GA6/2	8–42	ICP-AES & Redox Potential
15	Samaria GA6/3	42–54	ICP-AES & Redox Potential
16	Samaria GA7/1	0–8	ICP-AES & Redox Potential
17	Samaria GA7/2	8–40	ICP-AES & Redox Potential
18	Samaria GA7/3	40–55	ICP-AES & Redox Potential
19	Samaria GA8/1	0–5	ICP-AES & Redox Potential
20	Samaria GA8/2	5–15	ICP-AES & Redox Potential
21	Samaria GA8/3	15–31	ICP-AES & Redox Potential
22	Samaria GA8/4	31–48	ICP-AES & Redox Potential
23	Samaria GA8/5	48–60	ICP-AES & Redox Potential
24	Samaria GA9/1	0–20	ICP-AES & Redox Potential
25	Samaria GA9/2	20–44	ICP-AES & Redox Potential
26	Samaria GA9/3	44–54	ICP-AES & Redox Potential
27	Samaria GA10/1	0–7	ICP-AES & Redox Potential
28	Samaria GA10/2	7–15	ICP-AES & Redox Potential
29	Samaria GA11/1	0–4	ICP-AES & Redox Potential
30	Samaria GA11/2	4–19	ICP-AES & Redox Potential

Note: The GA code in Samaria represents systematic test pits.

According to the four phases of Redox potential, oxidation involves the loss of electrons and reduction implicates the net gain of electrons by an atom, molecule or ion (Schaetzel & Anderson 2005; Verpraskas 1999). Although Redox measurements are semi-quantitative, they are a useful proxy to the measure of soil potential. Soils and their structural integrities undergo irregular periods of oxidation and reduction, and these are expressed as Redox conditions (De Beer et al. 2016; Maharana et al. 2018; Vepraskas 1999). For example, in oxidising conditions, iron (Fe) and manganese (Mn) cations (and their related minerals) tend to be motionless and impart a brown or red colour to the soil. This is due to the free entry of oxygen into the soil, which leads to a brown or red coating on the soil. The displacement of iron oxides is coordinated by the behaviour of water and atmospheric conditions (e.g. oxygen). Reducing changes the soil to shades of grey, green, or other pale hues (De Beer et al. 2016; Maharana et al. 2018; Mausbach & Richardson 1994; Schaetzl & Anderson 2005). In the context of soil surface environments, during periods when water is obstructed or hindered, water may saturate the soil openings and consequently result in poorly aerated soils (Ahn 1970; Fitzpatrick, Wright & Stevens 1993). In turn, these redox conditions may force smaller organisms to acquire oxygen from the iron compounds by reducing the iron from the ferric form to a ferrous one (Ahn 1970:99–101). A number of studies (e.g. Chen & Thompson 2021; Maharana et al. 2018; Shoemaker et al. 2017; Wilmoth 2021) have shown that ferrous iron constantly moves in the soil surface environment and can be stopped by oxidation back to the ferric form.

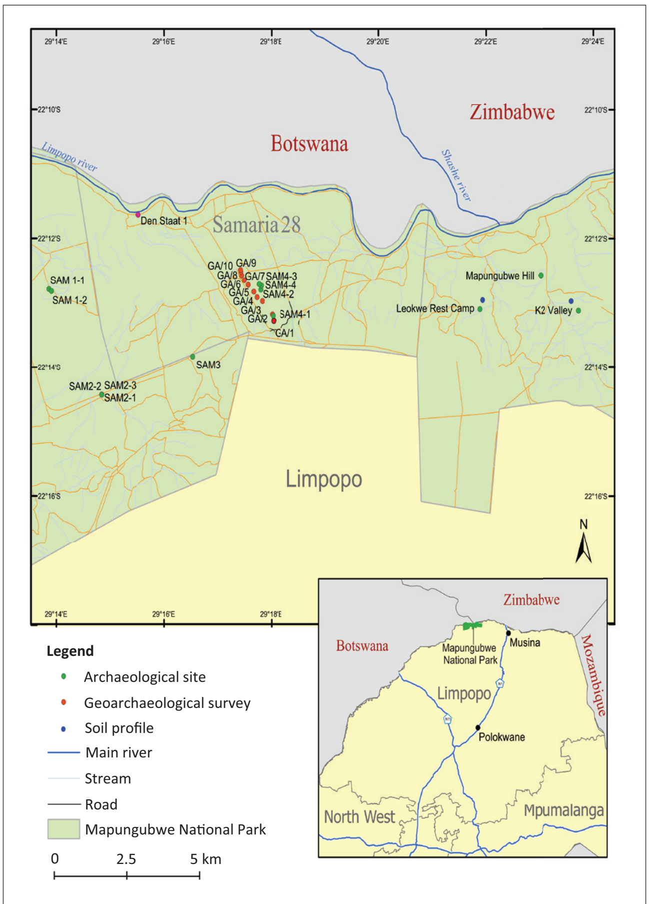
As observed elsewhere (e.g. Chen & Thompson 2021; Fitzpatrick et al. 1993; Mausbach & Richardson 1994; Schaetzl & Anderson 2005; Shackley 2004), Redox conditions affect iron oxides found in soils and, in turn, they are affected by the nature of biological activities and hydrological cycles. The analysis of geochemical data provides a context for comparing the Redox results to assess the moisture contents. As such, the integration of electrochemical potential and geochemical characterisation is important for this study as it helps to understand past people's interaction with their surroundings.

Methodological approach

To develop a geochemical and an electrochemical signature, a series of systematic geoarchaeological borehole surveys, across archaeological landscapes of the middle Limpopo Valley, were conducted 500 metres apart to document and retrieve palaeoenvironmental data from buried soil surfaces. The boreholes reached the bedrock (*ca.* 2.5 m variably). The borehole surveys began from the higher grounds of Samaria farm towards Denstaat and the middle Limpopo Valley (see Figure 2).

The bulk of the surveys were conducted in Samaria archaeological areas that are consistent with the local archaeological context and occupation sequences at Mapungubwe (Huffman 2000; Sulas, Antonites & Chauke 2012). The region was specifically selected because it showed undisturbed horizons whereas those around the middle Limpopo Valley (Leokwe Rest Camp, K2, and Mapungubwe) have disturbed sequences resulting from tourism-related activities and extensive research excavations. Soil profiles and sediments from exposed gully streams were documented as well as cored. This article reports on soil samples in isolation because the surveys targeted predetermined buried soil horizons and their significance in capturing information about changing environmental conditions and soil paedogenic processes.

The electrochemical (Redox) potential was analysed by mixing 10 grams of sediment with 20 mL (measured using a 40 mL syringe) de-ionised water and a magnetic stirring device for about 30–45 s. The pH and Redox measurements were measured using a PL700 series bench top multi-parameter meter and silicon chip probe electrode. Three replication measurements were run per sample and the full results are given in the data and results section. The data gathered from archaeological deposits was processed at two different locations: at the ASL Chemex laboratory in Johannesburg for Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and University of Pretoria (South Campus Laboratory) for electrochemical analysis. Eight trace elements, namely copper (Cu), iron (Fe), manganese (Mn), phosphorus (P), nickel (Ni), zinc (Zn), chromium (Cr) and magnesium (Mg) were selected because they are significant proxies of past and present environmental conditions. Notably, the concentration of these elements influences mineralogy of soil parent material, soil moisture regime, and characteristics of the groundwater (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992; Nxumalo 2016, 2019).



Source: Sulas, F., Pikirayi, I. & Nxumalo, B., 2013, 'Geoarchaeological survey and soil sampling at Mapungubwe, June 2013: Technical report', University of Pretoria, Pretoria

FIGURE 2: Map showing locations of the geoarchaeological survey in red dots and archaeological sites in green and blue dots.

Results

Geoarchaeological surveys

The geoarchaeological surveys recorded soil cover, landforms and landscape sequences.

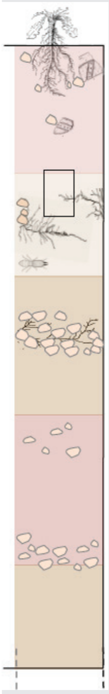
Published and unpublished sources (e.g. FAO 2004; Nxumalo 2019, 2021; Sulas et al. 2012) show that the reddish-brown soils are linked to the red weathering Karoo sandstone, and inclusions of aeolian deposit from Kalahari sands. Meanwhile, the dark brown sediments cannot be traced to a known geologic origin but occur in abundance in the valley bottoms with organic rich profiles, low lying water tables and biological activities (FAO 2004; Nxumalo 2019, 2021; Sulas et al. 2012). Accordingly, 30 loose soil sediment samples were retrieved from the borehole survey and soil sampling across Samaria settlement complexes as well as Leokwe Rest Camp (LKC) and K2 Valley for multi-element chemical and electrochemical analysis (see Table 1). Soil samples from the predetermined buried sediments in Denstaat, Leokwe Rest Camp, K2 and Samaria area are presented in Table 2. Essentially, Samaria provided undisturbed archaeological landscapes (control site) with a potential for the recovery of palaeoenvironmental proxies and comparisons with the greater region. The soil samples from the middle Limpopo Valley were processed to generate chemical elements as shown in Table 3.

The concentration levels for the eight chosen elements characterising a modern surface are as follows: Cu (1 ppm – 40 ppm), Fe (0.5% – 5%), Mn (437 ppm), P (300–650), Ni (1 ppm – 450 ppm), Zn (10 ppm – 300 ppm), Cr (5 ppm – 120 ppm) depending on rock (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992; Tisdale et al. 1985). Felsic and sedimentary rocks have high (Cr) and Mg concentrations that vary from 0.75% to 2% (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992; Oze, Bird & Fendorf 2007; Tisdale et al. 1985). These standard values are used as controls for interpreting the chemical signature of buried soils.

The chemical sequence from the 11 samples collected from Samaria (GA1/1 to GA11/1) shows both high and low element concentrations. Phosphorus, manganese, chromium and iron contents decrease with topography towards the Limpopo River floodplain: from high values

TABLE 2: Samaria Geoarchaeological Soil profile (GS 7/1 soil profile).

Profile	Geographic coordinates and Field notes
SAMARIA GS 7/1	S 22°12′39′′ – E 29°17′44′′ The area continues from GS 06 (*ca.* 500 m away), similar in topography, consists of sparsely distributed baobabs, some green leafed tree (possibly *Colophospermum mopane*), acacia vegetation and low grasses. Many ceramics are scattered on the site (black in colour, probably K2 or Mapungubwe period), with some being washed downslope.



Depth (cm)	Description	Unit	Sample	Photograph
0–8	Reddish light brown soils (7.5YR 3/3 on dry and 3/4 on wet soil); some fresh roots and ceramics	Topsoil	Bulk	
8–20	Light brown soils (5YR 3/4 on dry and wet sample); many rootlets, some biological activity, very fine sand silty loam	subsoil	Micromorphology (11 cm – 19 cm) and Bulk	
20–40	Coarse deposit (*ca.* 3 cm – 5 cm small pebbles); may have been coursed by flooding. Coarse material seems to have been washed site. Some fresh roots	Alluvial, very coarse deposit?		
40–55	Reddish brown soils (7.5YR 3/3 on dry and wet sample); well sorted and very fine silty loam	Buried soil	Bulk	
55–60	Very coarse layer. Dark brown soils (10YR 2.5/2); very fine silty loam	Buried alluvium?		

Source: Adapted from: Nxumalo, B., 2016, *Hydrological modelling of rainfall patterns and societal demise in the Mapungubwe landscape, South Africa*, Unpublished MA thesis, University of Pretoria

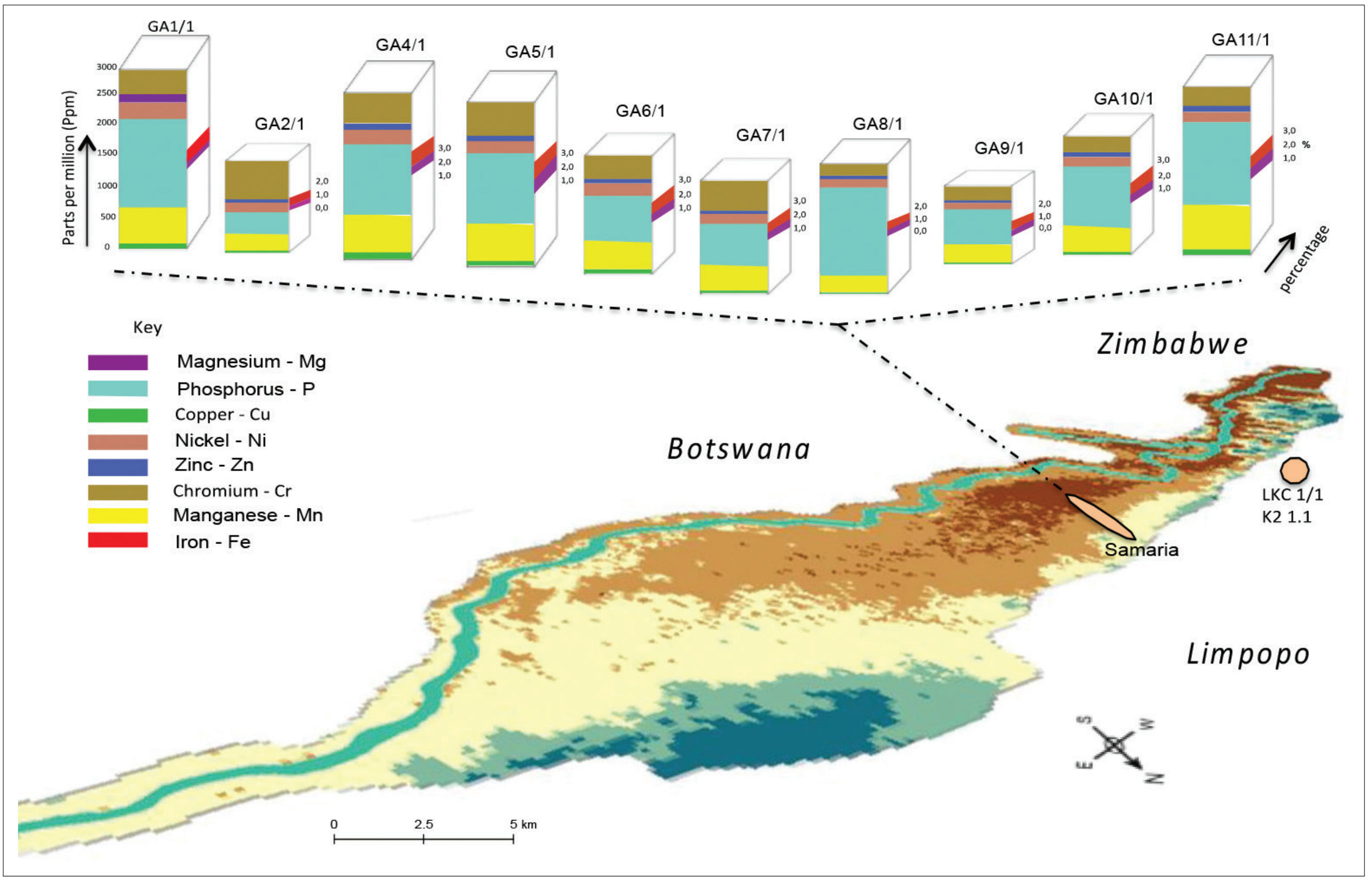
TABLE 3: A presentation of ICP-AES results in part per million (ppm) and percentage of trace elements from the Shashe-Limpopo Confluence zone: Denstaat, Leokwe Rest Camp (LKC), K2, and Samaria.

Sample	Ppm						%	
	Copper (Cu)	Manganese (Mn)	Phosphorus (P)	Nickel (Ni)	Zinc (Zn)	Chromium (Cr)	Iron (Fe)	Magnesium (Mg)
Denstaat 1/1	47	743	950	70	65	193	4.73	1.26
LKC1/1	27	349	310	208	31	242	2.99	9.42
K2/1.1	14	196	360	31	14	40	1.6	0.4
Samaria GA1/1	41	507	2190	193	49	445	3.21	1.94
Samaria GA2/1	22	275	340	103	26	641	1.82	0.75
Samaria GA4/1	40	541	1280	189	47	490	3.54	2.71
Samaria GA5/1	29	538	900	184	42	442	3.25	2.06
Samaria GA6/1	24	396	570	129	36	303	2.58	1.51
Samaria GA7/1	22	365	440	115	28	302	2.36	1.2
Samaria GA8/1	17	246	2210	43	35	179	1.48	0.49
Samaria GA9/1	17	245	450	66	24	196	1.68	0.61
Samaria GA10/1	26	331	780	81	37	187	2.25	1.01
Samaria GA11/1	39	532	830	81	56	171	2.96	1.08

Source: Adapted from: Nxumalo, B., 2016, *Hydrological modelling of rainfall patterns and societal demise in the Mapungubwe landscape, South Africa*, Unpublished MA thesis, University of Pretoria
Note: The trace element analysis were carried out by ASL Chemex laboratory, Johannesburg.
GA, systematic test pits.

on higher ground (Profile GA1/1:P 2190 ppm, Mn 507 ppm, Zn 49 ppm, Cr 445 ppm, Fe 3.21%) to lower values in the central area (GA7/1: P 440 ppm, Mn 365 ppm, Zn 28 ppm, Cr 302 ppm, Fe 2.36%). The profiles located further towards the Limpopo River show a less coherent chemical signal with alternating patterns of high and low values (see Figure 3).

Increased values of the eight trace elements are high in Profile GA8/1 (P 2210 ppm, Mn 246 ppm, Zn 35 ppm, Cr 179 ppm, Fe 1.48%), followed by GA9/1 which exhibits low concentrations (P 450 ppm, Mn 246 ppm, Zn 35 ppm, Cr 179 ppm, Fe 1.48%). Lastly, concentrations further increase for profile GA10/1 located at the edge of the floodplain (P 331 ppm, Mn 780, zinc – 37 ppm, Cr 187 ppm, Fe 2.25%) and profile GA 11/1 (phosphorus – 830 ppm, manganese – 532 ppm, zinc – 56 ppm, chromium – 171 ppm, Iron – 2.36%). These patterns indicate that the concentrations of the eight elements follow an increasing trend and some sudden peaks (both increases and decreases) as one descends towards the Limpopo River floodplain. The geochemistry of Denstaat 1/1 shows high levels of the eight elements. This suggests that soil potential and water content availability have been sufficient for a long time, even though the Shashe-Limpopo



Source: Adapted from: Nxumalo, B.S., 2019, 'Integrating geoarchaeological approaches and rainfall modelling as a proxy for hydrological changes in the Shashe–Limpopo Basin, South Africa', *South African Archaeological Bulletin* 74(211), 67–77

GA, systematic test pits.

FIGURE 3: The geochemistry of the Samaria area using eight trace elements from the Inductively Coupled Plasma Atomic Emission Spectroscopy results.

Basin now is dry and perceived as unfavourable for human habitation. In fact, the Denstaat profile exposes (P 950 ppm, Mn 743 ppm, Zn 65 ppm, Cr 193 ppm, Fe 4.73%). However, the profiles around K2 1/1 and Leokwe Rest Camp (LKC 1/1) vary significantly (see Table 4 and Figure 4). Notably, there are two sample areas of Leokwe Rest Camp (LKC1) characterising the upper section profiles and (LKC2) of the lower section profiles but are reporting on only one.

The geochemical analysis by ICP-AES in Denstaat and the broader middle Limpopo Valley (Leokwe Rest Camp and K2) shows high element concentrations of chromium, manganese, iron and phosphorus elements (as shown in Figure 3 and Figure 4). Similar levels can also be observed in Samaria. The fluctuating concentrations of the eight selected elements observed in the study area may point to the varied nature of the physical and chemical composition of soil parent material (e.g. Karoo sandstone outcrops which can be linked to increased chromium concentration).

The eight elements can also be linked to ground water percolation in what is now pan sediments or drier areas of the middle Limpopo Valley. Research on precipitation patterns in the Shashe-Limpopo Basin shows that the region is subject to unpredictable variability (Nxumalo 2019). This means that the way in which a season unfolds determines the rates of rainfall which may come in a heavy downpour or extended periods of drying before the next rains. However, this study did not explore what happens to the ground when rainfall water enters the ground. To examine and understand moisture or water characteristics in the region, electrochemical potential was carried out beyond existing rainfall data published in Nxumalo (2019).

Electrochemical sequence

Electrochemical sequencing is commonly used in the natural sciences field to understand the degree of reduction and oxidation in a chemical reaction. It is also used to modulate compound stability, which is important because it aids understanding availability of nutrients and metal in soil surface environments. This article explores early applications of Redox analysis to map out the electrochemical sequence for Iron Age settlements in the middle Limpopo Valley (as shown in Table 4).

The overall measurements obtained ranged from pH values of 4.3 to 2.3 and Redox readings of 190 mV – 237 mV from Samaria to the Limpopo River (GA1/1 to GA11/3) as shown in Table 4. Electrochemical potential values suggest an environment where oxygen is poor and slow decomposition of organic matter (see Table 1). According to Allison (1973), the supply of oxygen to decaying organic matter dictates the nature of the microflora which brings about the decomposition

TABLE 4: Electrochemical potential results for Samaria and middle Limpopo Valley.

Number	Site	Depth (cm)	pH	millivolts (mV)
1	Denstaat 1/1	30–40	3.9	206
			3.7	203
			3.9	200
2	Leokwe Rest Camp (LKC) 1/1	10–35	4.3	115.1
			3.9	106.1
			4.0	110.1
3	K2/1.1	20–32	3.5	201
			3.6	203.8
			3.2	200.2
4	Samaria GA1/1	0–10	2.8	211.5
			2.6	216.5
			2.4	221.4
5	Samaria GA2/1	0–8	2.5	230.5
			2.5	228.0
			2.3	232.5
6	Samaria GA2/2	8–28	2.5	223.8
			2.6	222.8
			2.6	220.8
7	Samaria GA4/1	0–12	3.1	221.7
			3.1	219.1
			3.3	210.8
8	Samaria GA4/2	12–27	3.0	204.3
			3.2	206.1
			3.2	195.2
9	Samaria GA4/3	35–54	3.2	190.9
			2.9	190.0
			3.0	186.0
10	Samaria GA5/1	0–10	3.1	203.0
			3.0	204.7
			3.0	208.2
11	Samaria GA5/2	10–42	3.1	206.5
			3.1	204.0
			3.0	204.1
12	Samaria GA5/3	42–57	2.9	207.1
			3.0	207.0
			2.9	206.1
13	Samaria GA6/1	0–8	3.1	200.2
			3.1	206.4
			3.0	208.4
14	Samaria GA6/2	8–42	3.0	211.1
			2.9	203.4
			2.9	209.8
15	Samaria GA6/3	42–54	3.1	200.5
			3.1	197.4
			3.1	202.2
16	Samaria GA7/1	0–8	3.0	211.8
			3.0	210.0
			2.9	217.4
17	Samaria GA7/2	8–40	2.7	225.9
			2.8	218.9
			2.8	214.8
18	Samaria GA7/3	40–55	3.0	215.1
			3.0	210.2
			3.0	213.3
19	Samaria GA8/1	0–5	3.0	200.5
			3.2	190.3
			3.2	190.9
20	Samaria GA8/2	5–15	3.1	193.3
			3.2	191.2
			3.0	196.9

Table 4 continues on next column →

TABLE 4 (Continues ...): Electrochemical potential results for Samaria and middle Limpopo Valley.

Number	Site	Depth (cm)	pH	millivolts (mV)
21	Samaria GA8/3	15–31	2.9	213.0
			3.0	203.9
			3.0	201.6
22	Samaria GA8/4	31–48	3.3	187.5
			3.3	183.6
			3.4	179.2
23	Samaria GA8/5	48–60	3.3	183.5
			3.3	184.3
			3.4	181.2
24	Samaria GA9/1	0–20	2.9	205.4
			2.8	207.2
			2.8	208.6
25	Samaria GA9/2	20–44	3.0	202.2
			2.9	203.1
			2.9	203.8
26	Samaria GA9/3	44–54	2.8	208.1
			2.9	206.3
			2.9	206.5
27	Samaria GA10/1	0–7	2.4	230.4
			2.4	227.5
			2.5	224.2
28	Samaria GA10/2	7–15	2.3	233.1
			2.3	235.6
			2.2	236.3
29	Samaria GA11/1	0–4	2.3	237.0
			2.3	234.1
			2.4	230.3
30	Samaria GA11/2	4–19	2.6	216.5
			2.4	230.4
			2.3	233.0

Source: Nxumalo, B., 2016, *Hydrological modelling of rainfall patterns and societal demise in the Mapungubwe landscape, South Africa*, Unpublished MA thesis, University of Pretoria

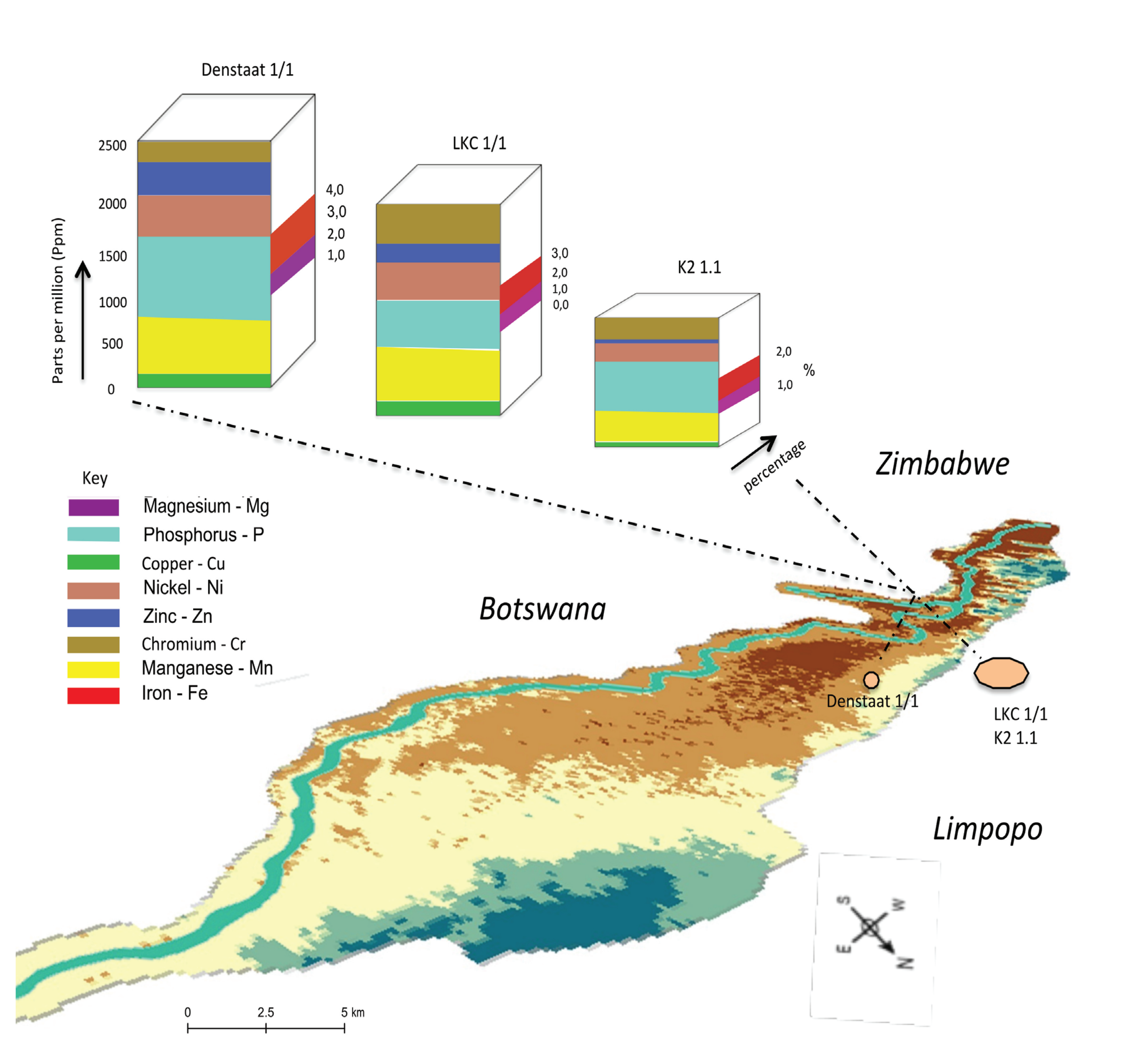
Note: The trace redox analysis were carried out by B. Nxumalo at the University of Pretoria, South Campus Laboratory.

GA, systematic test pits.

as well as the rate at which it decomposes and by products that form after. For example, conditions where oxygen quantities are inadequate, the decomposition process is hindered but ultimately the general aerobic break down products such as carbon dioxide, ammonia, water, and microbial cells are formed. The electrochemical sequence, therefore, suggests areas that have adequate ground water regimes. The Shashe-Limpopo Basin is an aquifer-dependent system where surface water flow percolates as groundwater down to greater depths downstream (Ekblom et al. 2012; FAO 2004; Gillson & Ekblom 2009). The water is discharged eastwards of the basin and south-easterly direction towards the Mozambique coastline. Focusing on the dataset from the middle Limpopo Valley (Mapungubwe, Leokwe Rest Camp and K2), pH values are generally acidic (3.1–4.3) and Redox potential is relatively low (106 mV – 217 mV; Table 4). The acidic pH values characterise the soil samples for much of the lower grounds of the middle Limpopo Valley. Although these values are not a proxy for the volume of water, they nonetheless provide information on ground water content.

Discussion

New data originating from the research presented in this article and palaeoenvironmental proxies suggests that the



Source: Adapted from: Nxumalo, B., 2016, *Hydrological modelling of rainfall patterns and societal demise in the Mapungubwe landscape, South Africa*, Unpublished MA thesis, University of Pretoria

FIGURE 4: The geochemistry of Denstaat 1/1, K2 Valley 1.1, and Leokwe Rest Camp (LKC) 1/1 using eight trace elements from the Inductively Coupled Plasma Atomic Emission Spectroscopy results.

growth of settlements in the middle Limpopo Valley may have been influenced by favourable environmental factors such as adequate moisture availability. This supports the long-held view that the middle Limpopo Valley had more favourable catchment areas (consistent aquifer regeneration) and floodplains that served as an important setting for agropastoral farming (Huffman 2007; Manyanga 2003, 2007; O'Connor & Kiker 2004). What emerges here is that the geochemical and electrochemical sequence is influenced by a variety of geomorphological and hydrological characteristics that make up the middle Limpopo Valley an ideal setting for human settlements as well as the use of the land. However, this view that the area got populated because of favourable environmental conditions can be criticised for environmental deterministic logic for which human acts and sustenance pursuits are strongly influenced by environmental factors. As witnessed in other archaeological inquiries on African State systems (e.g. Jenne-Jenno in Mali and Aksum in Ethiopia), environmental changes played a major part in societal transformations (Butzer 1996; Kusimba 1999; McIntosh & McIntosh 1984). Conclusions drawn from environmental deterministic views feature prominently when humans and environments are concerned, but they need to be supported with empirical evidence and models of environmental change. Indeed, assimilating relationships between environmental proxies and society is complex, but there has been renewed confidence in environmental determinism from this study and others based on chemical element and electrochemical analysis to identify anthropogenic as well as environmental footprints (see Fleisher & Sulas 2015; French, Sulas & Madella 2009; Nxumalo 2019, 2021; Pikirayi 2006; Sulas & Madella 2012).

Properties of elements

In soil, copper (Cu) is fixed and immobile because it is subject to absorption, precipitation, organic chelation, complexation and microbial fixation (Haluschak et al. 1998). For example, Cu precipitates with sulphides, carbonates and hydroxides because it is tightly held on organic and inorganic exchanges (Haluschak et al. 1998). Cu functions in oxidation (bulk of Cu adsorption occurring on Fe and Mn oxides), photosynthesis and metabolism; consequently, a significant component for plant growth (Kabata-Pendias & Pendias 1992). The element of iron (Fe) precipitates predominantly as an oxide and hydroxide, commonly absorbed by plants in the form of Fe^{2+} (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992). The solubility of Fe is controlled by pH in soil solution, which is essential to all organisms and a good indicator for stable vegetation and moisture content.

In soil, manganese (Mn) occurs in soils as Mn^{2+} which is absorbed by plants (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992). Mn forms high amounts of hydroxides and oxides (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992). It is essential for plant nutrition, common in surface horizons as a result of adsorption by organic matter and clay. In fact, electrochemical potential along with pH controls Mn solubility in soil. For instance, as pH decreases, the solution of manganese concentration increases. According to some studies (e.g. Gahoonia et al. 1994; Proudfoot 1976; Sulas & Madella 2012), phosphorus (P) is present in all ecosystems. Increased rates of P across archaeological sites are key indicators of early habitation sites and land use types. As such, large quantities of P are linked to substantial human occupation and land use. Chromium (Cr) commonly occurs in soil profiles with decomposing organic matter, and promotes the reduction of Cr^{6+} to Cr^{3+} which may contribute to reduced plant availability (Haluschak et al. 1998; Kabata-Pendias & Pendias 1992). Moreover, oxidation results in the transformation of Cr and this prohibits its mobility and toxicity. Nickel (Ni) is released as Ni^{2+} upon weathering and it precipitates with Fe and Mn oxides. Nickel is adsorbed onto clay and other organic fractions (Kabata-Pendias & Pendias 1992).

Zinc is highly mobile in soil solution and its weathering leads to the release of Zn^{2+} and this is controlled by the presence of silicates (e.g. clay), pH as well as hydrous oxides (Haluschak et al. 1998:38). This process is well reflected in some of the Samaria profiles such as GA 10/11 and GA 11/1 (see Table 4), which exhibit clay rich soils and acidic pH conditions. Magnesium (Mg) is an essential plant nutrient that contributes to plant growing conditions. According to Pansu and Gautheyrou (2006), increased amounts of Mg result in clay silicate dispersion and in turn reduces soil porosity as well as infiltration rates. This is often linked to increased availability of pan sediments providing sources of water to humans and animals as seen in Samaria.

Significant amounts of water in the middle Limpopo Valley percolate and gradually flow underground due to underlying geomorphic and geologic structure as well as human activities. A number of elements (e.g. phosphorus, chromium, manganese and iron) are useful proxies for understanding regions with enhanced moisture levels (Kabata-Pendias & Pendias 1992). Notably, moisture content is influenced by climate and forms part of soil surface environments and landscape regimes, since it is related to evapotranspiration rates and temperature changes (Misra & Tyler 1999). Moreover, moisture content helps shape soil solution chemistry and nutrient intake in the ecosystem. In turn, changes in element concentrations across soil surface environments have several ecological implications on plants and ground water levels (Misra & Tyler 1999). For instance, soil moisture is a fundamental regulator of plant productivity and ecological changes.

In this study, chemical elements from the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) results in the middle Limpopo Valley (e.g. Denstaat, Leokwe Rest Camp, K2, and Samaria) were compared to the electrochemical potential results or moisture signals. The availability of the eight elements in relatively large quantities means that vegetation and ground water availability in the study area have been available for a long time, even though today the area is arid. Results generated from optically stimulated luminescence (OSL) dating of soil surface deposits in Samaria have been dated to about AD 1237–1697, thus associated with the Iron Age and post-Iron Age occupation history at Mapungubwe (Nxumalo 2021). The implications of these dates and results presented in this article suggest that while environmental changes occurred, some areas in middle Limpopo Valley such as Samaria remained occupied even after the decline of the Mapungubwe State. The underlying geology and soil surface environments could have played a critical role in this regard, safeguarding the underground flow of water, making the area conducive. It is worth noting that the episodes of cooler and drier conditions impact the availability and concentration of elements. The archaeological record is characterised by evidence of water storage facilities that would have served as reservoirs during periods of droughts at Mapungubwe (Huffman 1996, 2008; Kuper 1982). However, it is difficult to say how past inhabitants of the middle Limpopo Valley may have exploited these ground water characteristics during periods of long-term drying.

Studies by authors such as Huffman (2007), Manyanga et al. (2000) and O'Connor (2001) have shown that the middle Limpopo Valley's socio-political complex evolved around agropastoral activities taking place at the Shashe and Limpopo floodplains. This means that societies settled in stockades around the hills for supposed protection while farming occurred in the floodplains. However, past historical rainfall patterns suggest that flooding would have been an imminent threat (Nxumalo 2019, 2021). Continuous threats from excessive water availability (flooding) may have imposed political instabilities, and some groups may have relocated to areas offering favourable environmental conditions such as Great Zimbabwe. The electrochemical potential suggests moisture levels can be correlated with published rainfall patterns in Nxumalo (2019), meaning that the Shashe-Limpopo Basin is characterised by unpredictable weather conditions linked to flooding. In turn, changes of weather conditions may have had several implications for farming activities and continued destabilisation of a political authority, leading to the decline of the middle Limpopo Valley. This article highlights conclusions made by authors such as Huffman (1996, 2000), Norström and Holmgren (2005), and Tyson and Lindesay (1992), that climate variability (too much of water) may have imposed social and economic instability leading to readjusted ways of subsistence and the decline of the middle Limpopo Valley. Several scholars (e.g. Manyanga 2006; Smith et al. 2007) have demonstrated that changing weather patterns would have been complemented with local adaptations to successfully inhabit the Shashe-Limpopo Basin. More importantly, climate change is not the only determinant factor towards human migrations on landscape (Manyanga et al. 2006; Nxumalo 2019).

The comparative assessment of the pH and Redox readings from the middle Limpopo Valley indicates an environment where oxygen is poor, and decomposition of organic matter is slow. This is observed in the sample readings for Samaria (GA2/2, GA9/1–10/1) and the middle Limpopo Valley (K2/1.1), all exhibiting decomposing organic material. It is worth noting that these conditions also lead to the formation of organic acids. These conditions result from oxygen depletion which stimulates the activities of anaerobic bacteria and produces organic acids (e.g. carbon dioxide, hydrogen, methane, hydrogen sulphides) and resistant plant materials that anaerobes cannot utilise (Allison 1973; Chen & Thompson 2021; Wilmoth 2021). As such, the middle Limpopo Valley is characterised by acidic pH values, especially in soil samples characterised by abundant organic matter and waterlogged valley bottoms. These conditions are useful for arable soils wherein waterlogging from floodplains and underlying geology causes anaerobic conditions providing improved soil nutrient for farming and human occupation during the early Mapungubwe periods. Even today, the Shashe-Limpopo Basin provides arable land for both commercial and subsistence farming activities. However, the shallow pan sediments and bouncing aquifer systems (i.e. water tables) allow the waterlogged regions to drain excess water away, the intermediate products, organic acids are quickly oxidised to the usual aerobic products (Allison 1973; Chen & Thompson 2021). These electrochemical potential conditions can also explain the exploitation of ground water in large quantities (ca. 850 mm^3 annually) by commercial farms and mines in the Limpopo province (FAO 2004). While this was 20 years ago, the demand has not decreased, but has, in fact, increased with more farming activities in the area.

In fact, the Shashe-Limpopo Basin is utilised by modern societies as a reflection of local knowledge whose roots can be traced in the historic past of the region (Manyanga et al. 2000). This is further supported by the displacement of chemical elements, which points to adequate groundwater levels. Together, the geochemistry and electrochemical results (ICP-AES, pH and Redox) indicate that the research area has adequate water bodies which could be linked to the underground aquifer systems. The ICP-AES and Redox conditions are not a direct measure of rainfall or available ground water but a proxy of available moisture sequences in the soil surface. In turn, these may have had consequential implications for the Iron Age farming societies in the middle Limpopo Valley. The combined analysis of geochemical and electrochemical data in this article allows us to begin reframing questions around changing environmental conditions and the decline of state societies. These results show the potential to predict future environmental changes and contributions to debates around societal developments along riparian ecological zones such as Mapungubwe. The present study contributes to debates on socio-cultural transformations in the middle Limpopo Valley. For example, inhabitants in this region may have greatly benefitted from the constant regeneration of groundwater tables as indicated by the geochemical and electrochemical potential results. This study indicates that we cannot ignore the role played by the environmental changes to determine human behavioural patterns of early agricultural societies.

Conclusion

In southern Africa, the middle Limpopo Valley represents an important area and strand of research that is characteristic of the earliest socio-political developments and farming institutions in Mapungubwe. The intended purpose of this work was to explore the complex nature of relationship between humans and their surroundings in the middle Limpopo Valley. The geomorphological and geological outlook of the middle Limpopo Valley also makes it a perfect study area for interrogating past people's interaction with the landscapes and environmental stresses linked to hydrological activity. This work combines geochemical and electrochemical data from soil sample analysis to model or predict aquifer behaviour and the occurrence of groundwater in the middle Limpopo Valley. Evidence from electrochemical and geochemical data indicates that adequate soil moisture regimes would have allowed constant ground water regeneration to the middle Limpopo Valley over time. This means that adequate soil moisture content may have been an essential resource for agricultural activities in the past. Moreover, these results suggest that we cannot ignore the role played by geology and climate to model potential societal behaviours of early agricultural societies. This is important when analysing archaeological sites located nearby riparian settings, especially the roles played by changing water regimes and farming institutions across river valley state systems. This study moves beyond traditional archaeological methods such as material discontinuity to show how past societies occupying floodplain ecologies may have interacted with their surroundings – as dictated to by the availability of water. As such, the article is relevant for scholars who are interested in understanding site formation processes by micro-analytical approaches and human interaction across abandoned archaeological landscapes.

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Competing interests

The authors declare that they have no financial or personal relationship(s) that may have inappropriately influenced them in writing this article.

Authors' contributions

The author B.S.N. conceptualised and drafted the article. F.S. helped with supervision of the project, methodological framing and analysing the geochemical signatures. I.P. helped with procuring funding for analysis and overall supervision.

Ethical considerations

Ethical clearance to conduct this study was obtained from the University of Pretoria, Faculty of Humanities Research Ethics Committee (No. 12378624).

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Data availability

The authors confirm that the data supporting the findings of this study are available within the article and/or its supplementary materials.

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References

Ahn, P.M., 1970, *West African Soils*, Oxford University Press, London.

Allison, F.E., 1973, *Soil organic matter and its role in crop production*, Elsevier Science Ltd, Amsterdam.

Anderson, I.P., Brinn, P.J., Moyo, M. & Nyamwanza, B., 1993, *Physical resource inventory of communal lands of Zimbabwe: An overview*, Natural Resource Institute Bulletin 60, Overseas Development Administration, Natural Resources Institute, Chatham, UK.

Bender, B., 2002, 'Time and landscape', *Current Anthropology* 43, 103–120.

Blenkinsop, T.G., 2011, 'Archean magmatic granulites, diapirism, and Proterozoic reworking in the Northern Marginal Zone of the Limpopo Belt', in D.D. Van Reenen, J.D. Kramers, S. McCourt & L.L. Perchuk (eds.) *Origin and Evolution of Precambrian High-Grade Gneiss Terranes, with Special Emphasis on the Limpopo Complex of Southern Africa*, Geological Society of America Memoirs, vol. 207, pp. 245–267, Geological Society of America, Boulder, CO.

Bradfield, J. & Antonites, A.R., 2017, 'Bone hoes from the Middle Iron Age, Limpopo Province, South Africa', *Quaternary International* 472, 126–134.

Bruno, D. & Thomas, J., 2008, *Handbook of Landscape Archaeology*, Routledge Handbooks Online Abingdon.

Butzer, K.W., 1996, 'Ecology in the long view: Settlement histories, Agrosystemic strategies, and ecological performance', *Journal of Field Archaeology* 23(2), 141–150. https://doi.org/10.1179/009346996791973909

Chen, C. & Thompson, A., 2021, 'The influence of native soil organic matter and minerals on ferrous iron oxidation', *Geochimica et Cosmochimica Acta* 292, 254–270. https://doi.org/10.1016/j.gca.2020.10.002

Chinoda, G., William, M.W., Nyikadzino, M.N. & Owen, R., 2009, *Baseline report on the geology of the Limpopo Basin area a contribution to the challenge program on water and food project 17 'Integrated water resource management for improved rural livelihoods: Managing risk, mitigating drought and improving water productivity in the water scarce Limpopo Basin*', Mineral Resources Centre, University of Zimbabwe, Harare.

Crumley, C.L., 2007, 'Reconstructing visual landscapes', *World Archaeology* 39(1), 51–69.

Davidson, D.A., Dercon, G., Stewart, M. & Watson, F., 2006, 'The legacy of past urban waste disposal on local soils', *Journal of Archaeological Science* 33(6), 778–783. https://doi.org/10.1016/j.jas.2005.10.017

De Beer, J., Seither, A. & Vorenhout, M., 2016, 'Effects of a new hydrological barrier on the temperatures in the organic archaeological remains at Bryggen in Bergen, Norway', *Conservation and Management of Archaeological Sites* 18(1–3), 99–115. https://doi.org/10.1080/13505033.2016.1182749

De Wit, M.J. & Roering, C., 1990, 'Episodes of formation and stabilization of the Kaapvaal craton in the Archean: An overview based on some selected recent data', in J.M. Barton (ed.), *The Limpopo belt: A field workshop on granulites and deep crustal tectonics, extended abstract*, pp. 42–52, Rand Afrikaans University, Pretoria.

Ekblom, A., 2004, *Changing landscapes: An environmental history of Chibuene, southern Mozambique*, Studies in Global archaeology 5, Department of Archaeology and Ancient History, Uppsala University, Uppsala.

Ekblom, A., Gillson L., Jan Risberg, J., Holmgren, K. & Chidoub, Z., 2012, 'Rainfall variability and vegetation dynamics of the lower Limpopo Valley, Southern Africa, 500 AD to present', *Palaeogeography, Palaeoclimatology, Palaeoecology* 363–364, 69–78. https://doi.org/10.1016/j.palaeo.2012.08.015

Fitzpatrick, R.W., Wright, M.J. & Stevens, R.M., 1993, *Drainage, sodicity and related problems of Vineyard Soils*, The Australian Wine Research Institute, Adelaide.

Fleisher, J. & Sulas, F., 2015, 'Deciphering public spaces in urban contexts: Geophysical survey, multi-element soil analysis, and artefact distributions at the 15th–16th-century AD Swahili settlement of Songo Mnara, Tanzania', *Journal of Archaeological Science* 55, 55–70. https://doi.org/10.1016/j.jas.2014.12.020

French, C.A.I. Sulas, F. & Madella, M., 2009, 'New geoarchaeological investigations of the valley systems in the Aksum area of northern Ethiopia', *Catena* 78, 218–233. https://doi.org/10.1016/j.catena.2009.02.010

Food and Agriculture Organization (FAO), 2004, *Drought impact mitigation and prevention in the Limpopo River Basin: A situation analysis*, FAO Subregional Office for Southern and East Africa, Harare.

Gahoonia, D.S., Raza, S. & Nielsen, N.E., 1994, 'Phosphorus depletion in the rhizosphere as influenced by soil moisture', *Plant and Soil* 159, 213–218. https://doi.org/10.1007/BF00009283

Gillson, L. & Ekblom, A., 2009, 'Untangling anthropogenic and climatic influence on riverine forest in the Kruger National Park, South Africa', *Vegetation History and Archaeobotany* 18, 171–185. https://doi.org/10.1007/s00334-008-0202-6

Haluschak, P., Eilers, R.G., Mills, G.F. & Grift, S., 1998, *Status of selected trace elements in agricultural soils of Southern Manitoba*, Technical report 1998-6E, University of Manitoba, Land Resource Unit, Brandon Research Centre, Research Branch, Agriculture and Agri-Food Canada.

Holland, M., 2011, *Hydrogeological characterisation of crystalline basement aquifers within the Limpopo Province, South Africa*, Unpublished Ph.D. thesis, Faculty Natural and Agricultural Sciences, University of Pretoria, South Africa.

Holmgren, K., Lee-Thorp, J.A., Cooper G.R.J., Lundblad, K., Partridge, T.C., Scott, L. et al. 2003, 'Persistent millennial-scale variability over the past 25 thousand years in southern Africa', *Quaternary Science Reviews* 22, 2311–2326.

Huffman, T.N., 1996, 'Archaeological evidence for climatic change during the last 2000 years in Southern Africa', *Quaternary International* 33, 55–60. https://doi.org/10.1016/1040-6182(95)00095-X

Huffman, T.N., 2000, 'Mapungubwe and the origins of the Zimbabwe culture', *South African Archaeological Society Goodwin Series* 8, 14–29. https://doi.org/10.2307/3858043

Huffman, T.N., 2007, *Handbook to the Iron Age: The archaeology of pre-colonial farming societies in Southern Africa*, University of KwaZulu-Natal Press, Scottsville.

Huffman, T.N., 2008, 'Climate change during the Iron Age in the Shashe-Limpopo Basin, Southern Africa', *Journal of Archaeological Science* 35(7), 2032–2047. https://doi.org/10.1016/j.jas.2008.01.005

Kabata-Pendias, A. & Pendias, H., 1992, *Trace elements in soils and plants*, CRC Press, Boca Raton, FL.

Kuper, A., 1982, *Wives for cattle: Bride-wealth and marriage in southern Africa*, Routledge and Kegan Paul, London.

Kusimba, C.M., 1999, *The rise and fall of Swahili States*, Altamira Press, Walnut Creek, CA.

Maggs, T.M. & O'Connor, T.G., 2000, 'African naissance: An introduction', in M. Leslie & T. Maggs (eds.), *African naissance: The Limpopo valley 1000 years ago*, Goodwin Series, vol. 8, pp. 1–3, The South African Archaeological Society, Cape Town.

Maharana, C., Srivastava, D. & Tripathi, J.K., 2018, 'Geochemistry of sediments of the Peninsular rivers of the Ganga basin and its implication to weathering, sedimentary processes and provenance', *Chemical Geology* 453, 1–20. https://doi.org/10.1016/j.chemgeo.2018.02.019

Manyanga, M., 2003, 'Settlement patterning in the Shashi-Limpopo valley: Reflections from surveys in Maramani and lower Mzingwani area', in F. Chami, G. Pwiti & C. Radimilahy (eds.), *Climate change, trade and modes of production in sub-Saharan Africa*, Studies in the African Past 3, pp. 21–38, DUP, Dar es Salaam.

Manyanga, M., 2006, *Resilient landscapes: Socio-environmental dynamics in the Shashi-Limpopo Basin, Southern Zimbabwe c. AD 800 to the present*, Societa Archaeologica Uppsaliensis, Uppsala.

Manyanga, M., 2007, *Resilient landscapes: Socio-environmental dynamics in the Shashi-Limpopo Basin, Southern Zimbabwe, c. AD 800 to present, studies in Global Archaeology 11*, Uppsala University, Uppsala.

Manyanga, M., Pikirayi, I. & Ndoro, W., 2000, 'Coping with dryland environments: Preliminary results from Mapungubwe and Zimbabwe phase sites in the Mateke Hills, south-eastern Zimbabwe', in M. Leslie & T. Maggs (eds.), *African Naissance: The Limpopo Valley 1000 Years Ago*, vol. 8, pp. 69–77, The South African Archaeological Society Goodwin Series, Cape Town.

Mausbach, M.J. & Richardson, J.L., 1994, 'Biogeochemical processes in hydric soil formation', *Current Topics Wetland Biogeochem* 1, 68–127.

McIntosh, S.K. & McIntosh, R.J., 1984, 'The early city in West Africa: Towards an understanding', *The African Archaeological Review* 2, 73–98. https://doi.org/10.1007/BF01117226

Meyer, A., 2000, 'K2 and Mapungubwe', in M. Leslie & T. Maggs (eds.), *African Naissance: The Limpopo valley 1000 years ago*, vol. 8, pp. 4–13, The South African Archaeological Society Goodwin Series, Cape Town.

Misra, A. & Tyler, G., 1999, 'Influence of soil moisture on soil solution chemistry and concentrations of minerals in the calcicoles Phleum phleoides and Veronica spicata grown on a limestone soil', *Annals of Botany* 84, 401–410. https://doi.org/10.1006/anbo.1999.0941

Murray, K.S., Rogers, D.T. & Kaufman, M.M., 2004, 'Heavy metals in an urban watershed in southeastern Michigan', *Journal of Environmental Quality* 33(1), 163–172. https://doi.org/10.2134/jeq2004.1630

Norton, S., 2007, 'Atmospheric metal pollutants – Archives, methods and history', *Water Air Soil Pollution* 7, 93–98.

Norström, E. & Holmgren, K., 2005, 'Rainfall driven variations in 13C composition and wood anatomy of breonadia salicina trees from South Africa between AD 1375 and 1995', *South African Journal of Sciences* 101, 162–168.

Nxumalo, B., 2016, *Hydrological modelling of rainfall patterns and societal demise in the Mapungubwe landscape, South Africa*, Unpublished MA thesis, University of Pretoria.

Nxumalo, B.S., 2019, 'Integrating geoarchaeological approaches and rainfall modelling as a proxy for hydrological changes in the Shashe–Limpopo Basin, South Africa', *South African Archaeological Bulletin* 74(211), 67–77.

Nxumalo, B., 2021, *The role of hydrological changes in the demise of Iron Age state societies in southern Africa: An integrative study of Mapungubwe, South Africa*, Ph.D. thesis, University of Cambridge.

O'Connor, T.G., 2001, 'Effect of small catchment dams on downstream vegetation of a seasonal river in a semi-arid African Savanna', *Journal of Applied Ecology* 38, 1314–1325. https://doi.org/10.1046/j.0021-8901.2001.00680.x

O'Connor, T.G. & Kiker, G.A., 2004, 'Collapse of the Mapungubwe society: Vulnerability of pastoralism to increasing aridity', *Climatic Change* 66, 49–66. https://doi.org/10.1023/B:CLIM.0000043192.19088.9d

Oze, C., Bird, D.K. & Fendorf, S., 2007, 'Genesis of hexavalent chromium from natural sources in soil and groundwater', *Proceedings of the National Academy of Sciences of the United States of America* 104(16), 6544–6549. https://doi.org/10.1073/pnas.0701085104

Pansu, M. & Gautheyrou, J., 2006, *Handbook of soil analysis. Mineralogical, organic and inorganic methods*, Springer, Berlin.

Pikirayi, I., 2006, 'The demise of Great Zimbabwe, AD 1420–1550: An environmental re-appraisal', in A. Green & R. Leech (ed.), *Cities in the world, 1500–2000*, pp. 31–47, Maney Publishing, Leeds.

Pikirayi, I., 2018, 'Water and large-scale societies in southern Zambezia, 900–1900 CE in F. Sulas & I. Pikirayi (eds), *Water and Society from Ancient Times to the Present: Resilience, Decline, and Revival*, pp. 136–154, Routledge, London.

Pikirayi, I., Sulas, F., Musindo, T.T., Chimwanda, A., Chikurumbike, J., Mtetwa, H. et al., 2016, 'Great Zimbabwe water', *Wiley Waters* 3(2), 195–210. https://doi.org/10.1002/wat2.1133

Pikirayi, I., Sulas, F., Nxumalo, B., Sagiya, M.E., Stott, D., Kristiansen, S.M. et al., 2022, 'Climate-smart harvesting and storing of water: The legacy of dhaka pits at Great Zimbabwe' *Anthropocene* 40, 100357. https://doi.org/10.1016/j.ancene.2022.100357

Pomposi, C., Funk, C., Shukla, S., Harrison, L. & Magadzire, T., 2017, 'Distinguishing southern Africa precipitation response by strength of El Niño events and implications for decision-making', *Environmental Research Letters* 13(7), 71–12.

Proudfoot, B., 1976, 'The analysis and interpretation of soil phosphorus in archaeological context', in D.A. Davidson & M.L. Shackley (eds.), Geoarchaeolgy *Earth Science and the Past*, pp. 94–113, Duckworth, London.

Roering, C., Van Reeenen, D.D., Smit, C.A., Barton, J.M., Jr. De Beer, J.H., De Wit, M.J. et al., 1992, 'Tectonic model for the evolution of the Limpopo Belt', *Precambrian Research* 55(1–4), 539–552. https://doi.org/10.1016/0301-9268(92)90044-O

Sadr, K., 2008, 'An ageless view of first Millennium AD southern African ceramics', *Journal of African Archaeology* 6(1), 103–129. https://doi.org/10.3213/1612-1651-10105

Schaetzl, R.J. & Anderson, S., 2005, *Soils: Genesis and morphology*, Cambridge University Press, Cambridge.

Scoones, I., 1996, *Hazards and opportunities: Farming livelihoods in dryland Africa lessons from Zimbabwe*, Zed Books, London.

Shoemaker, C.M., Ervin, G.N. & Di Orio, E.W., 2017, 'Interplay of water quality and vegetation in restored wetland plant assemblages from an agricultural landscape', *Ecological Engineering* 37(Part A), 705–714. https://doi.org/10.1016/j.ecoleng.2017.08.034

Smith, A., 1970, 'Trade and the Rozwi Mambo', in R. Gray & D. Birmingham (eds.), *Pre-colonial African Trade: Essays on trade in central and southern Africa before 1900*, pp. 265–289, Oxford University Press, London.

Smith, J., 2005, *Climate change and agropastoral sustainability in the Shashe-Limpopo River basin from AD 900*, Unpublished Ph.D. thesis, University of the Witwatersrand, Johannesburg.

Smith, J., Lee-Thorp, J. & Hall, S., 2007, 'Climate change and agropastoralist settlement in the Shashe–Limpopo River Basin', *South African Archaeological Bulletin* 62, 115–125.

Sulas, F. & Madella, M., 2012, 'Archaeology at the micro-scale: Micromorphology and phytoliths at a Swahili stonetown', *Archaeological and Anthropological Sciences* 4(2), 145–159.

Sulas, F. Kristiansen, S.M. & Wynne-Jones, S., 2019, 'Soil Geochemistry, Phytoliths and Artefacts from an Early Swahili Daub House, Unguja Ukuu, Zanzibar', *Journal of Archaeological Science* 103, 32–45.

Sulas, F., Pikirayi, I. & Nxumalo, B., 2013, 'Geoarchaeological survey and soil sampling at Mapungubwe, June 2013: Technical report', University of Pretoria, Pretoria.

Sulas, F.A., Antonites, C. & Chauke, C., 2012, *Geoarchaeological reconnaissance of the Mapungubwe landscape and its environs, 24–25 October 2012*, Technical report, University of Pretoria, Pretoria.

Tisdale, S.L., Nelson, W.L. & Beaton, J.D., 1985, *Soil fertility and fertilizers*. 4th edn., Macmillan Publishing Company, New York.

Tyson, P.D. & Lindesay, J.A., 1992, 'The climate of the last 2000 years in southern Africa', *The Holocene* 2, 271–278.

Tyson, P.D. & Preston-Whyte, R.A., 2000, *The weather and climate of Southern Africa*, Oxford University Press, Oxford.

Venter, F.J., Scholes, R.J. & Eckhardt, H.C., 2003, 'The abiotic template and its associated vegetation pattern', in J.T. Du Toit, K.H. Rogers & H.C. Biggs (eds.), *The Kruger experience, Ecology and management of savannah heterogeneity*, pp. 83–129, Island Press, Washington, DC.

Vepraskas, M.J., 1999, *Redoximorphic features for identifying aquic conditions*, N. Carolina Agricultural Research Service Technical Bulletin no. 301, North Carolina State University, Raleigh, NC.

Wilmoth, J.L., 2021, 'Redox heterogeneity entangles soil and climate interactions', *Sustainability* 13(18), 10084. https://doi.org/10.3390/su131810084

Wilson, C.A., Davidson, D.A. & Cresser, M.S., 2009, 'An evaluation of the site specificity of soil elemental signatures for identifying and interpreting former functional areas', *Journal of Archaeological Science* 36(10), 2327–2334.

Wood, M., 2000, 'Making connections: Relationship between international trade and glass beads from the Shashe-Limpopo area', *South African Archaeological Society Goodwin series* 8, 78–90.

Zhu, T. & Ringler, C., 2010, *Climate change implications for water resources in the Limpopo River Basin*, International Food Policy Research Institute, Washington, DC, pp. 1–16.