

Archaeometallurgy Study of Iron Production in Southeastern Africa During the Zulu Kingdom
Period (1818-1879)

by

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ABSTRACT

Despite the historical, archaeological, and oral evidence concerning iron production during the Zulu Kingdom period, limited geochemical research has been conducted to associate iron artifacts and smelting by-products with potential iron ore deposits. As a result, the sources of the ores used by Zulu ironworkers and the extent to which the bloomery process altered or preserved their chemical signatures remain poorly understood. This lack of geochemical provenance data limits the ability to determine whether iron implements used within the Zulu Kingdom were produced from a single regional ore source or from multiple geological sources exploited by different groups of ironworkers. This study therefore employed petrography and geochemical methods to identify possible ore sources and evaluate chemical changes throughout the iron-production *chaîne opératoire*.

The results suggest that Zulu ironworkers smelted ores from a range of geological sources, likely guided by considerations of accessibility and ore quality. The geochemical analysis also indicates that, although the *amaCube* were significant iron producers, they did not exclusively produce all the iron implements used within the Zulu Kingdom. Furthermore, the results demonstrate that geochemical signatures remained sufficiently preserved after the bloomery process to allow direct correlations among the chemical compositions of ores, manufacturing by-products, and finished objects. Analysis of the Wosi production sequence showed that iron concentrations increased from ore to finished artifact, while concentrations of vanadium (V), rubidium (Rb), strontium (Sr), and nickel (Ni) generally decreased.

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DEDICATION

In loving memory of my late grandmother, Mary Adu-Gyamfi. Your love, strength, and the values you instilled in me continue to guide and inspire me. This thesis is dedicated to you.

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CHAPTER 1: INTRODUCTION

1.1 Research Background

African metallurgy is distinguished by its early development, technological diversity, innovation, and the cultural significance attached to metallurgical practices and products. Unlike metallurgical research in other parts of the world, studies of indigenous African metallurgy have benefited from a range of data sources that shows the technologies and manufacturing techniques adapted to local resources, knowledge, and expertise (Killick and Fenn, 2012, p. 568; Chirikure, 2015b). Documentary sources, oral histories, ethnographic studies, ethnoarchaeology, archaeology, and archaeometallurgy have contributed to an understanding of three complementary aspects of metallurgy.

First, technology studies have focused on manufacturing processes and the kinds and quality of objects made (Kiriamia, 1987; Miller, 2002; Bandama, Chirikure and Hall, 2013; Killick and Fenn, 2012; Bandama, 2013; Mathoho, Nyamushosho and Chirikure, 2023). Second, socioeconomic research has examined metal workers in society and the role of metallurgy in the accumulation of wealth and power in African societies (Miller, 2001; Chirikure and Rehren, 2006; Bandama, 2013). Third, the ritual practices and religious frameworks surrounding metal production and use (Schmidt and Mapunda, 1997).

The study of African metallurgy was once dominated by the view that metallurgical knowledge originated in Eurasia, based on the assumption that Africans could not have independently developed such complex technologies (Shaw *et al.*, 1969; van der Merwe, 1980). However, the field increasingly recognizes that these technological developments occurred entirely within an African cultural framework (Daoust, 2014; Chirikure, 2015b).

Knowledge of the technological, socio-economic, and religious dimensions of metallurgy remains uneven across metal-producing societies on the continent. Some regions, including parts of West and East Africa, has rich historical archives and have benefited from ethnoarchaeological research on metal production and its socio-economic and ritual dimensions (Schmidt, 1997; Baužytė et al., 2023; Iles and Lyaya, 2015). In southern Africa, by contrast, ethnographic accounts, archaeological investigations, and archaeometallurgical studies have constituted the principal sources for understanding the production and use of metals. Laboratory archaeometallurgy, which involves “the application of techniques from earth and engineering sciences to gain technical and cultural information from slags, ores, and even collapsed furnaces” (Chirikure, 2018, p. 3), is among the most interdisciplinary approaches to the study of metallurgy. Its application has increased over the past two decades, although it has been applied unevenly across precolonial metalworking societies (Killick and Fenn, 2012).

In southern Africa, iron metallurgy has a long history of research. Most work has focused on early metallurgy dating to the first millennium AD, or Early Iron Age (Killick and Miller, 2014; Miller, Killick and Van der Merwe, 2001; Miller, 2002; Miller and Killick, 2004), on technology (Whitelaw, 1991; Miller and Whitelaw, 1994; Miller, 2002; Miller, Mulaudzi and Killick, 2002; Miller and Killick, 2004; Chirikure and Rehren, 2006; Hall *et al.*, 2006; Bandama, 2013; Bandama, Chirikure and Hall, 2013; Mathoho *et al.*, 2016; Mathoho, Nyamushosho and Chirikure, 2023;), and large-scale iron production (Thondhlana, 2012; Killick and Miller, 2014). Other studies have focused on the socioeconomic (Miller and Whitelaw, 1994; Chirikure, 2007) and spatial organization of production (Greenfield and Miller, 2004) based upon comparisons with more historically recent metal-producing societies in the region. By contrast, studies of second millennium AD (Later Iron Age) metallurgy have explored gold, tin, copper,

brass, and iron technologies, as well as both large and small-scale production, drawing on historical, ethnographic, and technological data (Hall, 1980; Maggs, 1982; Maggs and Miller, 1995 and Bandama, Chirikure and Hall, 2013).

Amongst this corpus of research, archaeometallurgy studies have overwhelmingly concentrated on metallurgical practices of early farming communities in parts of northern South Africa, Botswana, and Zimbabwe (Grant, 1999; Miller, Killick and Van der Merwe, 2001; Chirikure and Rehren, 2006; Chirikure, 2006; Hall *et al.*, 2006; Killick and Miller, 2014; Molofsky *et al.*, 2014; Mathoho, Nyamushosho and Chirikure, 2023; Mathoho *et al.*, 2016). Other, more recent historical metallurgical traditions documented through oral histories and archaeological evidence, such as those associated with the Zulu Kingdom, have not received the same research attention. Smelting remains, such as slags reduced ores, furnaces, tuyeres, and finished items, have not been subjected to physical and chemical analysis to develop a more holistic understanding of metallurgical technologies in southern Africa.

The principal aim of this study is to improve the current understanding of iron-production technologies within the Zulu Kingdom in southeastern Africa. The study focuses on iron ore sourcing and the effects of smelting on the chemical composition of iron products dating to the Zulu Kingdom period (c. 1818- 1879). The main objective of this study is to determine the chemical composition of sampled pre-industrial iron artifacts, smelting by-products (slag and bloom), and iron ores used by Zulu ironworkers. Through the application of geochemical methods and analytical techniques, this research seeks to: (1) establish the sources of iron ore used in the manufacturing of iron implements; and (2) examine changes in the chemical composition of raw materials through the production sequence, from iron ore to finished product. These new technological data will provide insights into the manufacture of iron objects and the

organization of iron production in relation to the political, socio-economic, and cosmological understanding of Zulu society, as understood through archaeological research, documentary evidence, and oral histories.

1.2 Research Questions and Hypotheses

Current knowledge of pre-industrial ironworking in southeastern Africa is derived from several sources. These include historical narratives based on oral traditions (Webb and Wright, 1986; Kuper, 1987; Delegorgue, 1997), studies of museum collections (Maggs, 1991; Maggs, 1993; Moffett, Maggs and van Schalkwyk, 2017), and archaeological or archaeometallurgical studies (Hall, 1980; Roodt, 1993; Miller and Whitelaw, 1994; van Schalkwyk, 1994; van Schalkwyk, 1994; Maggs and Miller, 1995; Greenfield, van Schalkwyk and Jongsma-Greenfield, 1997; Miller, 2001; Greenfield and Miller, 2004; Fowler and van Schalkwyk, 2025b). Previous ore-sourcing studies in southeastern Africa have examined ore sourcing for tin (Grant, 1999), copper (Hall *et al.*, 2006), and bronze production (Molofsky *et al.*, 2014).

For this thesis, the key research questions that I explored include:

1. What ore source(s) were exploited by Zulu ironworkers in iron production during the Zulu Kingdom era?
2. What is the chemical composition of iron artifacts, smelting by-products (slag and bloom), and iron ore?
3. What is the effect of smelting on the chemical composition of iron artifacts through the production sequence?

The sourcing of ores used by ironworkers in the southeastern lowlands remains an important area of archaeometallurgical research (Miller and Whitelaw, 1994). Although previous studies have examined the mineralogy and characterized materials from selected historical

assemblages in the region (Whitelaw, 1991; Miller and Whitelaw, 1994; Miller, 2002; Miller, Killick and Van der Merwe, 2001; Killick and Miller, 2014). Zulu iron metallurgy has not been investigated using geochemical provenance studies linking iron artifacts to potential iron ore deposits. This gap in available data and research underscores the need for an archaeometallurgy investigation that examines not only the technological processes involved in iron production but also whether iron objects can be linked to any ore sources known based on oral history, archaeological research, and geological research within the study area.

Previous archaeological and ethnohistorical research suggests that Zulu iron workers strategically located smelting sites close to iron ore sources and hardwood to facilitate the smelting process (Maggs, 1992, p. 67; Roodt, 1996, p. 94; Moffett, 2020, p. 4). However, there remains limited understanding of where the iron implements used by different communities throughout the kingdom were produced. It is generally assumed that smiths at different localities across the kingdom produced for either the local population, at the King's demand or both.

On the one hand, ironworkers throughout the kingdom may have been responsible for the manufacturing of hoes, axes, adzes, and smaller implements such as knives and awls to meet local demand (Maggs, 1992, p. 83). On the other hand, oral testimony indicates that the *amaCube*, who were situated within the Thukela River Basin, produced hoes for the kingdom (Webb and Wright, 1986, p. 14).

Iron smelting sites south of the Thukela River are often located near hematite outcrops associated with the Pietermaritzburg formation (Whitelaw, 1991, p. 32), while other sites occur near the magnetic ore-bearing Mozaan shales (Maggs, 1991). Early Iron Age smelting sites in the southeastern lowlands have also been identified in the central parts of the Thukela River Basin,

adjacent to outcrops containing amphiboles with varying concentrations of hematite and magnetite (van Schalkwyk, 1994; van Schalkwyk, 1994; Greenfield and Miller, 2004).

In this thesis, I tested three main hypotheses derived from oral history and previous archaeological research:

1. If the bloomery process does not significantly alter the chemical composition of ores, then a direct relationship exists between the chemical composition of ores, manufacturing by-products, and finished iron objects.

Null hypothesis: If the bloomery process significantly alters the chemical composition of ores, then there is no direct relationship exists between the chemical composition of ores and finished iron objects.

2. If Zulu ironworkers exploited a range of iron ore deposits for smelting activities, then there would be significant variation in the chemical composition of slag, bloom, and iron artifacts from archaeological sites.

Null hypothesis: The absence of significant chemical variation in iron-making by-products and objects is a result of using the ores from the same source.

3. If iron objects from Royal *amakhanda* were made exclusively by *amaCube* smiths, then iron objects would only exhibit a chemical composition of the source ore material used by *amaCube* smiths in the Nkandla area.

Null hypothesis: If the chemical composition in the iron-making by-products and finished objects from the Royal *amakhand*a do not match the chemical composition of source materials used by *amaCube* smiths, then the finished objects from the Royal *amakhand*a were not made exclusively by *amaCube* smiths.

1.3 Zulu Metallurgy

Metallurgy is widely regarded as an important technology in the military expansion and agricultural development of the nineteenth-century Zulu Kingdom, as well as in the development of Bantu-speaking communities more broadly (von Kapff, 2012; Dondofema, Matope and Akdogan, 2017). Zulu metallurgy was mainly characterized by ironworking and brass smithing (Fowler and van Schalkwyk, 2025b, p. 6). According to Roodt (1993, p. 110), the principal distinction between Zulu metallurgy and the metallurgical traditions of earlier Bantu-speaking communities in the region lay in the social and religious ideologies associated with iron smelting.

1.3.1 Zulu Ironworkers

Zulu ironworkers occupied a high social position and were regarded as the king's necessity (*insila*) (Raum, 1973; Costin, 1991). Their social standing was comparable to that of other specialized practitioners, including healers and diviners (Raum, 1973, pp. 214-217). According to Raum (1973, p. 217), Zulu smiths were described as the "foundation of the people" and the "strength of the nation" and were praised as the "weaponer" (*inyana yemkhonto*). As in some West African societies, ironworkers were accorded considerable status, while their craft was associated with taboos, mystical beliefs (*umnyama*), and ritual practices (Webb and Wright,

1986). The knowledge and rituals associated with ironworking were transmitted through the male lineage and were often restricted to families within chiefdoms (Maggs, 1992).

Iron smelting and forging were complex technologies, as the reduction process to remove slag (*amanyela*) and produce a high-quality bloom or ingot (*isgaxa sensimbi*) required knowledge and skills (Miller, 2002). Although smelting and forging or smithing constituted distinct stages of iron production, historical accounts do not always clearly distinguish between the specialists responsible for each activity. Nevertheless, differences in skill and specialization appear to have produced a hierarchy among Zulu metalworkers (Webb and Wright, 1986). The royal smith, who primarily produced brass ornaments, occupied the highest position in this hierarchy, followed by spear makers and hoe makers, respectively (Maggs, 1992).

By the nineteenth century, the manufacture and distribution of iron tools were subject to the authority of the Zulu king or *inkosi* (Maggs, 1992). While historical accounts often debate the independence of ironworkers, it is evident that the production was overseen by political authorities at both the chiefdom and kingdom levels (Raum, 1973; Costin, 1991). This is supported by Magg's (1992) reconstruction of precolonial ironworking in KwaZulu-Natal.

Although the scale of metal production during the Zulu kingdom era is not fully established, historical and archaeological evidence suggests that iron production mostly aligned with the demands of the Zulu king and the size of the military establishment (Maggs, 1992; Raum, 1973).

1.3.2 Spatial Organization of Zulu Iron Production

Earlier spatial investigation into Bantu-speaking iron metallurgy has indicated that smelting was mostly done in isolation away from the settlement due to ritual restrictions (Reid and MacLean, 1995; Greenfield and Miller, 2004). Based on Late Iron Age evidence from areas

north of Mpumalanga, Huffman (1990) argued that ironworking residues recovered from nineteenth-century village sites primarily represented forging and smithing activities conducted within settlements, while smelting took place in secluded locations outside the villages. Greenfield and Miller (2004), however, identified both spatial and temporal distinctions in metallurgical activities at the ninth- to tenth-century AD settlement of Ndondondwane. They argued that while forging and smithing took place within the village during its occupation, smelting activities occurred outside its confines (Greenfield and Miller, 2004). Smelting activities may have been done within the village after its abandonment (Greenfield and Miller, 2004; Greenfield and van Schalkwyk, 2003). More recent archaeological evidence from the ezinGwegweni *amakhanda*, including possible smelting or forging furnace, slag fragments and other metallurgical remains, suggests that smelting may also have occurred within settlements (Fowler and van Schalkwyk, 2025; Fowler and van Schalkwyk, 2026).

1.3.3 Iron Smelting Furnace Technology

Pre-industrial iron-smelting furnaces in southern Africa are broadly classified into three categories based on the shape: tall-shaft furnaces, low-shaft furnaces and bowl furnaces (Chirikure and Bandama, 2014b, p. 299). Factors such as furnace size, shape, airflow mechanisms, and heat-retention capacity affected the efficiency with which the raw materials were processed and the quality and usability of the resulting bloom. (Chirikure and Bandama, 2014b).

Iron-smelting furnaces were reportedly constructed to a depth of approximately 35 centimetres below ground, with a superstructure extending about 15 centimetres above the surface. They were connected to bellows through clay tuyeres, which directed air into the furnace and helped maintain the temperatures required for smelting (Roodt, 1996, p. 94). Archaeological

evidence indicates that Zulu furnaces were predominantly bowl-shaped (Figure 1.1 and Figure 1.2).

Excavations at Hluhluwe in the Sitezi area revealed the use of tuyere pipes, providing evidence of the airflow system used during smelting (Hall, 1980). The site also contained a distinctive arrangement of evenly spaced furnaces. This pattern differed from that identified at Mabhija, where furnaces occurred in pairs (Figure 1.3). Unlike Hluhluwe, Mabhija has the largest evidence of slag recorded in the eastern lowlands. The documented bowl furnaces contained openings through which tuyeres were inserted, allowing airflow to be controlled using skin bellows (Maggs, 1982). According to Maggs (1982, p. 140), furnaces from Hluhluwe and Mabhija represent a unique tradition which can be traced from “Tugela northwards” stretching to the “Mfolosi and Hluhluwe rivers”.



Figure 1.1: Bowl furnace with a short stack excavated at P74S01 (Smithy 2) (Reprinted after Fowler and van Schalkwyk 2026, fig. 3. B).



Figure 1.2: Paired bowl furnaces from Mabhija in the Tugela Basin, KwaZulu-Natal, South Africa (photo credit: KwaZulu Natal Museum Archives) (after Maggs 1982).

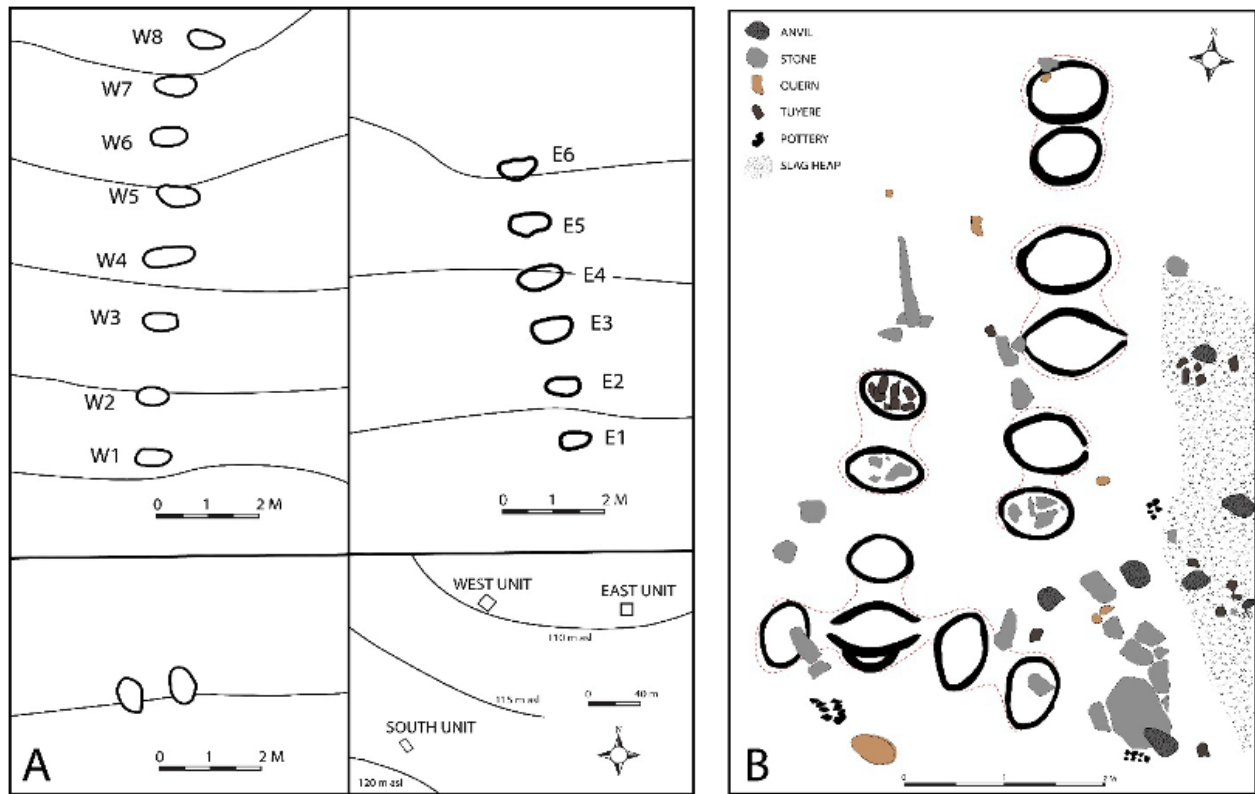


Figure 1.3: Metalworking layouts at (A) Smelting sites near the Hluhluwe River (redrawn from Hall 1982) and (B) Mabhiya Site A (redrawn from Maggs, 1982). After Fowler and van Schalkwyk (2025).

1.3.4 Zulu Iron Products

Zulu ironworkers produced mainly iron tools and weaponry (Maggs, 1991; Maggs, 1992; Maggs, 1993; Moffett, Maggs and van Schalkwyk, 2017). The production of iron ornaments appears to have been relatively uncommon, as archaeological evidence suggests that iron was used predominantly for utilitarian tools and weaponry (Roodt, 1993). Ornaments were instead commonly produced from brass, known as *ithusi elimhlophe*, which was highly valued in Zulu society (Maggs and Miller, 1995). Brass was used to manufacture personal adornments for the king, elite members, royal women of the *isigodlo*, high-ranking men (*izikhulu*), and distinguished warriors (Roodt, 1996, p. 95).

1.3.4.1 Iron Spears

Iron spears were central to the military operation of the Zulu Kingdom, especially the short stabbing spear known as the *iklwa*, an innovation under King Shaka, which was used in close combat with shields (*isihlangu*) (Eldredge, 2014; Roodt, 1996). Other documented spear types were used for throwing (*umkhonto*, *isijula*, *ingcula*, *inhlendla*); hunting (*unhlekwane*, *ingcawe*, *isijula*); ceremonial purposes (*isiphapha*); and for animal sacrifice (*umkhonto wokuhlaba*) (Roodt, 1996; Maggs, 1991). Maggs (1991, p. 132) categorized Zulu iron spearheads into five types: ogee-sectioned blades with double-foliate forms; broad ogee-sectioned blades with leaf-shaped forms; diamond-shaped spearheads commonly identified as Zulu spearheads; ogee-sectioned blades with square-sectioned tangs; and flat blades with thin, round-sectioned tangs (Figure 1.4).



Figure 1.4: Zulu Kingdom era iron spears accessioned at the KwaZulu-Natal Amafa Research Institute, Pietermaritzburg. A and B: Corroded spearhead with tangs (Accession date - 1978), C: Foliate spearhead with spikes on tang (Accession date: 1941, Site: uMgungundlovu), (Accession date: 1978, Site: uMgungundlovu) (Photos credit: Zulu Kingdom Archaeology Project (ZKAP)).

1.3.4.2 Battle Axes

The battle axe, known as the *isizenze*, was used for both warfare and hunting (Maggs, 1993). Maggs's (1993, p. 184) typology of Zulu battle axes held in museum collections classifies their blades into five forms: triangular, winged, crescent-shaped, bayonet-shaped, and sickle-shaped. Battle axes also held considerable political and ceremonial significance in Zulu society. They were carried by men who occupied positions of political authority or held senior military

ranks, thereby symbolizing status, leadership, and power. According to Maggs (1993), functional Zulu battle axes differed from ceremonial axes in both form and purpose. A typical Zulu battle axe had a broad, winged blade with a concave rear edge, whereas ceremonial axes were characterized by slender, elongated wings and long, thin handles (Maggs, 1993).

1.3.4.3 Iron Hoes

Iron hoes were among the largest iron implements produced by Zulu ironworkers and held considerable social, economic, and symbolic significance (Maggs, 1991; Moffett, Maggs and van Schalkwyk, 2017). Before the widespread use of iron hoes, similar agricultural implements were made from cattle shoulder blades and were known as *isiPanga* (Moffett, Maggs and van Schalkwyk, 2017).

Iron hoes manufactured and used by the Zulu ironworkers typically had long, narrow tangs and ellipsoidal or oval-shaped blades (Moffett, Maggs and van Schalkwyk, 2017) (Figure 1.5). They were produced primarily for agricultural purposes and were essential to food production (Kotze, 2021). Because of the high demand for hoes, a substantial proportion of smelted iron bloom may have been allocated to their manufacture. Older iron hoes were sometimes reforged into hoes (Moffett, Maggs and van Schalkwyk, 2017; Maggs, 1991).

In addition to their agricultural function, iron hoes had important social and symbolic value. During the nineteenth century, they were used as a medium of exchange for acquiring commodities, including cattle, and were sometimes presented as part of bride price in fulfilment of *ilobolo* obligations (Moffett, Maggs and van Schalkwyk, 2017).



Figure 1.5: Zulu iron hoe of circular shape with tapering shaft (Photo credit: The Trustees of the British Museum, BM Af1999,15.1). B: Heavily corroded iron hoe (Accession date: 1941, Site: uMgungundlovu). C: Worn iron hoe (Accession date: 1938, Site: uMgungundlovu). A and C are accessioned at KwaZulu-Natal Amafa Research Institute, Pietermaritzburg. (Photos credit: Zulu Kingdom Archaeology Project (ZKAP)).

1.4 Organization of the Thesis

This thesis is organized into five main chapters. Chapter One introduces the background to the study, identifies the research gap, outlines the research questions and hypotheses, provides an overview of Zulu metallurgy, and explains the motivation for the research.

Chapter Two reviews the literature on previous archaeological and archaeometallurgical studies conducted within the southern African context. It also traces the development of archaeometallurgy as a discipline and defines its principal concepts and approaches.

Chapter Three describes the materials examined in the study, including iron ores, slags, blooms, and metal artifacts dating to the period of the Zulu Kingdom. It also introduces the study area, identifies the locations from which the samples were collected, and provides an overview of the geology of KwaZulu-Natal. The chapter further presents the research methodology, including the analytical techniques and instruments employed, as well as the sample-preparation procedures and laboratory protocols followed during the study.

Chapter Four presents the analyses and results obtained through qualitative petrographic analysis, quantitative inductively coupled plasma mass spectrometry (ICP-MS), and semi-quantitative scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS).

Chapter Five discusses the technological and geochemical insights into iron production during the period of the Zulu Kingdom, based on the results obtained through the various analytical techniques. It also presents the overall conclusions of the study, discusses the challenges encountered, and provides recommendations for future research.

CHAPTER 2: LITERATURE REVIEW

2.1 Defining Archaeometallurgy

Through scientific analysis, metal artifacts have offered insights into the historical and cultural developments of post-Neolithic civilizations, including their technological, economic, and social evolution (Gentelli *et al.*, 2021). Archaeometallurgy may be broadly defined as the scientific study of ancient and pre-industrial metal production, distribution, use, and consumption through the application of techniques derived from the physical sciences (Chirikure, 2015b). The field emerged from the need for specialized archaeological inquiry into the role of metallurgy in early technological development (Craddock, 1995). As a subfield of archaeology, archaeometallurgy developed through the integration of cultural-historical approaches with scientific methods of investigation (Dolfini, 2024; Gonca, 2024; Killick, 2014).

To provide a comprehensive understanding of past metallurgical practices, archaeometallurgy draws upon multiple research methods and disciplines, including, archaeology, materials science, ethnoarchaeology, geology, history, and chemistry. These approaches are used to investigate broader social questions concerning the sourcing, production, exchange, use, and consumption of metals in both prehistoric and historical contexts (Gonca, 2024).

Recent literature has broadened the definition of archaeometallurgy beyond the technical processes involved in metal smelting. The field now encompasses the acquisition of raw materials and the relationships between metallurgical practices, human societies, and cultural systems (Chirikure, 2007; Hauptmann, 2020; Miller, 2002; Miller and Killick, 2004). Pernicka (2014), for example, defines archaeometallurgy as the interdisciplinary study of ancient

metallurgical processes, including the production and use of metal artifacts. This expanded definition combines archaeological investigation with scientific analysis, including chemical composition and isotopic analyses, to examine the technological, cultural, and economic dimensions of past metalworking.

Archaeometallurgical research therefore traces the entire production sequence, from the mining and smelting of ores to the manufacture, distribution, use, and eventual deposition of metal objects (Rehren and Pernicka, 2008). This broader perspective emphasizes the importance of examining the complete technological chain rather than focusing exclusively on smelting or the finished product.

Similarly, Killick and Fenn (2012, p. 559) defined archaeometallurgy as a “study that examines all aspects of the production, use and consumption of metals from 8000 BCE to the present”. Killick (2014, p.11) further emphasizes that archaeometallurgy is inherently interdisciplinary because no single researcher can master all the specialized fields upon which it draws. The field therefore depends on expertise from a wide range of disciplines to develop a comprehensive understanding of pre-industrial metal production.

According to Killick (2014, p. 11), these disciplines include socio-cultural anthropology, archaeology, ethnography, history, philosophy, mineralogy, petrology, chemistry, geology, metallurgy, ceramic technology, numismatics, forestry among others.

2.2 Chaîne Opératoire in Iron Metallurgy

To understand smelting effects on the chemical composition of the materials sampled in this study, it is necessary to understand the stages, techniques, and decisions involved in the iron-production process. In archaeometallurgical research, the concept of the *Chaîne opératoire* offers

a comprehensive outline for examining the entire technological sequence of iron production, from the mining of raw materials to finished objects (Daoust, 2014) (Figure 2.1).

The term *chaîne opératoire* refers to the step-by-step process of creating finished metal artifacts, from the initial selection of raw materials to the final product (Leroi-Gourhan, 1964). This process involves “the transformation of ore, a natural substance, into functional iron objects entails passing through a series of technical stages during which the material undergoes chemical and physical transformations” (Fluzin, 2014, p. 65).

Transforming iron ore into finished products requires a sequence of chemical and physical processes involving additional materials and agents, including fuel and oxidizing agents (Bauvais, 2009; Bauvais and Fluzin, 2009). The process of iron smelting is thus a technical and complicated technology that requires special expertise and knowledge. According to Hauptmann (2020, p. 6), “the chain of these activities shows that miners and metallurgists have always had the know-how.”

The effectiveness of the smelting process and the quality of its outputs are therefore determined not only by the quality of the ores and the type of the furnace but also by the expertise of the metalworkers and the decisions made throughout the production sequence (Stepanov *et al.*, 2022a, p. 22). Such decisions may include the choice of ores and smelting techniques, the choice of fuel, the regulation of airflow and temperature, and the timing of stages of production.

In studies of southern African metallurgy, the *chaîne opératoire* approach involves analysing the complete sequence associated with iron production within their cultural, social, and environmental contexts (Killick, 2001; Killick, 2004; Daoust, 2014;). According to Chirikure

(2018, p. 3), the broader sequence of iron production includes “mining, clay extraction, charcoal preparation, smelting, smithing and use of metal objects.” These production processes were also “imbued with religious, sociocultural, and symbolic attributes, all of which were inseparable from the associated technology” (Chirikure, 2018, p. 3). The *chaîne opératoire* approach therefore allows researchers to examine not only the technical processes involved in metallurgy but also the skills, choices, and knowledge systems through which those processes were organized.

This approach therefore helps researchers understand the specific techniques, skills and knowledge systems employed by pre-industrial societies in metalworking, thereby providing insights into socio-economic organization, cultural practices and technological innovation within these communities (Stoellner, 2013). By situating technological sequences within their broader social and cultural settings, this framework provides insights into the socio-economic organization, cultural practices, technological innovations, and environmental adaptations of pre-industrial metalworking communities

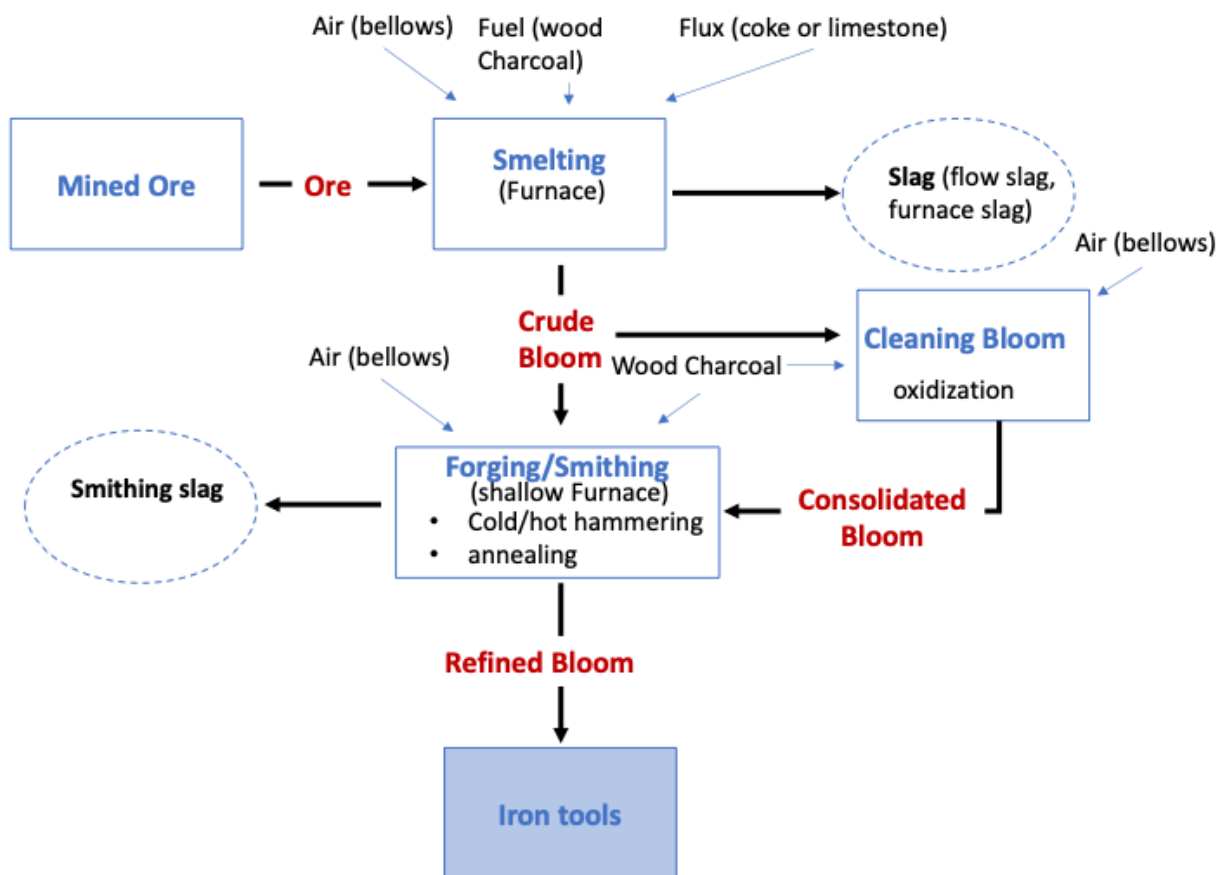


Figure 2.1: The *chaînes opératoires* for iron production (redrawn from Bandama, (2013))

2.3 The Early Developments in Archaeometallurgy

The science of studying metals can be traced back to the seventeenth century, but between the eighteenth and nineteenth centuries, scientific research of metallurgy gained much academic interest (Giardino, 2022). During this period, the scientific examination of metal artifacts focused primarily on their classification according to typology and chronology (Dizé, 1790; Jürgensen and Petersen, 1836), the measurement of alloy constituents (Hausmann, 1815; Becquerel, 1832; Roloff, 1810), and chemical compositional analysis (Goebel, 1842; Mallet, 1849).

Goebel's research in 1842 explored how chemical analysis can help identify the origins of ancient civilizations by studying metallic artifacts using scientific techniques (Goebel, 1842). Thus, by examining the composition of ancient metal objects, such as tools, weapons and ornaments, it was possible to trace the source material and gain insights into the trade routes, technological knowledge and cultural connections of past societies.

Around the same time, quantitative analytical techniques were introduced in studying metallurgy (Pearson, 1796; Gmelin, 1783; Klaproth, 1815; Berzelius, 1836; Wibel, 1863; Wibel, 1864; Berthelot, 1906). Klaproth (1815), for example, investigated the chemical composition of metal artifacts and developed one of the earliest quantitative analyses of archaeological metals. His analysis of Roman coins represented an important development in the application of quantitative chemistry to archaeological and metallurgical research. This work contributed to the foundations upon which later methods of characterizing metal artifacts were developed (Klaproth, 1815).

Subsequently, studies by Fellenberg (1866) and von Bibra (1873) further contributed to the development of archaeometallurgy through the systematic compositional analysis of iron artifacts. Their research provided information about the extraction, reduction, and manufacture of iron and contributed to a broader understanding of the technological and cultural developments associated with ironworking in antiquity (Fellenberg, 1866; von Bibra, 1873).

By the early twentieth century, the science of studying ancient metals had achieved a more comprehensive theoretical framework for research on technological change, cultural development, and production systems (Childe, 1963; Childe, 2009; Trigger, 1986; Wailes, 1996; Rowlands, 1971; Leroi-Gourhan, 2009; Tylecote, 1962; Smith, 1975). Advances in analytical

instrumentation, including spectrometry techniques, further expanded the study of ancient metallurgical practices (Otto, 1939; Stos-Gale and Gale, 2009).

Developments in emission spectrometry enabled researchers to detect elements at trace concentrations while requiring relatively small sample quantities. These advances strengthened the application of compositional and geochemical approaches to archaeological metals and contributed to the development of archaeometallurgy as an interdisciplinary field combining archaeological interpretation with scientific analysis (Rehren and Pernicka, 2008).

2.4 Iron Ore Sourcing Studies - A General Overview

The science of tracing iron artifacts to potential ore sources has been widely applied across various regions. Studies have shown that, despite the chemical transformations associated with smelting, iron products and smelting by-products can retain geochemical signatures that enable their correlation with potential ore sources (Coustures *et al.*, 2003; Blakelock *et al.*, 2009; Charlton *et al.*, 2010; Chirikure, 2014b; Chirikure and Bandama, 2014b; Crew, 2021).

In archaeometallurgy, applied geochemistry, which involves the characterization of elements and compounds, can be applied to ores, slags, blooms, furnace remnants and finished metal artifacts to understand the technology and geological source materials (Chirikure, 2014a). Geochemical methods continue to develop through the advancement in analytical instruments and laboratory techniques, enabling the chemical characterization and microscopic examination of archaeological materials with increasing precision (Pollard, 2007; Pollard and Bray, 2007; Pernicka, 2014).

The analysis of trace and major elements in ores, smelting by-products, and finished objects can assist in provenance of iron-production materials (Radivojević *et al.*, 2010). Recent

archaeometallurgical studies have employed analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) to characterize major and trace elements. These techniques have proved valuable for examining iron-production processes, identifying possible ore sources, and assessing the effects of smelting on the chemical composition of iron-production materials (Desaulty *et al.*, 2008; Gentelli *et al.*, 2021).

Desaulty *et al.* (2009) conducted a comparative analysis of medieval iron artifacts used in the construction of churches in Beauvais and Rouen, France, and iron ore samples obtained from the Pays de Bray region. Using major- and trace-element analyses of slag inclusions, they concluded that the chemical signatures of the iron used in the churches did not correspond with those of the sampled ores from Pays de Bray (Desaulty *et al.*, 2009).

Similarly, Leroy *et al.* (2012) investigated the provenance and distribution of iron ores and products in the Ariège region of France. The study sought to define the chemical signatures of ores from the region and compare them with slag inclusions in artifacts recovered from various archaeological sites. The findings revealed a complex regional iron market involving products derived from multiple sources, particularly at sites such as Montréal-de-Sos, which was located near important trade routes (Leroy *et al.*, 2012). Objects recovered from Castel-Minier were produced primarily from local ores, whereas most of the objects from Mirabat Castle appear to have originated outside the Ariège region, possibly because of an ore-for-charcoal exchange treaty (Leroy *et al.*, 2012).

Isotope-ratio analysis of prehistoric iron artifacts and associated smelting by-products has also proved valuable in provenance research (Dillmann *et al.*, 2017; Braun *et al.*, 2013).

Archaeometallurgical studies have examined isotopes of iron (Milot *et al.*, 2016; Braun *et al.*,

2013; Milot *et al.*, 2020), tin (Begemann, 1999; Hausteine, 2010), osmium (Junk, 2003; Braun *et al.*, 2013; Liss, Levy and Day, 2020), lead (Schwab *et al.*, 2006; Degryse *et al.*, 2007; Degryse, Schneider and Muchez, 2009; Radivojević *et al.*, 2010; Molofsky *et al.*, 2014; Rademakers *et al.*, 2019; Gentili *et al.*, 2021; Ciarlo *et al.*, 2022) and strontium (Degryse *et al.*, 2007; Dufour *et al.*, 2007; Degryse, Schneider and Muchez, 2009; Braun *et al.*, 2013).

Braun *et al.* (2013) analysed rhenium-osmium (Re-Os) isotope ratios in iron ores, slags, and blooms from an Early Iron Age smelting site in the Black Forest of southern Germany. They concluded that osmium isotopes, because of their highly siderophile characteristic, may preserve diagnostic geochemical signatures throughout the smelting process and are therefore potentially suitable for provenance studies of pre-industrial iron. A major limitation of this analytical approach, however, is the requirement for enough slag inclusions to obtain reliable isotope-ratio measurements (Braun *et al.*, 2013).

In a similar study, Degryse *et al.* (2007) used Thermal Ionization Mass Spectrometry (TIMS) to analyse and compare lead (Pb) and strontium (Sr) isotope signatures from Roman to Byzantine iron artifacts and iron ore samples from the ancient territory of Sagalassos, Turkey. Their findings, based on multivariate analysis, revealed that the ores used were derived from multiple sources, highlighting the diverse origins of the materials (Degryse *et al.*, 2007; Degryse, Schneider and Muchez, 2009).

These studies demonstrate the value of different analytical techniques in iron-provenance research. However, a multi-method approach is often preferable because it can help mitigate the limitations associated with individual analytical techniques (Rehren and Pernicka, 2008). Schwab *et al.* (2013), for example, combined chemical compositional analysis with lead-isotope analysis to examine iron finds from southern Germany. They concluded that the raw materials

used for iron smelting in the Manching region were obtained from bog-ore deposits near the Danube River.

In another multi-method study, Dillmann *et al.* (2017) combined osmium-isotope-ratio (Os) analysis with trace-element analysis to compare the chemical signatures of approximately 31 iron artifacts. The analysed materials included chariot tyres, blooms, and bipyramidal semi-finished iron objects. The study sought to determine the origins of the iron and examine its circulation among sites in the North Alpine region towards the end of the First Iron Age. The findings indicated that the ores used to produce the blooms and wheel tyres were locally sourced, whereas the remaining objects were potentially produced from ores of different geographical origins (Dillmann *et al.*, 2017).

2.5 Archaeometallurgy in Southern Africa

Archaeometallurgical research in southern Africa has increasingly incorporated modern geochemical methods and analytical techniques to investigate past iron working practices. Through these approaches, studies of the geochemical signatures of iron artifacts (Begemann *et al.*, 1999; Miller, 2002; Hall *et al.*, 2006; Mathoho, Nyamushosho and Chirikure, 2023), furnace types (Whitelaw, 1991; Chirikure, 2006; Chirikure and Bandama, 2014a), and smelting by-products have provided important insights into the sources of raw materials (Grant, 1999; ; Haustein, 2010; Bandama, Chirikure and Hall, 2013; Molofsky *et al.*, 2014), and manufacturing processes employed by ironworkers (Chirikure, 2006; ; Miller, 2002; Thondhlana, Martín-Torres and Chirikure, 2016; Bandama, 2020; Mathoho, Nyamushosho and Chirikure, 2023;).

2.5.1 Southern African Early Iron Age Iron Technology

As noted earlier in this chapter, archaeometallurgical techniques have been widely applied in southern Africa to reconstruct pre-industrial iron-smelting technologies. Mathoho, Nyamushosho and Chirikure (2023) employed a multidisciplinary approach that combined petrographic and chemical analyses, including optical microscopy, X-ray fluorescence (XRF), and scanning electron microscopy (SEM). These methods were used to determine the composition and microstructure of iron ores, tuyere fragments, and iron-smelting remains recovered from Mutoti 2, an Early Iron Age site in northern South Africa. The results of the study indicate that ironworkers at Mutoti 2 utilized a bloomery process in which iron ore was heated with charcoal under reducing conditions to produce a spongy bloom (Mathoho, Nyamushosho and Chirikure, 2023). The presence of tuyeres and the composition of the associated slags suggest that the smelting process was carefully controlled. This evidence reflects the ironworkers' detailed understanding of temperature regulation, airflow, and the reducing conditions required for effective iron production.

In another study conducted at Shankare Hill in the northern Lowveld, Thondhlana, Martín-Torres and Chirikure (2016) reconstructed iron-smelting technology through an archaeometallurgical investigation of titanium-rich iron slags. They concluded that the technology represented a typical bloomery process comparable to the extractive technologies documented at other iron-smelting sites in the northern Lowveld (Killick and Miller, 2014; Miller, Killick and Van der Merwe, 2001).

The integration of archaeological evidence with scientific analysis has demonstrated the technical expertise of ironworkers and the significance of iron production in the historical development of southern Africa. Bandama, Chirikure and Hall (2013) investigated Iron Age

metal production in the southern Waterberg region of South Africa using quantitative wavelength-dispersive X-ray fluorescence (WD-XRF) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). These techniques were used to characterize the chemical composition and microstructure of smelting by-products. From their studies, iron workers utilized a bloomery process with locally available hematite ores. The production system was described as “self-fluxing” because the silica required for slag formation was supplied through the deliberate erosion of the furnace walls rather than through the addition of a separate mineral flux (Bandama, Chirikure and Hall, 2013, p. 263).

Other mixed-method studies have also contributed to the identification of changes and continuities in metal-production practices over time, thereby providing evidence for reconstructing broader socio-economic dynamics. Miller and Whitelaw (1994) combined archaeological investigation with laboratory analysis to compare the metallurgical technology at kwaGandaganda with contemporaneous iron artifacts and smelting by-products from other ironworking sites in southern Africa. Their comparative analyses revealed little variation between the iron artifacts from kwaGandaganda and assemblages from other southern African sites, including Tsodilo Hills and Broederstroom (Miller and Whitelaw, 1994). The smelting and forging technologies employed at kwaGandaganda were also similar to those documented at the Early Iron Age sites of Divuyu and Nqoma in the Tsodilo Hills of Botswana (Miller and Whitelaw, 1994).

2.5.2 Iron Ore Sourcing

Iron workers were knowledgeable about the environment and exploited the resources available for smelting (Bauvais and Fluzin, 2009; Bandama, Chirikure and Hall, 2013; Bandama, 2020; Chirikure, 2018; Huffman, 2007; Pfaffenberger, 2020). This knowledge is a testament to

their expertise, as established by studies done by Stepanov *et al.*(2022b) and Chirikure and Bandama (2013)

At kwaGandaganda, Miller and Whitelaw (1994) conducted detailed laboratory analyses of ferrous artifacts and two slag fragments using petrography, metallography, and chemical analysis. They concluded that ironworkers may have exploited two potential ore sources: haematite from the Pietermaritzburg Shale Formation and iron-rich sand from the Berea Red Formation (Miller and Whitelaw, 1994).

In the northern Lowveld of South Africa, Killick and Miller (2014) demonstrated the potential of chemical analysis and thin-section microscopy for identifying the sources of iron ores represented in ferrous slags. They comparatively analysed slag and iron ore samples using reflected-light microscopy, wavelength-dispersive X-ray fluorescence (WD-XRF), X-ray diffraction (XRD), and electron microprobe analysis (EMPA). The results suggested that the ores may have originated from the Phalaborwa and Schiel Complexes, as well as from the magnetite-ilmenite deposits of the Rooiwater Igneous Complex (Killick and Miller, 2014).

2.6 Conclusion

Archaeometallurgy has developed into an interdisciplinary field that combines archaeological inquiry with scientific methods to investigate the production, distribution, use, and consumption of metals in past societies. Early studies relied largely on typological classification, petrographic examination, and optical techniques to understand pre-industrial metallurgy. However, significant advances in analytical science, particularly in geochemistry and materials characterization, have transformed the field.

Improvements in mineralogical and chemical characterization, together with the development of quantitative analytical methods such as X-ray fluorescence (XRF), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), inductively coupled plasma mass spectrometry (ICP-MS), and isotope analysis, have enabled researchers to reconstruct technological processes and investigate the provenance of iron ores with greater precision. These developments have also demonstrated the value of integrating multiple analytical approaches with archaeological, historical, and ethnographic evidence to produce more comprehensive interpretations of pre-industrial metallurgical practices and technological choices.

The literature reviewed in this chapter further demonstrates that archaeometallurgical research in southern Africa has contributed substantially to the understanding of iron-production technologies, resource exploitation, and socio-economic organization in pre-industrial societies. Studies conducted across the region indicate that iron smelting was a technically complex and knowledge-intensive process embedded within broader cultural, social, ritual, and environmental contexts.

Overall, the integration of scientific laboratory methods with archaeological and historical evidence continues to refine interpretations of pre-industrial iron metallurgy. This interdisciplinary framework provides a strong foundation for investigating iron-production technologies, changes in chemical composition throughout the production sequence, and the sourcing of iron ores in southeastern Africa. It also establishes the analytical and theoretical basis for the present study of iron production during the period of the Zulu Kingdom.

CHAPTER 3: STUDY AREA, MATERIALS AND METHODS

3.1 Introduction

In archaeometallurgical research, laboratory investigation of archaeological materials enhances understanding of metallurgical remains and past production processes (Fluzin, 2014). Drawing on their archaeometallurgical research, Miller and Killick (2004), argue that the study of materials such as ores, slags, blooms, and metal artifacts should combine morphological assessment, microscopic examination, chemical analysis, and consideration of the archaeological context.

Different geochemical techniques have varying analytical capabilities, detection limits, and levels of precision (Chirikure, 2015a). Consequently, this study employed multiple analytical techniques to examine the sampled materials and address the limitations associated with relying on a single method (Fluzin, 2014; Dillmann *et al.*, 2017). These techniques included imaging, major- and trace-element analysis, and multivariate statistical analysis (Killick, 2014; Pollard and Bray, 2014; Dillmann *et al.*, 2017).

This chapter presents the study area, materials examined and the analytical methods employed in the study. It describes the sample-selection procedures, laboratory preparation methods, analytical protocols, and instruments used. The chapter also provides the cultural and historical context of the study area, identifies the sampling locations, and outlines the geology of the southeastern lowlands of South Africa.

3.2 Study Area

In this thesis, I primarily focused on archaeometallurgical materials from different sites within the Zulu Kingdom. The study area is situated in the southeastern lowlands of South

Africa. This area sits east to west between the central Midlands coast and from the White uMfolozi River in the north to the Thukela River in the south (Figure 3.1). This area is the core of the Zulu Kingdom territory and the epicentre of Zulu heritage and traditions.

Today, the Zulus constitute one of the largest groups among the Nguni-speaking peoples and occupy a prominent place in the historical and cultural development of modern South Africa. According to oral tradition, the ethnonym “Zulu”, meaning “people of the skies,” was adopted by Malandela, who is generally regarded as an important ancestor of the Zulu people (Derwent, 2006, p. 4).

The Zulu Kingdom was one of the most prominent political entities in nineteenth-century southern Africa and rose to prominence under rulers such as Shaka, Dingane, Mpande, and Cetshwayo (Kennedy, 1991). According to Gump (1988), the kingdom emerged during the early nineteenth century because of a complex combination of historical, political, cultural, and economic factors. These included changes in the regional political landscape, the emergence of new economic and trade networks, and the expansion of the military.

At its height, the Zulu Kingdom was a powerful and influential state that exercised considerable political and military authority across parts of southeastern Africa. During this period, settlements were structured in accordance with the political and administrative organization of the kingdom. They were generally divided into two principal categories: royal or military settlements known as *amakhanda*, which were associated with the king, and family homesteads known as *imizi*. These settlements occupied different positions and exercised varying degrees of authority within the governance structure of the kingdom (Fowler and van Schalkwyk, 2022, 2025) (Figure 3.2)

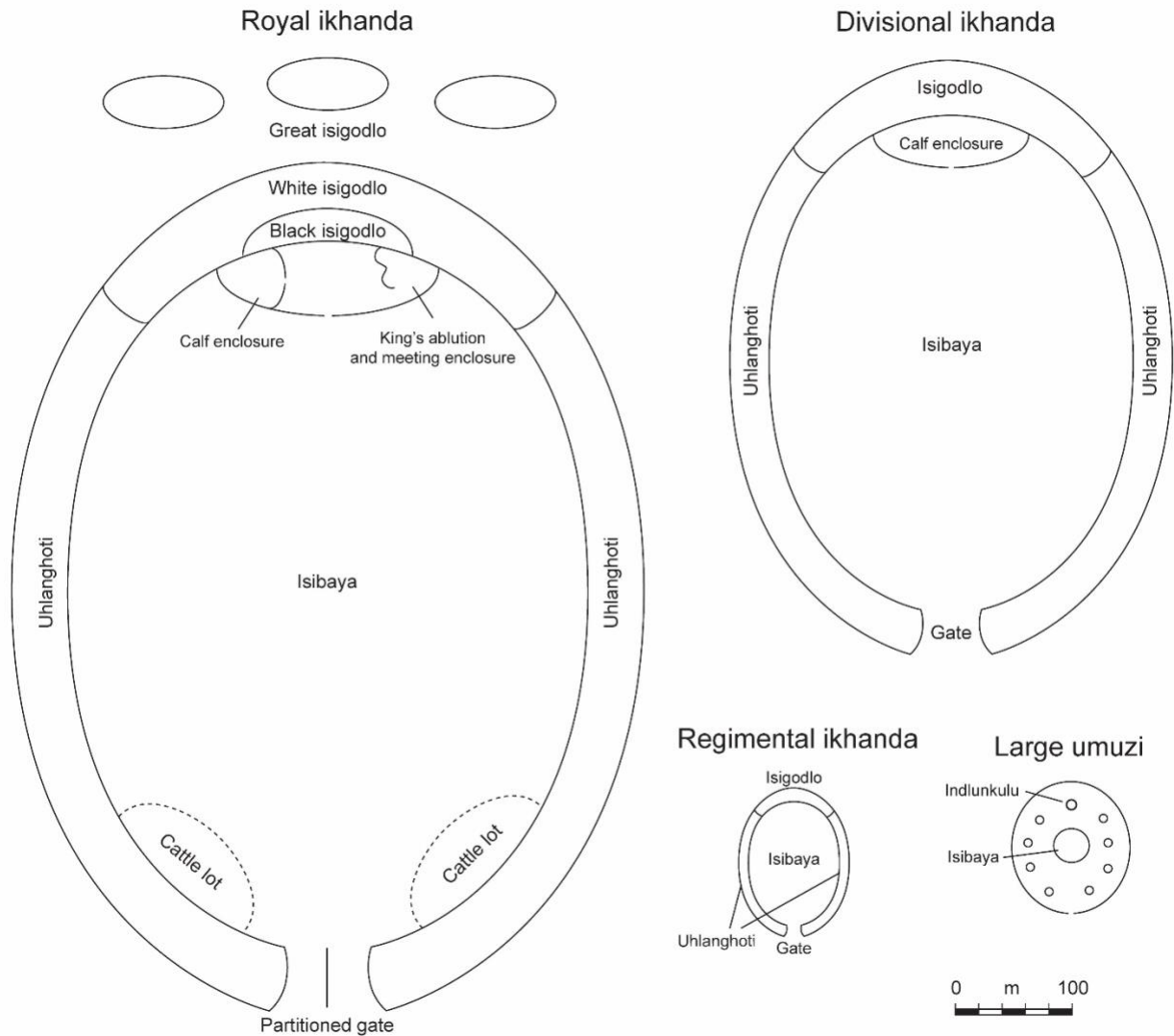


Figure 3.2: Layout of traditional Zulu amakhanda and homesteads. Reprinted after Fowler and van Schalkwyk 2022, fig. 3.

3.2.1 uMgundgundlovu

uMgundgundlovu, referred to in some historical records as Dingane's Royal Kraal, served as the capital of King Dingane, who lived from 1785 to 1840. The settlement was established in December 1829 in the emaKhosini Valley, between the uMkhumbane and Nzololo streams. The

name *uMgungundlovu* is derived from the isiZulu expression *ungungu we ndlovu*, meaning “the secret place of the elephant” (Derwent, 2006, p. 6).

uMgungundlovu was a large and carefully planned settlement that reflected the centralized political authority and organizational capacity of the Zulu Kingdom under King Dingane. Its layout consisted of a central cattle enclosure, or *isibaya*, surrounded by residential huts arranged in a circular formation, a pattern characteristic of Zulu royal and military *amakhandas* (van der Merwe and Pikirayi, 2019).

King Dingane abandoned *uMgungundlovu* in December 1838 following the defeat of his forces by the Voortrekkers at the Battle of Blood River, also known as the Battle of Ncome (Parkington and Cronin, 1979; von Kapff, 2012). Following the defeat, Dingane ordered the capital to be burned and migrated north of the *uMfolozi* River, where he established another capital (Parkington and Cronin, 1979).

Archaeological excavations conducted at the site over several decades have recovered a wide range of artifacts, including iron objects, faunal remains, brass crucibles, brass bangles, glass beads, grindstones, and ceramics (Parkington, 1974; Parkington and Cronin, 1979; Plug and Roodt, 1990; Roodt, 1993). Also, the two iron hoes sampled for this thesis were excavated at this site between 1939 and 1940.

3.2.2 *kwaDukuza*

The site of *kwaDukuza* in the *emaKhosini* occupies a significant place in the history of the Zulu Kingdom. Named after King Shaka’s third *ikhanda*, it is located near the Indian Ocean coastline at the present town of Stanger. *kwaDukuza* was established by King Shaka in late 1826

near the Mvoti River as his new royal capital (Fowler and van Schalkwyk, 2022; Fowler and van Schalkwyk, 2025a).

At kwaDukuza, King Shaka established military and administrative reforms such as the *imizi* and military barracks (Eldredge, 2014). The presence of an organized military establishment suggests that iron was an important resource at the site because it was required for the manufacture of weapons used in warfare and defence. The site is also where Shaka was assassinated in 1828 by his half-brothers, Dingane and Mhlangana (Eldredge, 2014).

3.2.3 *ezinGwegweni*

During the Anglo-Zulu War of 1879, British forces targeted Zulu military settlements to dismantle the kingdom's military infrastructure. On June 26, 1879, the regimental *ikhanda* of ezinGwegweni was among nine *amakhandas* destroyed by Wood's Flying Column, a British military unit, during the second invasion of the Zulu people (Laband, 2014; Thompson, 2006). The destruction of these settlements was intended to weaken the logistical and operational capacity of the Zulu army. It contributed to the eventual defeat of the kingdom and its subsequent incorporation into British-controlled territory (Laband, 2014).

ezinGwegweni was surveyed in 2022 by the Amafa Research Institute in KwaZulu-Natal and the Zulu Kingdom Archaeology Project (Fowler and van Schalkwyk, 2025a; Fowler and van Schalkwyk, 2022; Fowler and van Schalkwyk, 2025b). Archaeological investigations yielded a range of artifacts, including ceramics, lithic tools, furnace debris, and iron slag. Features such as middens and grain pits were also identified. The archaeological remains generally correspond with the layout and characteristics of a typical regimental *ikhanda*. However, no clear evidence of an *isigodlo* or a great *isigodlo* was identified (van der Merwe and Pikirayi, 2019; van der

Merwe, Fowler and Sadr, 2023). The furnace debris and iron slag documented by Fowler and van Schalkwyk (2025a) suggest that iron-smelting activities may have taken place at the site.

3.2.4 *Mamba*

Mamba is an important Early Iron Age settlement located in the Thukela River Valley of KwaZulu-Natal, South Africa. The site was occupied by mixed-farming communities between approximately the eighth and tenth centuries AD (Huffman, 2007; Van Schalkwyk, 1994, pp. 138-140). Materials from Mamba were included in this study because previous archaeological excavations at the site revealed evidence of iron-smelting activities. Analyses of recovered slag and ore fragments also suggest that ironworkers may have exploited locally available ore sources (Van Schalkwyk, 1994).

Also, the site's proximity to other Early Iron Age settlements, such as Wosi and Ndondondwane, further indicates a regional pattern of settlement, resource utilization, and metallurgical activity within the Thukela River Valley (Van Schalkwyk, 1994a; van Schalkwyk, 1994b; Coutu *et al.*, 2016). Collectively, these sites contribute to an understanding of the economic activities, social organization, and regional interactions of Early Iron Age communities in southern Africa. The archaeological evidence from Mamba is therefore important for examining iron production within the broader historical landscape of the region.

3.2.5 *Ndondondwane*

The Early Iron Age (EIA) site of Ndondondwane is located on the northeastern bank of the Thukela River in KwaZulu-Natal, South Africa (House *et al.*, 2023, p. 3). The site has been extensively studied to understand the social, economic and environmental aspects of Early Iron Age (EIA) communities. Initial surveys in the 1970s and later excavations in 1995 revealed a

unique settlement pattern characterized by shallow deposits and a short occupation period over the 9th to 10th Century AD (Greenfield, van Schalkwyk and Jongsma, 1997; van Schalkwyk; Maggs, 1984). Studies by Greenfield and Miller (2004) examined the spatial patterning of ironworking, highlighting the settlement's social organization and economic activities. Other studies have highlighted the site's chronology (Fowler, Greenfield and van Schalkwyk, 2000; Fowler and Greenfield, 2009), ceramics (Fowler, 2002; Fowler, 2011), local ecology and plant use (House *et al.*, 2023), environmental and subsistence studies (Greenfield and van Schalkwyk, 2008; Greenfield, 2006), taphonomic processes (Fowler, Greenfield and van Schalkwyk, 2004), and fauna (Fread, 2007; Arnold, Greenfield and Creaser, 2013; Coutu *et al.*, 2016).

3.2.6 Wosi

Wosi is an Early Iron Age archaeological site located in the lower Thukela River Basin of KwaZulu-Natal, South Africa. The site dates to approximately the seventh and eighth centuries AD and is important for understanding the social, economic, and technological practices of early farming communities in the region (van Schalkwyk, 1994).

Archaeological excavations at Wosi have revealed evidence of an organized settlement, including pottery, tools, and faunal remains (van Schalkwyk, 1994). These findings provide insights into subsistence practices that combined mixed farming with participation in regional exchange networks (van Schalkwyk, 1994).

In addition to subsistence evidence, iron smelting residues from Wosi had high manganese content, unlike Mamba, whose ore was obtained from titaniferous magnetite deposits. According to van Schalkwyk (1994, p. 94), iron workers probably sourced ore from “magnetite deposits discovered on the south bank of the Thukela, opposite the Wosi site”. The presence of

metallurgical remains and the identification of a potential nearby ore source make Wosi an important comparative site for this study. Its inclusion was important because it was the only site that has the complete materials to examine the chemical behaviour from ore to finished artefact.

3.3 Geological Overview of KwaZulu-Natal

Archaeometallurgical research requires a comprehensive understanding of the local geology, particularly with provenance studies (Thondhlana, Martínón-Torres and Chirikure, 2016). For this study, ore samples were collected from several geological formations and groups. These included amphibolites of the Mambulu Complex within the Tugela Group in the Tugela Basin; magnetite-rich shales of the Mozaan Group at Denny Dalton; magnetite-bearing shales of the Pietermaritzburg Formation at Jameson's Drift (Figure 3.3); banded iron formations within the Dwyka Group bedrock near Nkandla (Figure 3.4) and shales of the Pietermaritzburg Formation in the Ecca Group at Babanango.

KwaZulu-Natal is characterized by rocky topography that rises steeply from the coast towards the interior. Elevations increase to approximately 600–900 m above sea level in the hinterland and reach approximately 1,200–1,500 m (Camp, 1999). The geology of the province comprises a diverse sequence of rock formations that reflect the complex geological history of the region. These formations span the Archaean, Proterozoic, Palaeozoic, Mesozoic, and Cenozoic eras and include several supergroups and geological units that contribute to the province's diverse geological landscape (Camp, 1999) (Figure 3.5)

Nsuze and Mozaan groups belongs to the Pongola Supergroup. The Mozaan Group is mainly of siltstone and magnetite-bearing mudstone (Gold and Von Veh, 1995). This geology is known for iron ores and gold-bearing conglomerate (Groenewald, 2012; Hicks and Hofman,

2012). The Nsuze group comprises basalt, limestone, banded siltstone and sandstone in the lower part (Groenewald, 2012; Hira, 1998).

In the central to southern parts of the province, the primary geological sequence is the Proterozoic Natal Metamorphic Province (NMP) (Groenewald, 2012). The lithostratigraphy of the Natal Belt is characterized predominantly by granite and gneiss and is divided into three terranes namely; Tugela, Mzumbe and Margate (Thomas, 1989; Hira, 1998; McCourt et al., 2006; Bisnath et al., 2008; Clarke, 2008;).

The Margate Terrane forms the southern part of the Natal Belt and consists mainly of metamorphosed rocks that were later intruded by granitic materials (Thomas, 1989; McCourt et al., 2006; Bisnath et al., 2008). Some areas have relatively high levels of metamorphism, particularly near large intrusive rock bodies (Thomas, 1989; McCourt et al., 2006).

The Tugela Terrane is also interpreted as a remnant of an ancient ocean basin and contains a mixture of felsic and mafic rocks, schists, granitic rocks, and marble (Johnston et al., 2003). It is also important because it contains several mineral deposits, including sulphide ores, gold associated with quartz veins, and other metalliferous minerals (Thomas, 1989).

The Karoo Supergroup, which formed during the Palaeozoic and Mesozoic eras, comprises several distinct lithostratigraphic units. These include the Lebombo Group, characterized primarily by rhyolite and basalt; the Drakensberg Group, composed predominantly of basalt and associated dolerite; the Stormberg Group, which includes sandstone units such as the Molteno Formation; the Beaufort Group, characterized largely by mudstone and sandstone; the Ecca Group, which comprises sandstone and shale formations, including the Vryheid and

Pietermaritzburg formations; and the Dwyka Group, which is composed predominantly of diamictite (Groenewald, 2012).

Along the coast, unconsolidated sediments dominate the geological composition, representative of the Cenozoic era and enriched in minerals such as titanium and zirconium (Sudan, 1999; Groenewald, 2012). The Zululand group, forming a significant part of the coastal plain, consists of siltstone and sandstone (Groenewald, 2012). Within this group, the Cretaceous Mzinene formation has shallow marine glauconitic siltstones, sandstones with calcareous concretions and limestone beds which is like the St Lucia Formation (Sudan, 1999). The Makatini Formation comprises sandstone and marine siltstone (Sudan, 1999; Groenewald, 2012). This stratigraphic sequence defines the diverse geology of the region as seen in Figure 3.5.



Figure 3.3: Outcrops revealing exposed magnetite-rich shale interlayered by non-magnetic rich shale along the Jameson's Drift, KwaZulu-Natal, South Africa (source: Zulu Kingdom Archaeology Project Archives (ZKAP)).

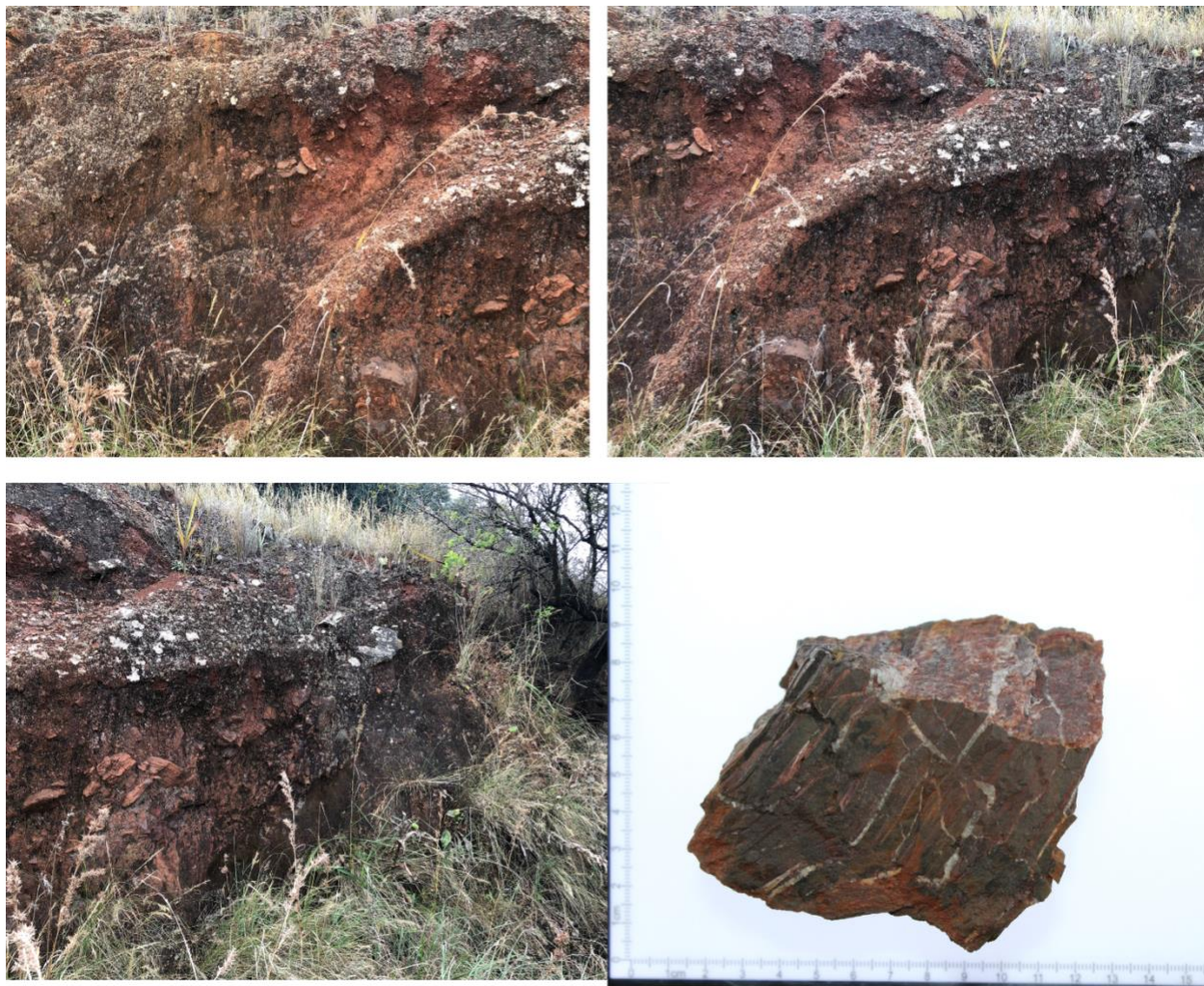


Figure 3.4: Exposed magnetic iron-banded formations around the Middle Tugela River, KwaZulu-Natal. (Source: Zulu Kingdom Archaeology Project Archives (ZKAP)).

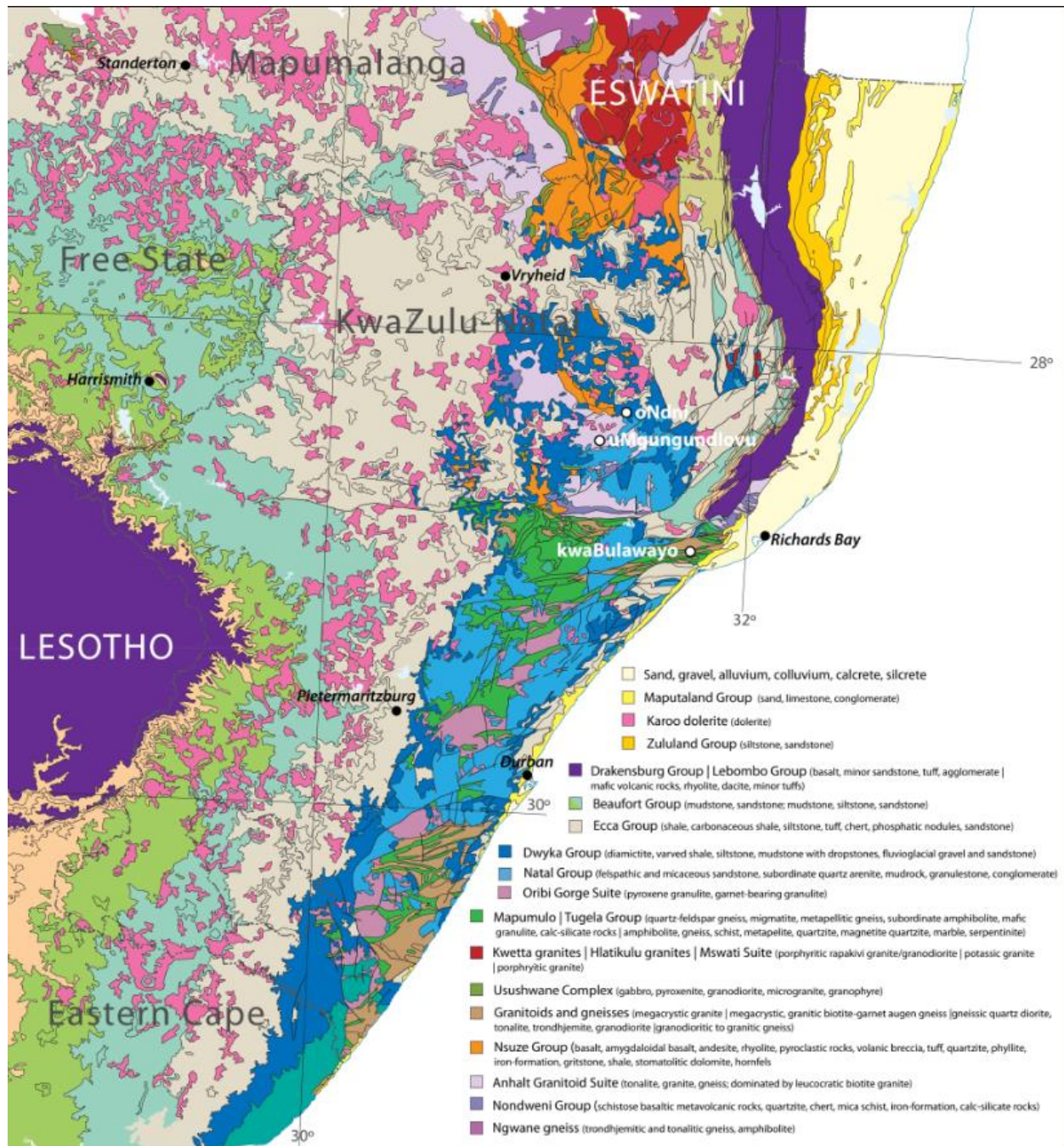


Figure 3.5: Simplified geological map of the province of KwaZulu-Natal (Reprinted with permission by Zulu Kingdom Archaeology Project (ZKAP) 2023).

3.4 Materials

This study focused on iron ores, iron artifacts, and the residual materials produced during smelting and forging, namely slags and blooms. The iron artifacts belong to the era of the politically independent Zulu Kingdom and cover much of the nineteenth century AD (c. 1816-1879). For analytical purposes, the sampled materials were grouped into archaeological materials dating to the period of the Zulu Kingdom and comparative materials from other relevant archaeological and geological contexts (Table 3.1)

3.4.1 Archaeological Samples

Archaeological examples of iron tools and implements are exceedingly rare. An effort was made in this study to target iron artifacts and by-products of secure provenience and determinate function. Archaeological samples included two iron hoes found at uMgungundlovu (Parkington, 1974; Roodt, 1993) (Figure 3.7, A and B), an iron ore fragment identified at KwaDukuza *ikhanda* (Fowler and van Schalkwyk, 2022) (Figure 3.8, G) and two ferrous slag fragments from ezinGwegweni *ikhanda* (Figure 3.10, F). The three sites, uMgungundlovu, KwaDukuza and ezinGwegweni, are within two kilometres of one another within the eMakhosini basin south of the White uMfolozi River (Figure 3.11).

3.4.2 Comparative Samples

Three regional sets of comparative samples were used to establish geochemical signatures for potential ore sources. First, iron ore samples from the Mozaan shales at Denny Dalton (Figures 3.8E and 3.8F) and ore from the Pietermaritzburg shales on the Babanango Plateau (Figure 3.8C) were also examined because of their proximity to the *amakhanda* in eMakhosini. Second, ore samples from the Pietermaritzburg shales in the Mhlatuze River catchment near

kwaBulawayo-2 were included. Third, ore samples from Nkandla (Figure 3.8A), Wosi (Figure 3.8B), and Jameson's Drift (Figure 3.8D) were examined to investigate potential ore sources associated with the amphibolites of the Tugela Group in the Thukela River Basin. Comparative slag and bloom samples were also obtained from the Early Iron Age sites of Ndondondwane, Wosi, and Mamba (Figures 3.9 and 3.10).

All archaeological materials used in this research are housed at the KwaZulu-Natal Amafa and Research Institute in Pietermaritzburg, South Africa. The geological ore samples were obtained during the Zulu Kingdom Archaeology Project and are housed in the Department of Anthropology at the University of Manitoba.

Table 3.1: Descriptions of sampled materials from archaeological sites and ore sources.

Archaeology sample							
Finds Number	Observation Code	Site Name	Accession Date	Type	Description	Context	Count
1939-M-101	NGU-20	uMgungundlovu	1939	Hoe	Tanged, kidney-shaped hoe blade with wear and folding on the blade. Possibly repurposed as an axe.	Surface collection, probably in the 1930s	1
1940-M-102	MGU-21	uMgungundlovu	1940	Hoe	Tanged, kidney-shaped hoe blade with wear and folding on the blade. Possibly repurposed as an axe.	Surface collection, probably in the 1930s	1
2022-M-118	DUK-9	kwaDukuza	2022	Ore find	Iron ore fragment	Locus 08 is associated with a few hammer stones found on the eastern side of the site.	1
2022-M-119 2022-M-120	GWE-14 GWE-18	ezinGwegweni	2022	In-situ Slag	2 pieces of metallic iron slag collected for analysis	Locus 06 is associated with hammer stones, anvils, sharpening stones, and a nearby furnace	2
Comparative sample							
1983-M-111	MAM-4	Mamba	1983	In-situ Bloom	Thin bloom mass that could be run off bloom of a tuyere	OU I, 4C, Area 2	1
1983-M-112	MAM-16	Mamba	1983	In-situ Slag	Tuyere fragment with slag mass on exterior (slag: 38 x 27 mm)	OU I, 6C, Area 2	1
1983-M-113	MAM-13	Mamba	1983	In-situ Slag	vitirified (glassy) slag mass	OU I, 4C, Area 2	1
1983-M-114	MAM-1	Mamba	1983	Bloom	fragment of bloom	OU I, 6C, Area 2	1
1983-M-115	MAM-12	Mamba	1983	In-situ Slag	vitirified (glassy) slag mass	OU I, 5B, Area 2	1
1996-M-116	NDO-17	Ndondondwane	1996	In-situ Slag	slag fragment	surface collection near 'Furnace Area': 4-6 E, 25-30 S	1
1996-M-117	NDO-3	Ndondondwane	1996	In-situ Bloom	fragment of bloom (50 x 60 mm)	surface collection near 'Furnace Area': 4-6 E, 25-30 S	1
1984-M-107	WOS-8	Wosi	1984	Ore source	Iron ore fragment from the Mambulu Complex within Tugela Group amphibolite	Grid 2, Trench 1, Level 2	1
1985-M-109	WOS-15	Wosi	1985	In-situ Slag	slag fragment	Grid 2, Level 2	2
1984-M-108	WOS-2	Wosi	1984	In-situ Bloom	Iron bloom fragment	Grid 2, Level 1	1
1985-M-110	WOS-19	Wosi	1985	Jeweller y "amulet"	half of a circular iron object with a central hole that van Schalkwyk interpreted as an amulet.	Grid 2. Quarter 1, Trench 6, Square A, Level 2	1
2023-M-157	DEN-7	Denny Dalton	2022	Ore source	Mozaan Shale	Denny Dalton	1
2023-M-158	DEN-6	Denny Dalton	2023	Ore source	Mozaan Shale	Denny Dalton	1
2023-M-156	JAD-5	Jameson's Drift	2023	Ore source	Pietermaritzburg shales	Jameson's Drift	1
2024-M-113	NKD-11	Nkandla	2024	Ore source	Iron Banded Formations (Dwyka Group bedrock	Nkanlida (Middle Thukela River)	1
2023-M-153	BAB-10	Babanango	2023	Ore source	Pietermaritzburg shales (Swazian Era leucocratic biotite granite	Babanango	1

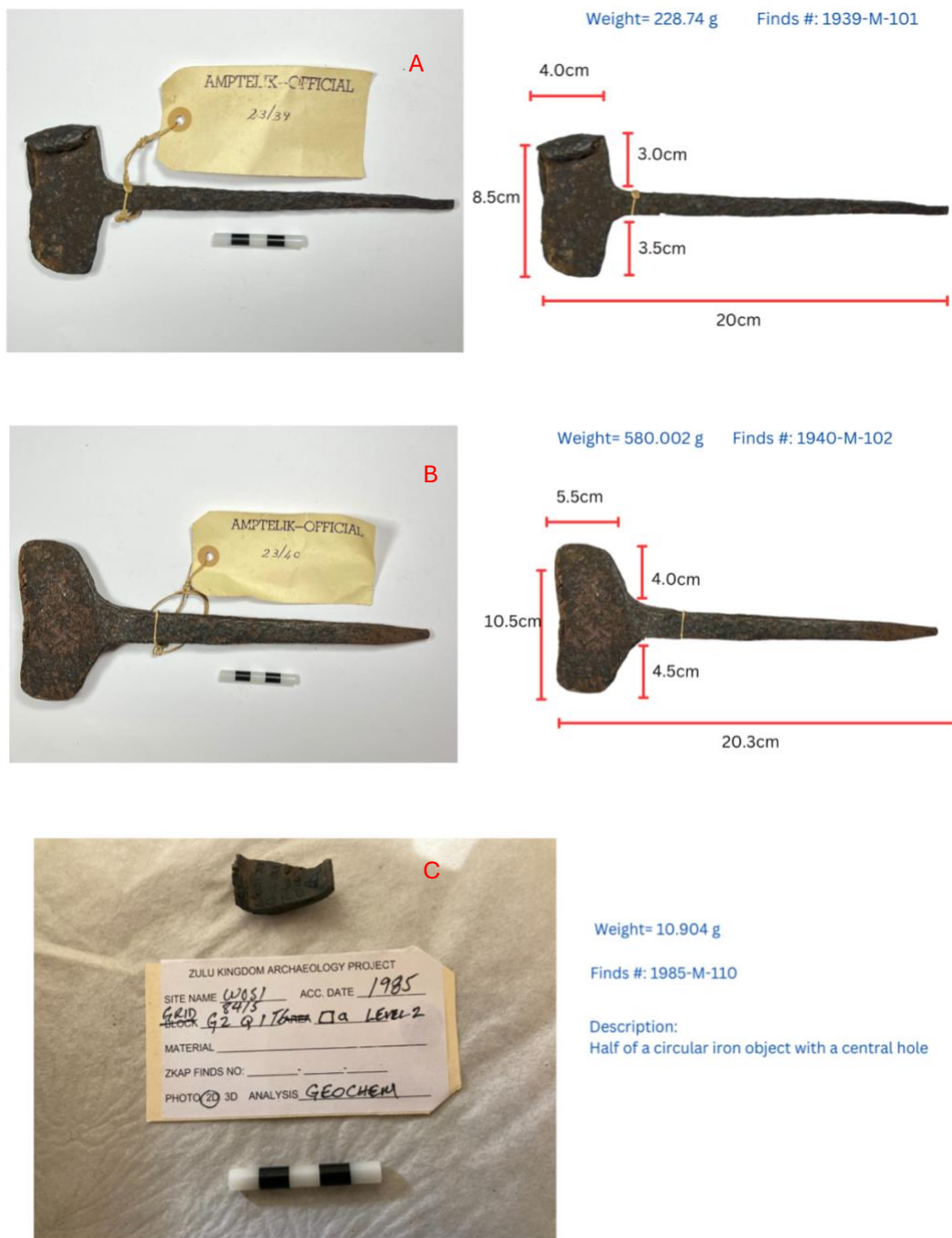


Figure 3.6: Metal samples used in this thesis. A: Iron hoe from uMgungundlovu. Accession date:1939. B: Iron hoe from uMgungundlovu. Accession date:1940. C: half of a circular iron object from Wosi. Accession date: 1985. Photos credit: KwaZulu-Natal Amafa Research Institute, Pietermaritzburg and Zulu Kingdom Archaeology Project (ZKAP)).



Figure 3.7: Ore samples from A: Iron Banded Formation in Middle Tugela River (Nkandla); B: Wosi; C: Pietermaritzburg Shales in Babanango Mines; D: Jameson's Drift; E-F: Mozaan Shales in Denny Dalton; G: kwaDukuza. Photos credit: Zulu Kingdom Archaeology Project (ZKAP).



A



Finds #: 1984-M-108



B



Finds #: 1983-M-111



C



Finds #: 1983-M-114



D



Finds #: 1996-M-117

Figure 3.8: Bloom samples from the Early Iron Age sites of A: Wosi; B-C: Mamba; and D: Ndondondwane. Photos credit: KwaZulu-Natal Amafa Research Institute, Pietermaritzburg and Zulu Kingdom Archaeology Project (ZKAP)).

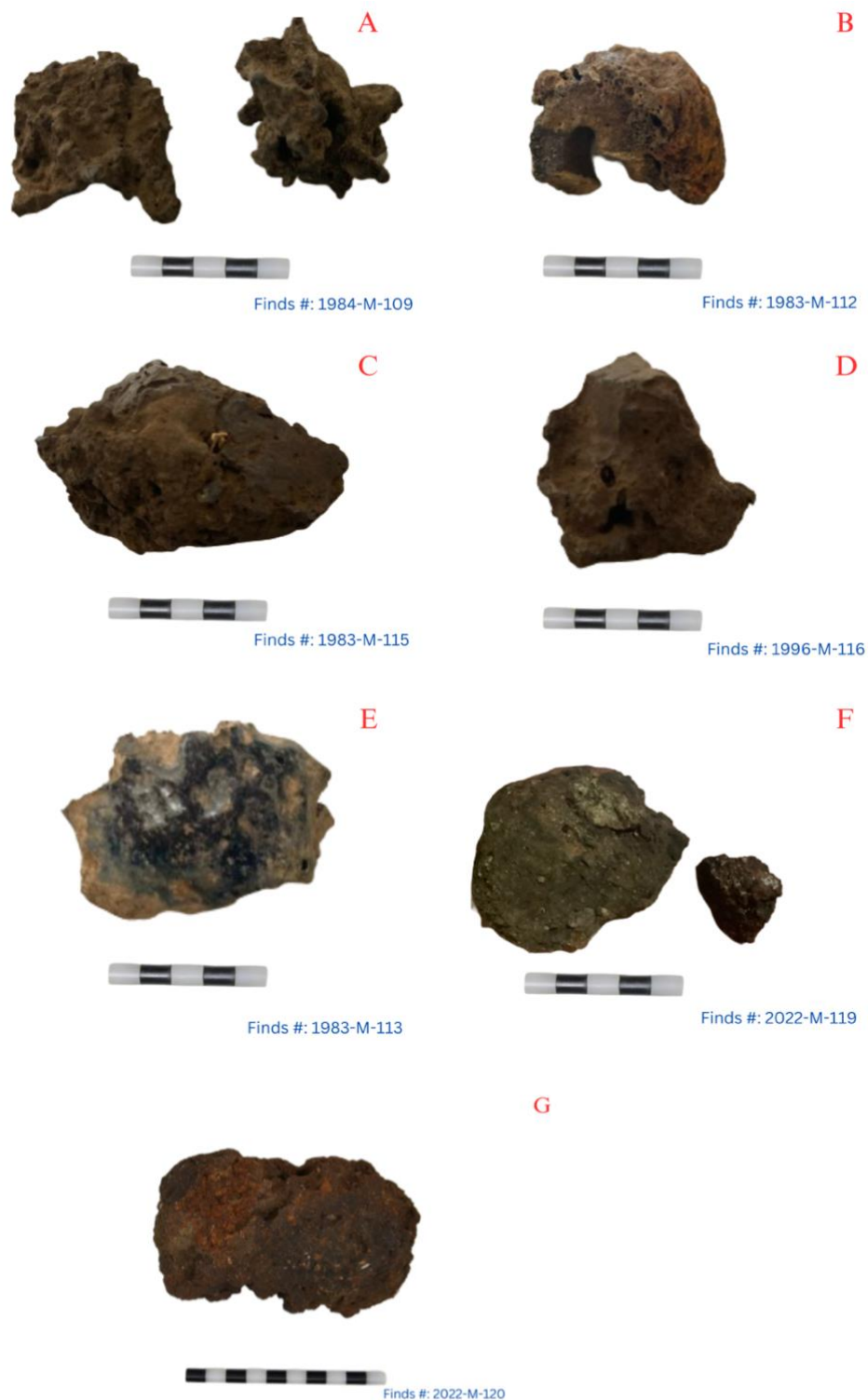


Figure 3.9: Slag samples from A: Wosi, B: Mamba with an attached piece of tuyere. C: Mamba. D: Ndongondwane. Mamba. F and G: ezinGwegweni. Photos credit: KwaZulu-Natal Amafa Research Institute, Pietermaritzburg and Zulu Kingdom Archaeology Project (ZKAP)).

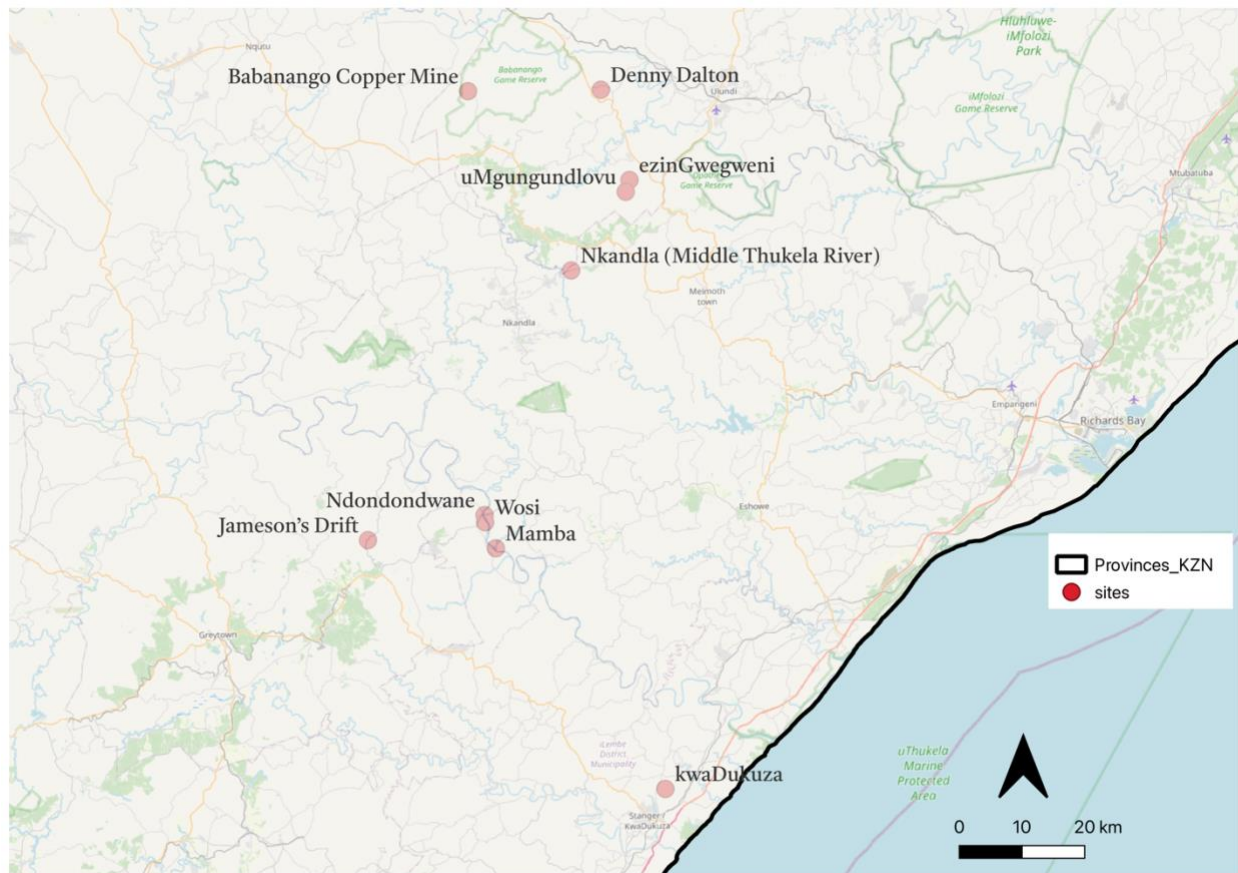


Figure 3.10: Map showing site locations of where materials were sampled. (Data source: Zulu Kingdom Archaeology Project (ZKAP))

3.5 Method, Techniques and Instrumentation

The primary methodological approach used in this research is archaeometallurgy, which is discussed extensively in Chapter Two. The subsections below focus on the techniques I used as well as the instrumentation.

3.5.1 *Imaging and Petrography*

Imaging of materials involved applying microscopic techniques (Miller and Killick, 2004; Chirikure and Rehren, 2006; Mathoho, Nyamushosho and Chirikure, 2023) and petrographic techniques (Miller and Killick, 2004; Killick and Miller, 2014; Maggs and Miller, 1995) to

polished and thin-sectioned materials. These techniques helped deduce information about the non-metallic inclusions and composition (Scott, 2014; Scott and Schwab, 2019). Imaging of metallurgical samples has long been conducted using optical microscopy (Baužytė *et al.*, 2023) or a light microscope. For this study, I used an Eclipse 50i POL Polarizing Microscope equipped with a Nikon LV-UEPI epi-illuminator at the University of Manitoba. Additionally, I used the Manitoba Institute of Materials' (MIM) Scanning Electron Microscopy (SEM) for high-resolution imaging of micro-points of interest as well as 2D micrographs.

3.5.1.1 Sample Preparation

The preparation process began with the cutting of the ore, slag, and bloom samples into manageable pieces using a mechanized cutting tool in the Polished Thin-Sections Laboratory at the University of Manitoba. After cutting, the samples were sent to Precision Petrographics Canada, where polished thin sections measuring 26 mm × 46 mm were prepared on standard glass slides (Figure 3.11). The thin sections were then analysed microstructures and capture photomicrographs for mineral identification.

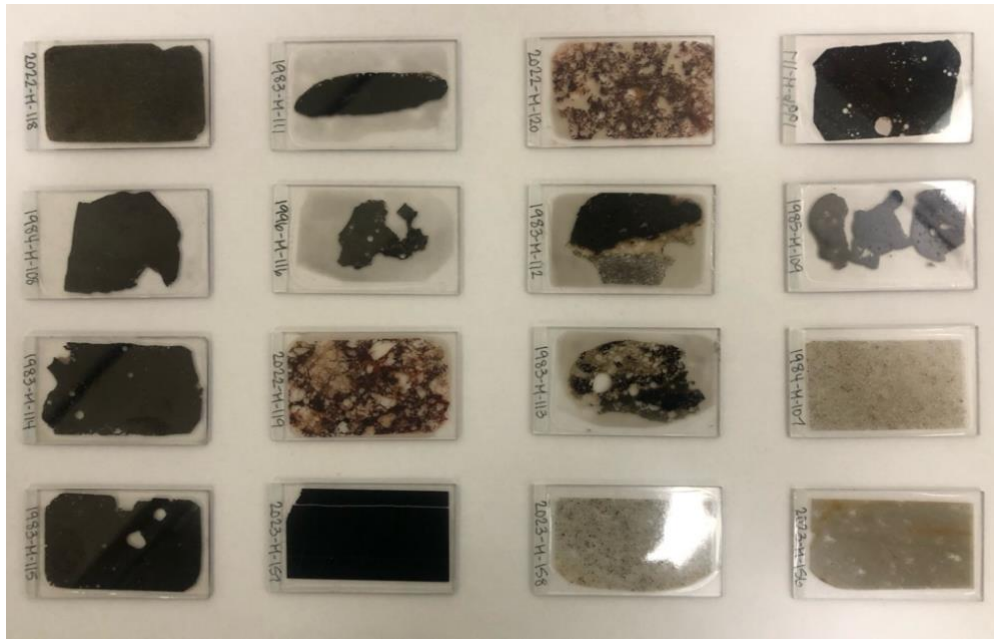


Figure 3.11: Petrographic thin sections of materials with dimension 26mm x 46mm, covered with 30 microns of epoxy on regular glass. (Source: Author)

3.5.2 Geochemical Analyses

For this thesis, sampled materials were chemically analysed for major and trace elements. These techniques involved identifying and quantifying the presence of major elements and trace elements (Scott, 2014; Scott and Schwab, 2019). Samples from the materials (ores, slags and blooms) were sent to Actlabs Canada for analysis using fusion inductively coupled plasma mass spectrometry (Fusion-ICP-MS). The iron artifacts, comprising two iron hoes and an amulet, were analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the University of Manitoba (Woodhead *et al.*, 2007).

The rationale for using LA-ICP-MS for the iron materials (hoes and “amulet”) was that Actlabs was unable to effectively conduct the geochemical analysis using the fusion method. Laser Ablation was therefore selected as the most suitable alternative. It is a minimally destructive analytical technique that allows for elemental analysis without causing significant

damage to the iron hoes (Pollard and Bray, 2014). The use of minimally destructive and non-destructive analytical techniques has become increasingly important in archaeometallurgical research, particularly when examining museum collections and culturally significant objects (Pollard and Bray, 2007; Pollard and Bray, 2014). This consideration was especially important for the Zulu iron hoes examined in this study.

To ensure comparability of the ICP-MS data, the concentrations of Si, Al, Fe, Mg, Mn, Ca, Na, K, Ti, and P were recalculated as major oxide percentages. This was achieved by converting the ppm values using the appropriate molecular weight ratios and dividing by 10,000. This standardization ensured consistency between the Fusion ICP-MS and Laser Ablation ICP-MS datasets for subsequent analysis. Again, Quanta FEG 650 Scanning Electron Microscopy (SEM), equipped with Energy-Dispersive X-ray Spectroscopy (EDS) at the University of Manitoba, was used for elemental mapping and point analysis of the materials. This involved spot analysis and map scans to characterize the compositional variations in spots of interest as well as areas of interest. This technique provided detailed information about the elemental composition of materials.

3.5.2.1 Scanning Electron Microscopy (SEM) Sample Preparation

Iron samples (Iron hoes and “Amulet”) were embedded in epoxy resin using a TP-7001B Mounting Press at the University of Manitoba (Figure 3.12). The preparation procedure involved the following steps:

1. Approximately 0.5 g of each metal sample was cut using a Dremel cutting tool.
2. Four grams of transparent polyacrylic compression resin powder were placed in the mounting press together with each metal sample.

3. The TP-7001B mounting press was set to a temperature of 220 °C and operated for 10 minutes under a constant pressure of 70 psi.
4. The mounting press was operated using specific parameter settings, with the ALT value set to 0001 and the SC value set to 5 to ensure consistency throughout the embedding procedure.
5. Upon completion of the heating cycle, the mounted samples were cooled to approximately 30 °C over a period of 12 minutes to allow the resin to solidify properly.
6. The controlled temperature, pressure, and cooling conditions ensured that the resin hardened without introducing defects, thereby preserving the microstructure of the metal samples for subsequent analysis and characterization.
7. To facilitate identification, each mounted sample was labelled, traced on paper, and photographed (Figure 3.10).

The metal samples embedded in epoxy resin were initially polished by hand using silicon carbide abrasive paper. Polishing began with a coarse grit of P-200 to remove the surface layer of resin, gradually progressing to a finer grit of P-1200. This step was essential to fully expose the metal surfaces while ensuring a smooth, defect-free finish for subsequent analysis.

Following the initial hand polishing, the metal samples embedded in epoxy resin underwent further mechanical polishing using a Struers LabForce-50 polishing machine at the University of Manitoba.

The polishing process was conducted in three stages to achieve the desired results. The polishing machine was operated at 250 RPM. The process involved several steps:

1. First, a 9 μm diamond suspension fluid was applied and polished for 7 minutes to remove any remaining surface irregularities.
2. Second, this was followed by polishing with a 3 μm diamond suspension fluid for 5 minutes, refining the surface further.
3. Finally, a 1 μm diamond suspension fluid was used for 2 minutes to produce a smooth, mirror-like finish, ensuring the samples were ready for imaging and elemental mapping analysis.

For elemental mapping and point analysis, all prepared samples were carbon-taped to allow conductivity and reduce charging (Figure 3.13). I used xT microscope Control V6.2.8 software for data processing. The SEM-EDS scanning parameters used included:

- Low vacuum
- 100 Pa chamber pressure
- High voltage- 20.00kV
- Working distance- 10- 15 mm

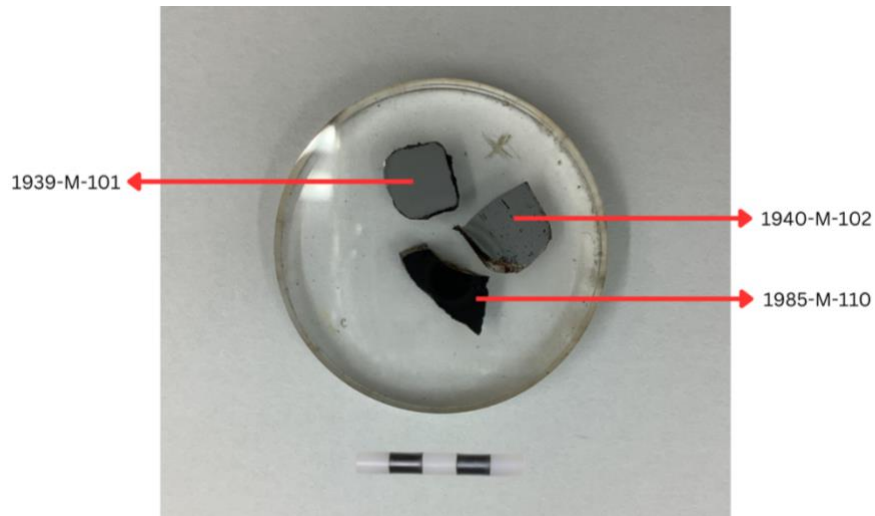


Figure 3.12: Metal samples embedded in epoxy resin. (Source: Author)

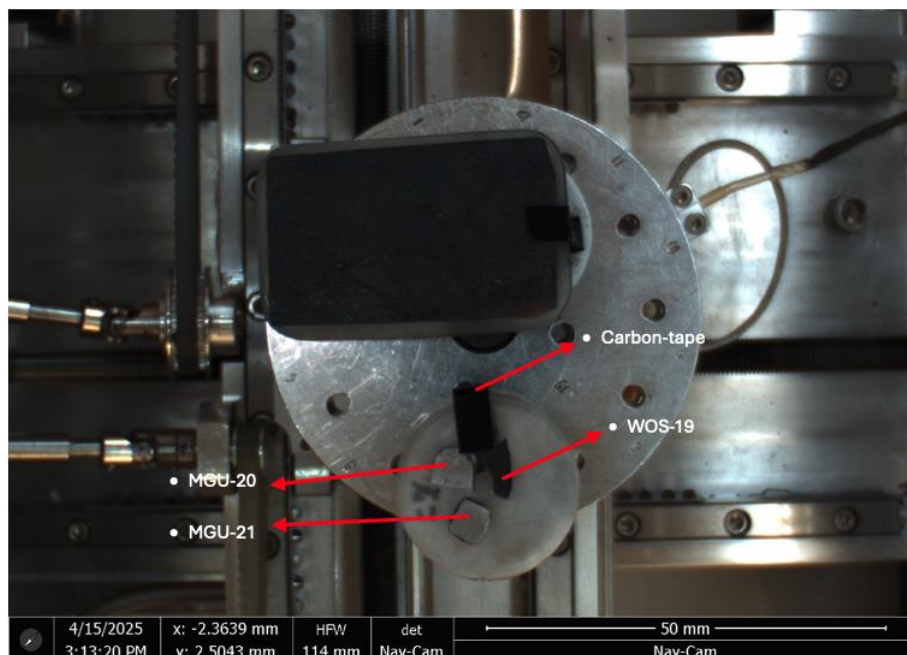


Figure 3.13: Navigational camera image showing samples on the stud held with carbon tape in the SEM instrument. (Source: Author)

3.5.2.2 Laser Ablation- ICP-MS

For the hoes and amulet samples, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was used to ablate three areas on each sample. This required minimal sample preparation as I used the embedded metal samples in epoxy resin (iron hoes and amulet). For data trimming, Iolite 4 software was used (Paton *et al.*, 2011). The parameters used were the following:

- Wavelength- 213
- Sample depth- 4.9 mm
- Gas- Argon (Ar) gas
- Makeup gas- 0.93 L/min
- Laser set-up- 30 μm
- Power- 0.16 mJ
- Fluence- 22.68/cm²
- Frequency 10 Hz

For reference materials, the following standards were used:

- National Institute of Standards and Technology (NIST) 610 glass
- BCR 2G

3.5.2.3 Fusion- ICP-MS

Ore, slag, and bloom samples weighing at least 5 g were sent to Actlabs Canada for major- and trace-element analysis using fusion inductively coupled plasma mass spectrometry (ICP-

MS). The samples were initially crushed to a nominal particle size of less than 2 mm and mechanically split to obtain representative subsamples. Each subsample was then pulverized until at least 95% of the material passed through a 105 μm sieve (Actlabs, 2025).

The pulverized samples were then added to either lithium metaborate or tetraborate before its put in the induction furnace. The resulting molten material was then dissolved in a about 5% solution of nitric acid and mixed until fully dissolved. The prepared solution was then introduced into the ICP-MS instrument for analyses of major oxides and trace elements. The fusion procedure was fully automated and performed using a robotic system to promote consistency, efficiency, and analytical accuracy (Actlabs, 2025).

3.6 Data Analysis

For data analysis, Microsoft Excel and XLSTAT statistical software, version 2024.4, were used to conduct multivariate statistical analyses, including principal component analysis (PCA) and element-ratio analysis. These analyses were used to examine patterns, similarities, and differences in the elemental compositions of the sampled materials.

Element-ratio analysis assessed the relative proportions of selected elements, while PCA was used to identify the variables that contributed most strongly to compositional variation. Together, these methods improved the interpretability of the analytical data and provided a more comprehensive basis for comparing the sampled materials and evaluating potential relationships among ores, smelting by-products, and finished iron artifacts.

3.7 Conclusion

This chapter outlined the study's analysed specimens and methods, including the analytical techniques, instruments, and protocols for sample preparation and laboratory analysis. It

described the materials examined, comprising iron artifacts, iron ores, slags, and blooms, together with their recorded provenience and geographical coordinates.

A multi-method analytical approach was adopted in recognition of the limitations associated with relying on a single technique in iron-provenience research. By integrating petrographic, geochemical, microscopic, and statistical analyses, the study generated a more comprehensive dataset for addressing the research questions and evaluating relationships among the ores, smelting by-products, and finished iron artifacts.

CHAPTER 4: DATA PRESENTATION AND RESULTS

4.1 Introduction

In this chapter, I present the analysis and results obtained using petrographic and geochemical methods. Petrographic analysis involved qualitative optical microscopy using a polarizing microscope. Geochemical data were obtained using quantitative inductively coupled plasma mass spectrometry (ICP-MS) and semi-quantitative scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). The data were processed and visualized using Microsoft Excel, XLSTAT statistical software version 2024.4.1, SEM xT Microscope Control software version 6.2.8, and Iolite 4 software for data trimming.

4.2 Ores

The ore samples included one archaeological sample from kwaDukuza (DUK-9) and geological samples from Jameson's Drift (JAD-5), Denny Dalton (DEN-6 and DEN-7), Wosi (WOS-8), Babanango (BAB-10), and Nkandla (NKD-11). Raw geochemical data, log10-transformed geochemical data, petrographic observations, and elemental-mapping results were used to characterize the chemical compositions of the ore samples and determine whether they could be chemically discriminated. A comparative analysis was also conducted to identify which geological ore samples most closely corresponded to the archaeological ore sample.

4.2.1 *Thin-Section Petrography Results*

The archaeological ore sample from kwaDukuza (DUK-9) was petrographically similar in mineral composition to the geological samples from Wosi (WOS-8), Denny Dalton (DEN-6 and DEN-7), and Jameson's Drift (JAD-5). These samples were dominated by silicate matrices containing quartz, fayalite and hematite (Figure 4.1). The large quartz crystals observed in JAD-

5 may indicate a felsic source (Baiyegunhi, Liu and Gwavava, 2017, p. 349). In contrast, the Nkandla ore sample (NKD-11) was a high-grade ironstone dominated by magnetite and hematite, with minor amounts of quartz (Figure 4.1).

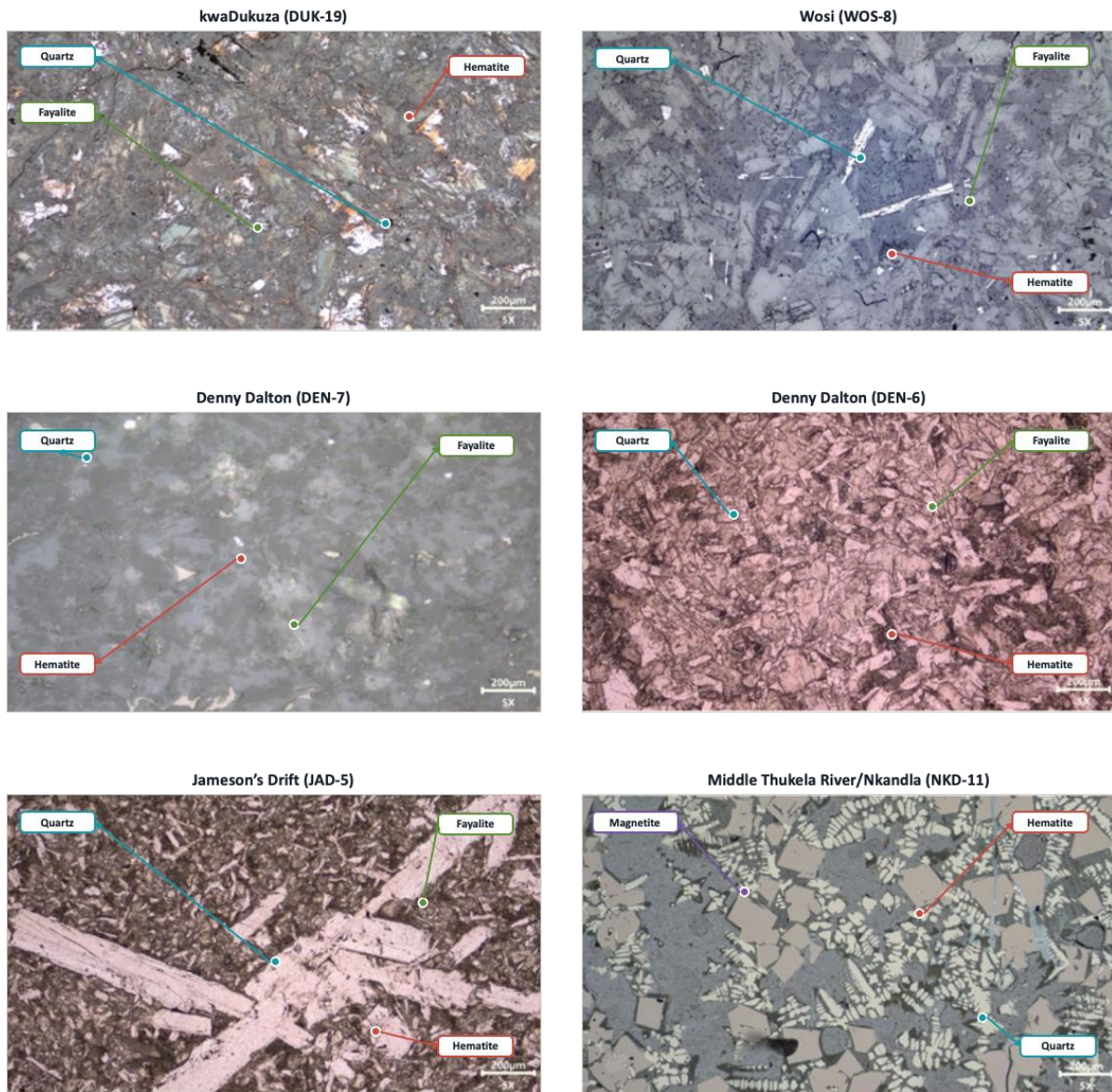


Figure 4.1: Thin-sectioned micrograph images of the ore samples under a light microscope. (Source: Author)

4.2.2 Chemical Composition

All analysed ore samples exhibited high SiO₂ concentrations, ranging from 32.27 to 59.55 wt.% (Figure 4.2 and Table 4.1). Al₂O₃ concentrations ranged from 12.32 to 13.46 wt.%, while Fe₂O₃ concentrations varied considerably, from 11.43 to 66.95 wt.% (Figure 4.2 and Table 4.1). Other major oxides, including MnO, MgO, CaO, Na₂O, K₂O, TiO₂, and P₂O₅, occurred in relatively low concentrations and did not constitute major components of the ore samples (Figure 4.2 and Table 4.1).

The ore sample from Babanango (BAB-10) contained very low concentrations of feldspar-associated oxides, including Al₂O₃, K₂O, Na₂O, and CaO. The most distinctive result was observed in the sample from the middle Thukela River near Nkandla (NKD-11), which contained a very high concentration of Fe₂O₃ (66.95 wt.%) and low concentrations of all other major oxides, including Al₂O₃, MnO, MgO, CaO, K₂O, Na₂O, TiO₂, and P₂O₅. The remaining ore samples contained Fe₂O₃ concentrations ranging from 12.23 to 17.77 wt.% (Figure 4.2 and Table 4.1). DEN-7 contained relatively high concentrations of MnO and K₂O but a low concentration of Na₂O, whereas JAD-5 contained a low concentration of K₂O.

The trace-element compositions varied among the analysed ore samples (Figure 4.3 and Table 4.2). The Babanango ore sample (BAB-10) was high in transition trace elements (TTEs), with an exceptionally high concentration of Cu (>10,000 ppm) and moderate to high concentrations of Cr (1,490 ppm), Co (116 ppm), Pb (159 ppm), and V (109 ppm) (Figure 4.3 and Table 4.2). These results indicate a strong association with copper-bearing minerals and substantial TTE enrichment.

The banded iron ore sample from the middle Thukela River near Nkandla (NKD-11) also contained TTEs, including V (42 ppm), Cr (20 ppm), Ni (40 ppm), and Co (9 ppm) (Figure 4.3 and Table 4.2). Large-ion lithophile elements (LILEs), including Sr (8 ppm) and Ba (14 ppm), were also detected, together with rare earth elements (REEs), such as Ce (15.6 ppm) and Nd (5.05 ppm), and a low concentration of the high-field-strength element (HFSE) W (9.6 ppm).

The two Denny Dalton ore samples showed contrasting trace-element patterns (Figure 4.3 and Table 4.2). The first sample, DEN-6, contained elevated concentrations of TTEs, including Cr (130 ppm), Co (41 ppm), Ni (70 ppm), Cu (130 ppm), and Zn (110 ppm). In contrast, DEN-7 contained lower concentrations of Cr (70 ppm), Co (14 ppm), and Ni (40 ppm), but higher concentrations of REEs, including Ce (80.2 ppm) and Nd (36.1 ppm). Both samples were enriched in LILEs, particularly Ba, which reached a concentration of 453 ppm (Figure 4.3 and Table 4.2).

Within the middle Thukela River Basin, the Wosi ore sample (WOS-8) was characterized by the highest Cr concentration (510 ppm), together with high concentrations of Sr (255 ppm) and Ni (190 ppm). By comparison, its Cu (60 ppm) and Zn (100 ppm) concentrations were lower. REEs, including Ce (26.2 ppm) and Nd (13.3 ppm), were also present at relatively low concentrations.

The Jameson's Drift sample (JAD-5) contained moderate concentrations of TTEs, including Cr (170 ppm), Co (40 ppm), Ni (60 ppm), Cu (120 ppm), and Zn (100 ppm). It also contained comparatively high concentrations of Sc (41 ppm) and V (308 ppm), but low concentrations of REEs, including La (13.2 ppm) and Ce (27.5 ppm) (Figure 4.3 and Table 4.2).

Finally, the ore nodule from kwaDukuza-2 (DUK-9) contained high concentrations of V (365 ppm) and Sc (43 ppm), together with moderate concentrations of Cr (100 ppm), Ni (60 ppm), and Zn (140 ppm). The REEs Ce (22.6 ppm) and Nd (17.2 ppm) occurred at moderate concentrations (Figure 4.3 and Table 4.2).

Table 4.1: Major element oxides in ore samples. Unit in weight percentage (wt%). (Source: Author)

Element oxides	Jameson's Drift	Wosi	Denny Dalton	Denny Dalton	kwaDukuza	Babanango	Nkandla
	JAD-5	WOS-8	DEN-6	DEN-7	DUK-9	BAB-10	NKD-11
	Geological ore	Geological ore	Geological ore	Geological ore	Archaeological ore	Geological ore	Geological ore
SiO ₂	52.74	53.87	51.72	59.55	49.63	54.21	32.27
Al ₂ O ₃	14.85	12.37	14.58	16.65	12.82	7.77	0.64
Fe ₂ O ₃ (T)	12.46	11.43	12.46	13.46	17.77	12.23	66.95
MnO	0.207	0.164	0.196	0.785	0.242	0.141	0.082
MgO	5.53	8.88	5.37	1.31	4.8	8.41	0.05
CaO	9.73	7.5	9.95	0.33	8.73	0.15	0.02
Na ₂ O	2.49	2.21	2.43	0.52	2.12	0.01	0.01
K ₂ O	0.29	0.78	0.82	1.88	0.6	0.01	0.01
TiO ₂	1.229	0.992	1.281	0.773	2.098	0.419	0.012
P ₂ O ₅	0.2	0.14	0.21	0.14	0.19	0.07	0.03

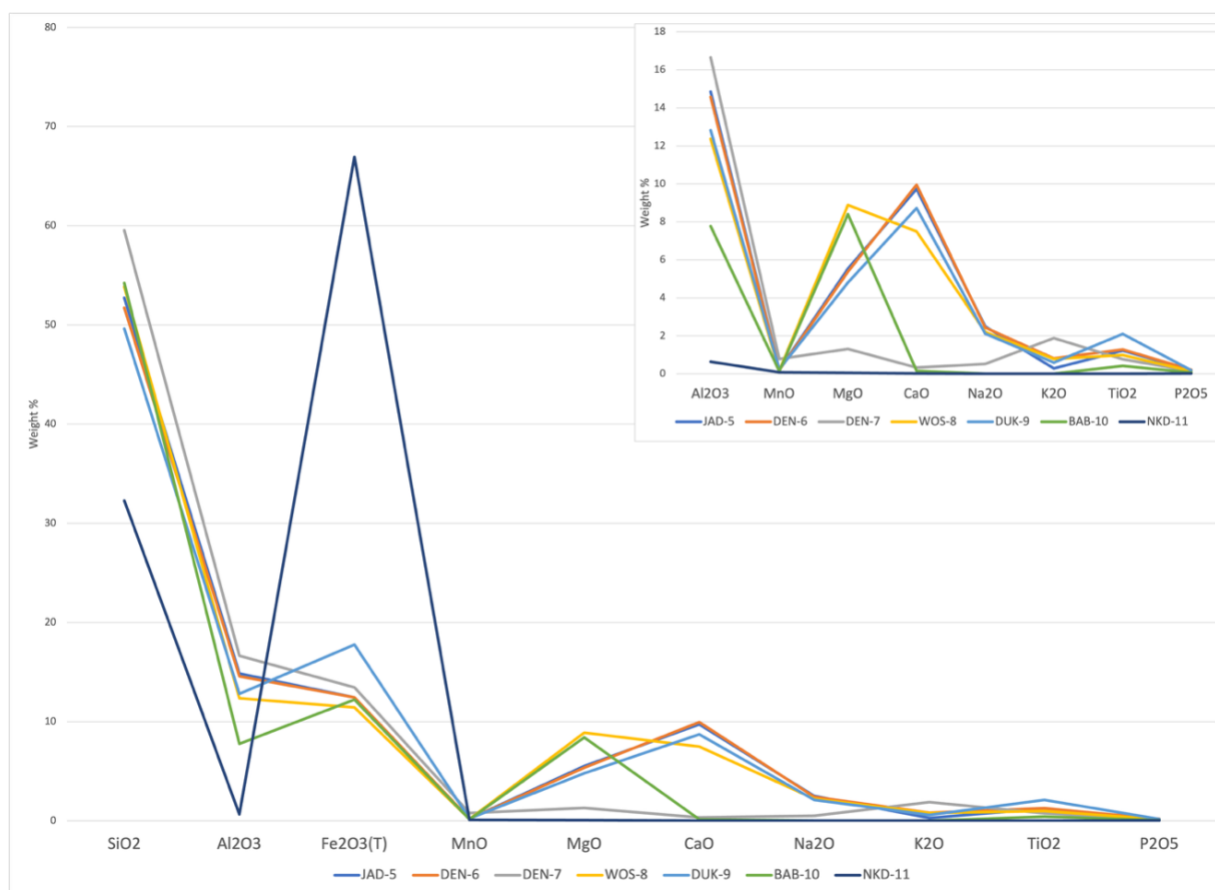


Figure 4.2: Major element oxide composition of geological ores and archaeological ore in weight percent (Wt%). The insert shows major oxide composition without Fe₂O₃ and SiO₂. (Source: Author)

Table 4.2: Trace element compositions of ore samples in parts per million (ppm). (Source: Author)

Element	Jameson's Drift	Denny Dalton	Denny Dalton	Wosi	kwaDukuza	Babanango	Nkandla
	JAD-5	DEN-6	DEN-7	WOS-8	DUK-9	BAB-10	NKD-11
	Ore source	Ore source	Ore source	Ore source	Ore find	Ore source	Ore source
Rare Earth Element (REE)							
La	13.2	13.2	40.3	13	13.6	12.3	6.98
Ce	27.5	27.8	80.2	26.2	22.6	20.9	15.6
Pr	3.36	3.35	8.81	2.85	3.46	2.4	1.39
Nd	16.3	16.5	36.1	13.3	17.2	8.99	5.05
Sm	3.83	3.98	7.82	3.33	4.44	1.71	1.04
Eu	1.18	1.27	1.42	1.08	1.5	0.293	0.361
Gd	4.46	4.7	6.63	3.58	5.22	1.67	0.96
Tb	0.74	0.81	1.09	0.63	0.95	0.29	0.18
Dy	4.45	5.08	6.51	3.61	5.89	1.72	1.24
Ho	0.9	1.02	1.3	0.74	1.24	0.36	0.28
Er	2.69	2.95	3.72	2.11	3.67	1.05	0.89
Tm	0.41	0.452	0.57	0.304	0.569	0.152	0.128
Yb	2.8	3.02	3.9	1.96	3.77	1.05	1.03
Lu	0.454	0.481	0.644	0.293	0.616	0.157	0.158
Sc	41	39	16	23	43	17	2
High Field Strength Element (HFSE)							
Y	26.9	29.7	38	20.9	34.8	8.9	7.4
Zr	119	121	147	84	135	52	7
Nb	9.5	7.6	17	5.5	7	4.3	0.5
Large Ion Lithophile Element (LILE)							
Rb	5	21	110	21	14	1	1
Sr	206	200	50	255	122	5	8
Ba	150	304	453	327	232	7	14
Th	1.57	1.88	15.3	1.84	1.12	1.29	0.46
U	0.33	0.42	5.24	0.45	0.26	6.53	1.8
Transition Trace Element (TTE)							
Cr	170	130	70	510	100	1490	20
Co	40	41	14	47	47	116	9
V	308	302	131	216	365	109	42
Cu	120	130	50	60	50	10000	260
Zn	100	110	80	100	140	80	30
Other Trace Elements							
Be	1	1	3	1	1	2	1
Hf	2.9	3.3	4.3	2.1	3.8	1.1	0.1
Ta	0.48	0.42	1.18	0.25	0.37	0.2	0.1
W	0.5	0.8	3.4	1.2	0.9	0.5	9.6
Tl	0.05	0.12	0.76	0.12	0.11	0.5	0.5
Pb	5	5	12	5	7	159	5
Ni	60	70	40	190	60	1390	40
Ga	18	20	23	18	20	27	3
Ge	1.4	1.6	1.6	1.4	1.5	0.9	8.2
As	5	8	5	5	5	5	16
Mo	2	2	3	2	2	3	2
Ag	0.5	0.5	0.5	0.5	0.5	25.1	0.5
Sn	1	1	4	1	1	2	1
Sb	0.2	0.2	0.4	0.2	0.3	0.2	0.6
Cs	0.6	0.4	8.7	0.3	0.3	0.1	0.1

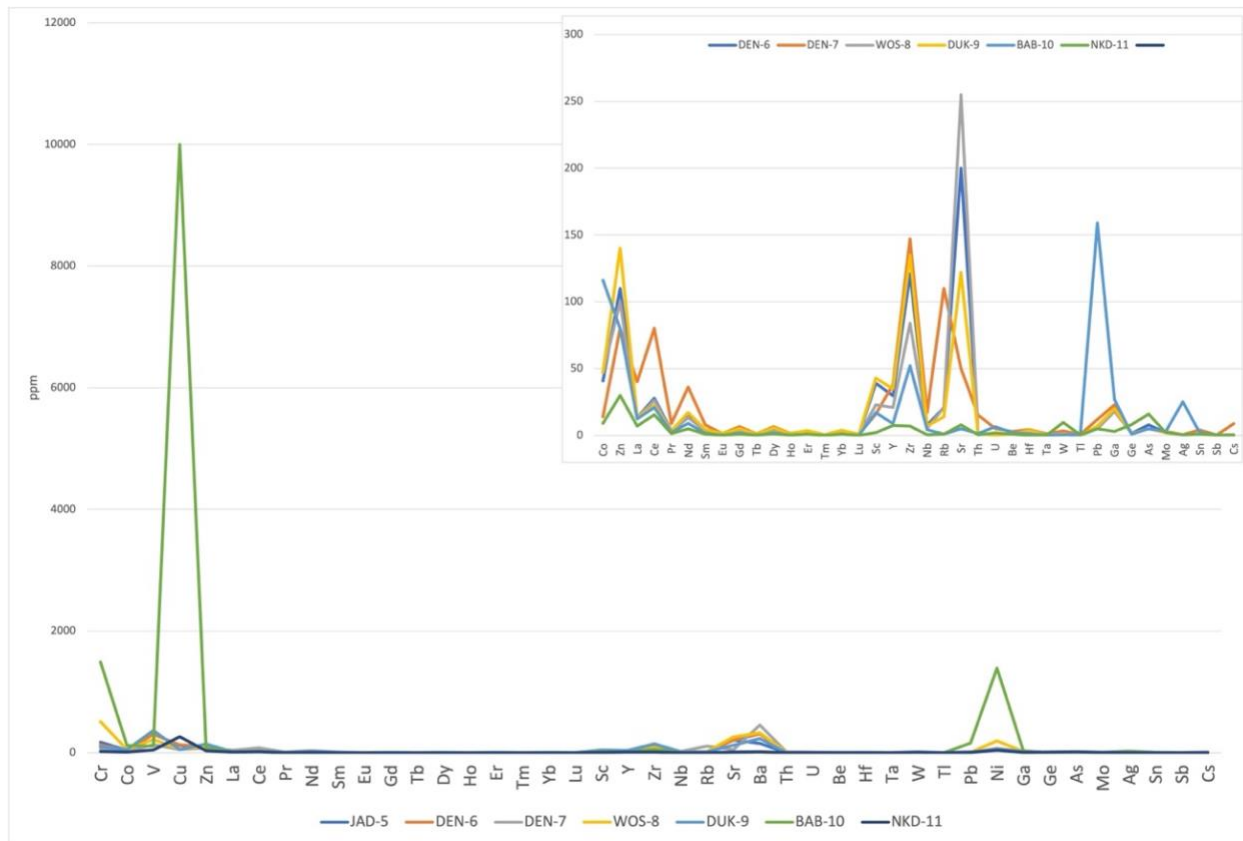


Figure 4.3: Trace element composition of geological ores and archaeological ore in parts per million (ppm). Insert shows trace element composition without Cu and Ni. (Source: Author)

4.2.3 Statistical Analysis

Using Log10 major and trace elements for the Principal Component Analysis (PCA), samples from Wosi (WOS-8), Jameson's Drift (JAD-5) and Denny Dalton (DEN-6) grouped closely together, indicating broadly similar geochemical compositions (Figure 4.4). In contrast, the Babanango (BAB-10) and Nkandla (NKD-11) samples plotted as outliers, reflecting distinct geochemical signatures that may indicate derivation from different geological sources (Figure 4.4).

The two Denny Dalton ore samples, DEN-6 and DEN-7, were geochemically distinguishable based on their relative rare earth element (REE) and titanium dioxide (TiO₂)

concentrations. DEN-6 contained lower REE concentrations, whereas DEN-7 contained a higher concentration of TiO_2 . Elemental biplots of MgO-Cu , $\text{Na}_2\text{O-MgO}$, $\text{Na}_2\text{O-U}$, $\text{P}_2\text{O}_5\text{-MnO}$, and Sr-U further demonstrated the geochemical heterogeneity between DEN-6 and DEN-7 (Figure 4.5). Although the Jameson's Drift (JAD-5), Denny Dalton (DEN-6), and Wosi (WOS-8) samples cluster, the Denny Dalton (DEN-7), Nkandla (NKD-11), and Babanango (BAB-10) samples were clearly discriminated (Figure 4.5).

The archaeological ore fragment recovered from the kwaDukuza *ikhanda* (DUK-9) (Fowler and van Schalkwyk, 2022) better correlates geochemically with the Denny Dalton (DEN-6) and Jameson's Drift (JAD-5) ore samples than with the Wosi sample (WOS-8) (Figure 4.6). These results suggest that DUK-9 may be sourced from an ore source in the vicinity of Denny Dalton or from another geologically similar source.

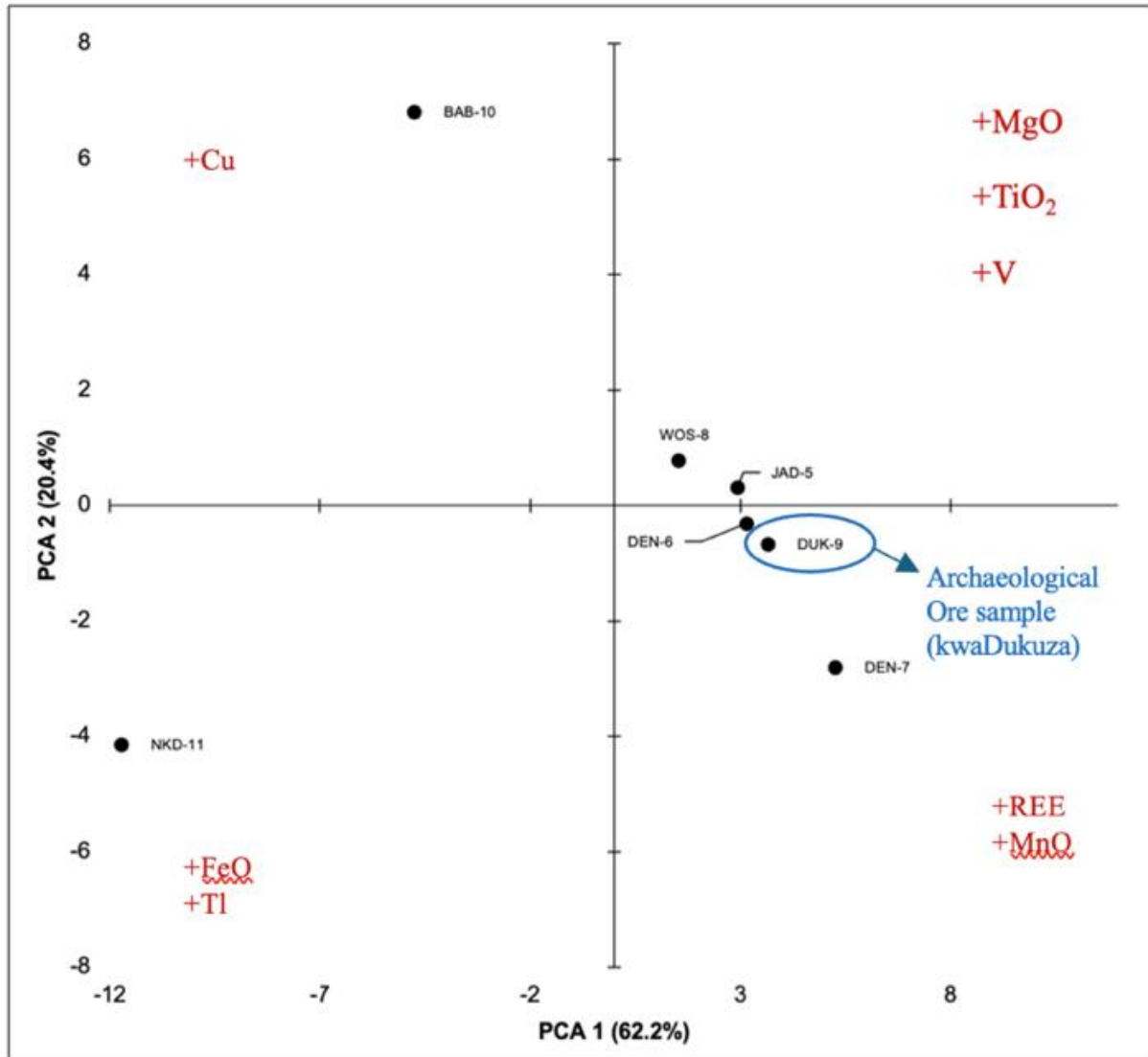


Figure 4.4: PCA correlation scatter plot observations of ore samples using transformed Log10 major and trace elements. (Source: Author)

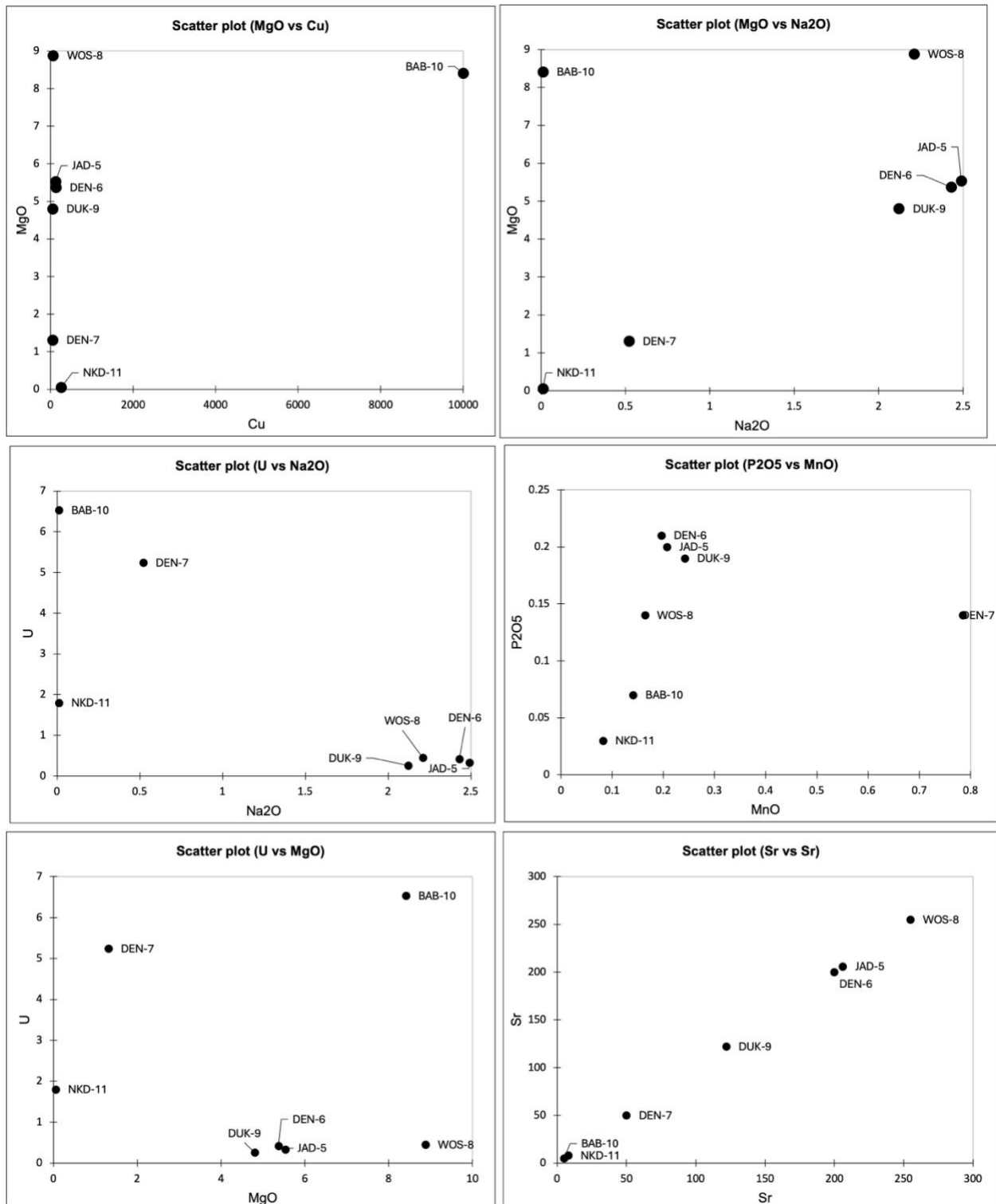


Figure 4.5: Scatterplots showing the element-to-element (MgO/Cu, MgO/Na₂O, U /Na₂O, P₂O₅ /MnO, MgO/U and Sr/ U) discrimination among the ore samples. (Source: Author)

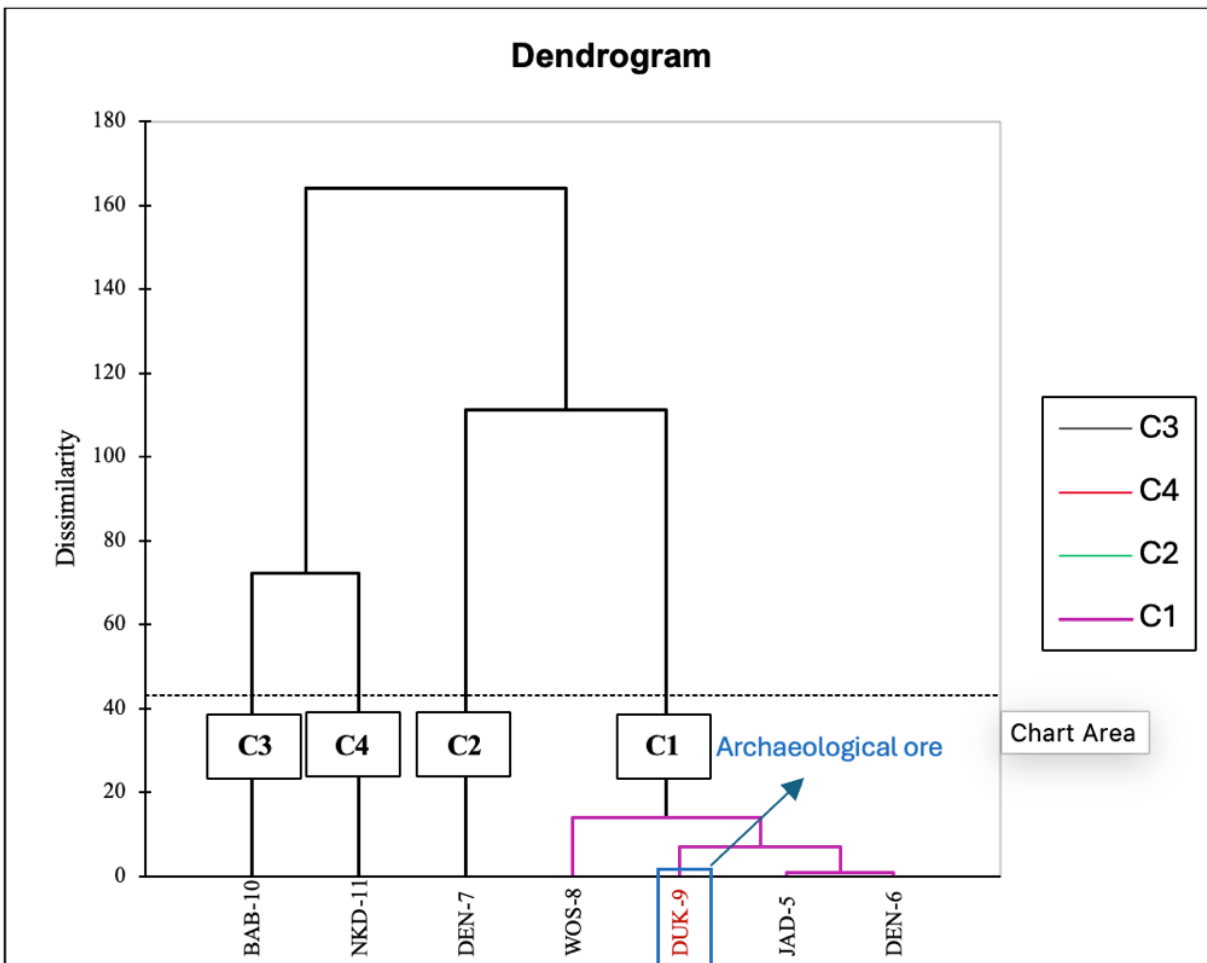


Figure 4.6: Agglomerative Hierarchical Clustering (AHC) showing the similarity between ore samples using raw ICP-MS data. (Source: Author)

MnO/TiO₂ ratios better distinguish DEN-7, NKD-11 and BAB-10, but JAD-5, DEN-6 and WOS-8 still group together because they have MnO/TiO₂ ratios less than 0.2 (Figure 4.7 and Figure 4.8). According to van Schalkwyk (1994; 1994), ore used at Mamba is high in titanium, whereas Wosi is high in manganese. MnO to TiO₂ ratio shows that ores from Wosi (WOS-8), Jamson's Drift (JAD-5), Babanango (BAB-10) and Denny Dalton (DEN-6) have high titanium oxide (TiO₂) and low manganese oxide (MnO), but Nkandla (NKD-11) is much lower in both oxides (Figure 4.7). This analysis confirms the characterization of the Wosi ore (WOS-8)

reported by van Schalkwyk (1994). Also, with a ratio of 0.12, DUK-9 falls within the Group 1 category (Figure 4.8).

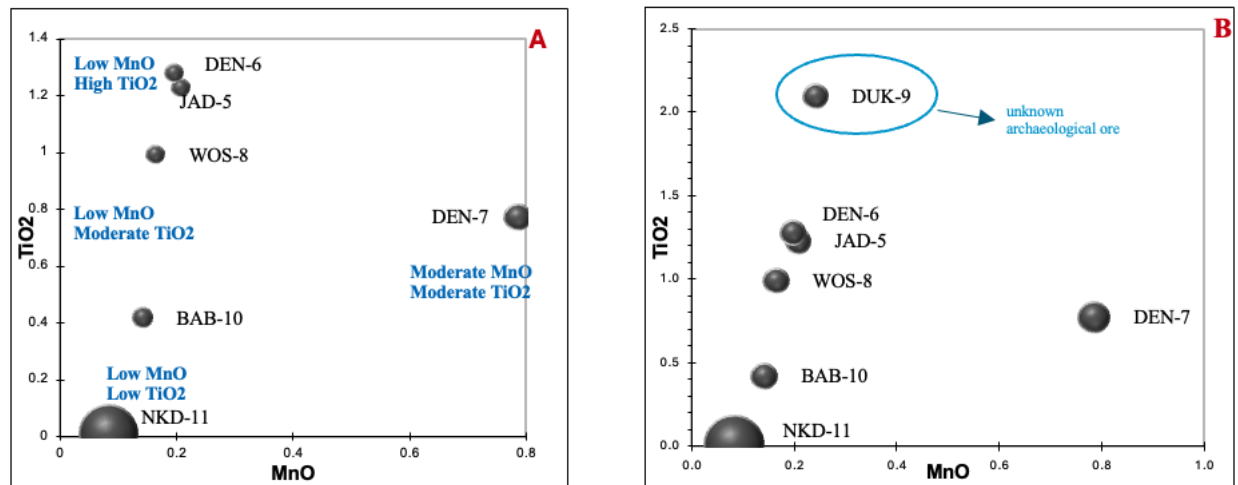


Figure 4.7: MnO/TiO₂ ratio scatter plots of ore samples A (without DUK-9) and B (with DUK-9), where bubble size corresponds to MnO concentration. (Source: Author)



Figure 4.8: MnO and TiO₂ concentrations (ppm) of ore samples and the corresponding MnO/TiO₂ ratios showing four major groupings. (Source: Author)

4.2.4 Conclusion

The geological ore samples from BAB-10, NKD-11 and DEN-7 represent unrelated sources, but JAD-5, DEN-6 and WOS-8 continue to group because of their very similar geochemistry and MnO/TiO₂ ratios. The unknown archaeological ore sample (DUK-9) fits with JAD-5, DEN-6 and WOS-8 group based on the Principal Component Analysis (PCA), Agglomerative Hierarchical Clustering (AHC) and MnO/TiO₂ ratios analysis.

4.3 Slags

4.3.1 *Thin-Section Petrography Results*

The petrographic analysis showed varying mineral composition in all samples (Figure 4.9). The ezinGwegweni samples, GWE-14 and GWE-18, were predominantly quartz with minor iron-oxide inclusions. The presence of silicates and the relative less of iron-rich phases are consistent with the high SiO_2 and low Fe_2O_3 concentrations recorded for these samples.

In contrast, the Mamba and Wosi slags contained dendritic iron-rich phases, like wustite, within fayalitic silicate matrices. Based on the opaque phases, other minerals present were ilmenite. Similarly, WOS-15 contained abundant dendritic iron oxides, although its high MnO concentration suggests that manganese-bearing iron silicates may also be present.

NDO-17 differed from the other slag samples. It was composed predominantly of iron-rich grains like wustite with fewer silicate minerals. This observation, together with the sample's chemical composition, may support its interpretation as an unconsolidated or partially consolidated iron bloom rather than a smelting slag.

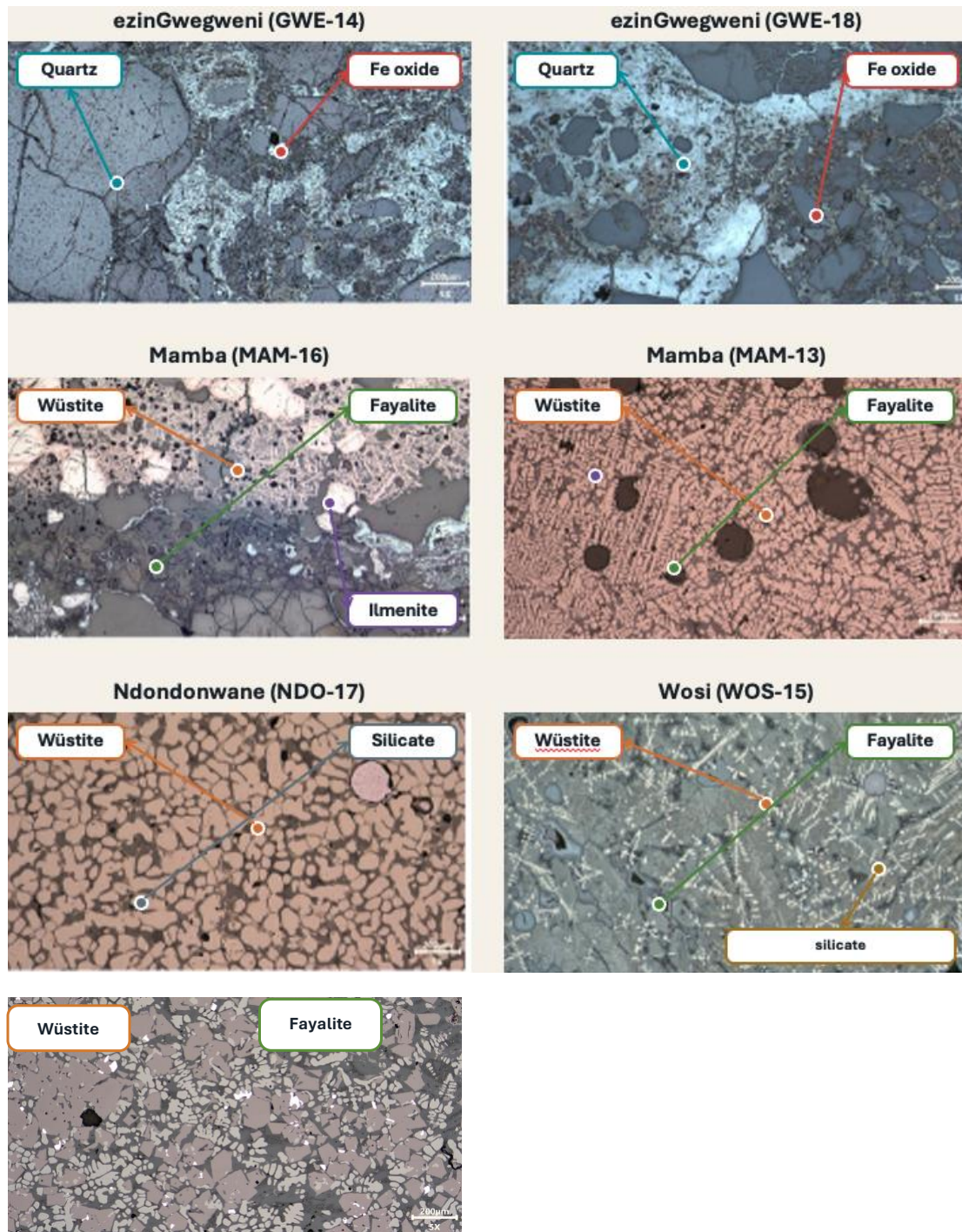


Figure 4.9: Thin-sectioned micrograph of slags showing mineral phases. (Source: Author)

4.3.2 Chemical Composition

The slag collection comprised materials from Mamba (MAM-12, MAM-13, and MAM-16), Wosi (WOS-15), Ndondondwane (NDO-17), and ezinGwegweni (GWE-14 and GWE-18). MAM-12 contained a very high concentration of iron oxide (Fe_2O_3), at 72.85%, with a low concentration of silicon dioxide (SiO_2), at 11.1%, and a moderate concentration of aluminium oxide (Al_2O_3), at 5.02%. In contrast, sample MAM-13 had a much lower Fe_2O_3 content (26.27%) and a significantly higher SiO_2 content (48.76%) (Figure 4.10 and Table 4.3). MAM-16, on the other hand, was moderately high in Fe_2O_3 (49.2%) and SiO_2 (27.3%). All slags from Mamba had elevated titanium dioxide (TiO_2) concentrations, particularly sample MAM-15 (10.09%), while MnO, MgO, CaO, and P_2O_5 concentrations were low across all samples (Figure 4.10 and Table 4.3).

The ezinGwegweni samples were characterized by high silica (SiO_2) and low iron oxide (Fe_2O_3) contents. Sample GWE-14 contained 65.39% SiO_2 , while sample GWE-18 had a similar concentration of 63.72% (Figure 4.10 and Table 4.3). The iron oxide (Fe_2O_3) concentrations in these samples were significantly lower, at 11.49% and 16.6%, respectively, than those of the remaining slags. The aluminium oxide (Al_2O_3) content ranged from 11.21% to 12.59%, while both samples exhibited relatively high sodium oxide (Na_2O) and potassium oxide (K_2O) values, indicating the possible use of silica fluxes.

The Wosi slag (WOS-15) had a high Fe_2O_3 content (63.8%) and a moderate SiO_2 content (23.88%). Notably, this sample contained the highest manganese oxide (MnO) concentration (5.192%). Other oxides present at low concentrations included Al_2O_3 (4.2%), MgO (1.4%), and

CaO (1.7%) (Figure 4.9 and Table 4.3). Relative to the other slag samples, Na₂O, K₂O, TiO₂, and P₂O₅ concentrations were very low (<1.0%) (Figure 4.10 and Table 4.3).

The Ndondondwane sample (NDO-17) was distinctive because of its extremely high iron oxide content (91.89%) and minimal silica content (7.39%) (Figure 4.10). This composition may suggest an inefficient smelting process, possibly resulting in a high ferrous content.

Alternatively, this sample may have been incorrectly identified as slag and may instead be an unused bloom. NDO-17 had low concentrations of other oxides, including Al₂O₃ (1.96%), SiO₂ (7.4%), and TiO₂ (0.542%), which were not typical of those in the other slag samples (Figure 4.10 and Table 4.3).

In terms of trace elements, MAM-12 contained high concentrations of transition trace elements (TTEs), including Co (27 ppm), Ni (60 ppm), and Cu (50 ppm). MAM-13 had higher concentrations of Cr (220 ppm) and the large-ion lithophile element (LILE) Rb (40 ppm), together with elevated concentrations of the rare earth elements (REEs) La (31.9 ppm) and Ce (61.3 ppm) (Table 4.4 and Figure 4.11). All Mamba slags contained extremely high vanadium (V) concentrations, especially MAM-12 (1,770 ppm) and MAM-16 (2,474 ppm) (Table 4.4 and Figure 4.11).

The Wosi slag (WOS-15) was characterized by comparatively low concentrations of TTEs, including Cr (80 ppm), Co (13 ppm), and Ni (<20 ppm) (Table 4.4). However, the Wosi slag recorded the highest tungsten (W) concentration, at 3.3 ppm. Other trace elements, such as V (151 ppm), occurred at moderate concentrations, while the REEs included La (26.7 ppm) and Ce (59.2 ppm) (Table 4.4).

The Ndondondwane slag (NDO-17) also had an exceptionally high vanadium concentration (1,144 ppm), similar to those of the Mamba slags (Table 4.4 and Figure 4.11). Cobalt (Co) and nickel (Ni) were present at moderate concentrations of 30 ppm each, while zinc (Zn) was relatively high at 110 ppm (Table 4.4). Rare earth element (REE) concentrations were generally lower than those in the Mamba and ezinGwegweni slags, with cerium (Ce) recorded at 20.2 ppm (Table 4.4).

The ezinGwegweni slags (GWE-14 and GWE-18) contained higher Cr concentrations, particularly sample GWE-18 (310 ppm), which had the highest concentration among all the analysed slags (Table 4.4 and Figure 4.11). The TTEs included Ni (140 ppm in GWE-18 and 90 ppm in GWE-14) and V (100–168 ppm). These slags (GWE-14 and GWE-18) also contained the highest Pb concentrations (40–57 ppm) and moderate REE concentrations, with Ce reaching 49.3 ppm in GWE-18 (Table 4.4 and Figure 4.10). Only the Babanango ore (BAB-10) had very high concentrations of Cr and Pb.

Table 4.3: Major element oxide compositions in slags. Unit in weight percentage (wt%).
(Source: Author)

Element oxides	Mamba	Mamba	Mamba	Wosi	Ndondondwane	ezinGwegweni	ezinGwegweni
	MAM-12	MAM-13	MAM-16	WOS-15	NDO-17	GWE-14	GWE-18
	In situ slag	In situ slag	In situ slag	In situ slag	In situ slag	In situ slag	In situ slag
SiO ₂	11	48.8	27.3	24	7.4	65.39	64
Al ₂ O ₃	5	10.4	9.82	4.2	2	12.59	11
Fe ₂ O ₃ (T)	72.85	26.3	49.2	64	92	11.49	17
MnO	0.3	0.1	0.26	5.2	1.7	0.252	0.2
MgO	1.5	3.79	2.33	1.4	0.4	0.43	0.3
CaO	2.7	6.2	1.96	1.7	1.8	0.7	0.5
Na ₂ O	0.2	2.29	0.69	0.2	0.1	3.14	2.5
K ₂ O	0.3	2.12	0.75	0.4	0.2	3.99	2.7
TiO ₂	10	0.7	9.71	0.4	0.5	0.17	0.2
P ₂ O ₅	0.1	0.78	0.09	0.3	0.2	0.09	0.2

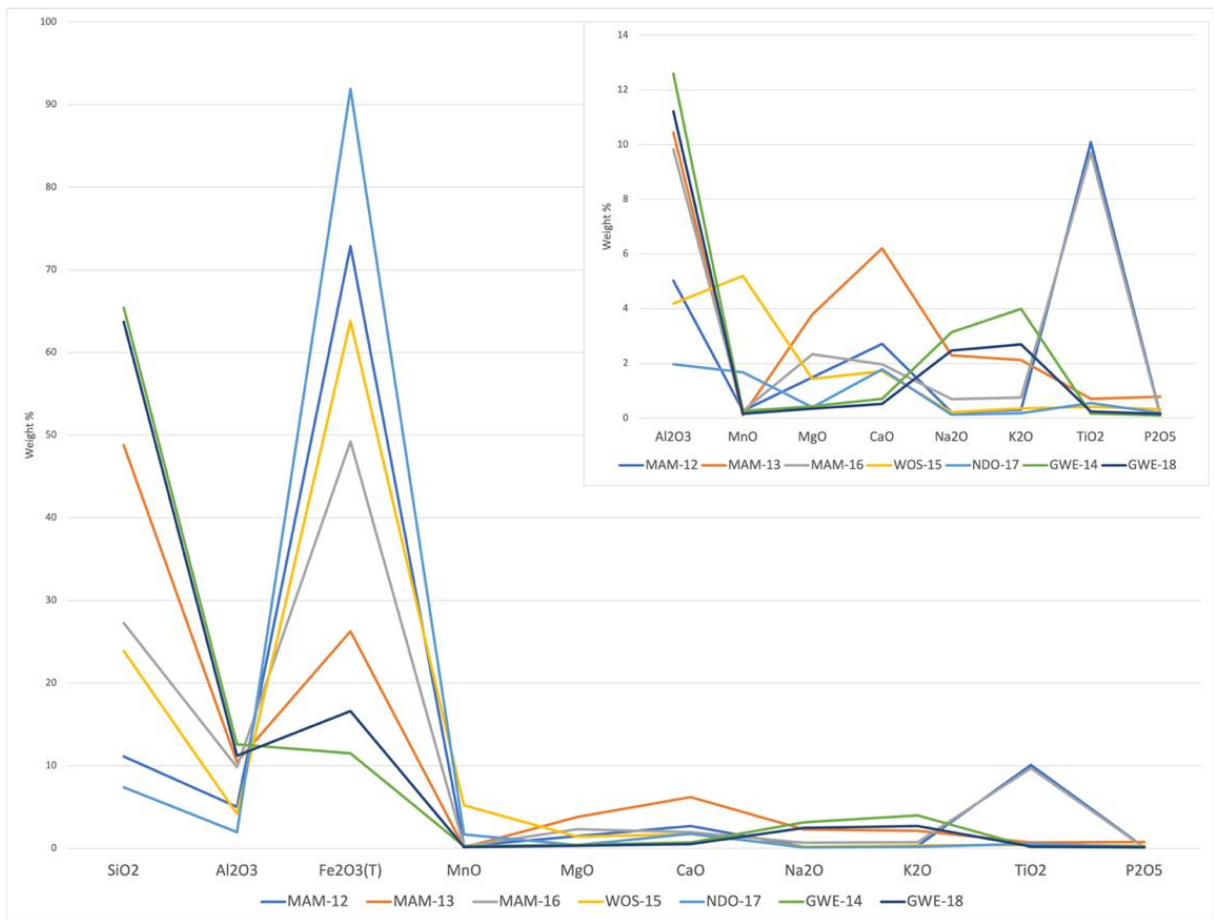


Figure 4.10: Major element oxide composition of slags in weight percent (Wt%). Insert shows major oxide composition without Fe₂O₃ and SiO₂. (Source: Author)

Table 4.4: Trace element compositions of slag samples in parts per million (ppm). (Source: Author)

Element	Mamba	Mamba	Mamba	Wosi	Ndondondwane	ezinGwegweni	ezinGwegweni
	MAM-12	MAM-13	MAM-16	WOS-15	NDO-17	GWE-14	GWE-18
	In situ slag	In situ slag	In situ slag	In situ slag	In situ slag	In situ slag	In situ slag
Rare Earth Elements (REE)							
La	4	31.9	15.1	26.7	14	18.1	15.3
Ce	8.66	61.3	29.8	59.2	20.2	43.6	49.3
Pr	1	6.7	3.23	5.4	2.1	3.27	2.99
Nd	3.89	27.5	13.8	23.2	7.97	12.4	11.7
Sm	0.83	4.67	2.67	4.62	1.65	2.05	2.42
Eu	0.263	1.16	0.582	1.21	0.37	0.502	0.422
Gd	0.83	3.45	2.32	4.72	1.6	1.7	2.01
Tb	0.13	0.49	0.35	0.77	0.23	0.26	0.33
Dy	0.7	2.45	1.87	4.19	1.27	1.4	2
Ho	0.14	0.5	0.38	0.85	0.26	0.27	0.41
Er	0.4	1.39	1.09	2.43	0.8	0.77	1.24
Tm	0.059	0.198	0.163	0.343	0.113	0.12	0.195
Yb	0.41	1.39	1.15	2.18	0.72	0.78	1.35
Lu	0.062	0.221	0.181	0.327	0.114	0.116	0.206
Sc	15	13	20	8	< 1	2	3
High Field Strength Elements (HFSE)							
Y	3.5	14.6	10.7	26.8	8.2	6.4	10.9
Zr	60	199	161	48	27	67	108
Nb	3.8	10.5	7.5	5.8	2.9	3.6	4.6
Large Ion Lithophile Elements (LILE)							
Rb	6	40	25	5	3	97	68
Sr	170	641	230	136	118	272	167
Ba	169	724	374	641	190	946	537
Th	0.87	4.72	5.34	1.36	0.76	6	10.2
U	0.3	1	1.02	0.58	0.43	1.2	2.06
Transition Trace Elements (TTE)							
Cr	40	220	140	80	< 20	170	310
Co	27	21	106	13	30	37	36
V	1770	107	2474	151	1144	100	168
Cu	50	50	30	20	40	10	30
Zn	< 30	30	120	< 30	110	< 30	< 30
Other Trace Elements							
Hf	1.5	4.7	3.8	1	0.5	1.8	2.8
Ta	0.18	0.52	0.41	0.23	0.11	0.31	0.38
W	0.9	1.1	< 0.5	3.3	< 0.5	1.2	1.2
Tl	< 0.05	0.07	0.08	< 0.05	< 0.05	0.48	0.37
Pb	< 5	< 5	< 5	< 5	< 5	40	57
Ni	60	60	110	< 20	30	90	140
Ga	42	12	42	9	41	15	14
Ge	< 0.5	0.7	0.9	0.5	1.6	0.6	0.7
As	< 5	6	< 5	< 5	< 5	5	6
Mo	< 2	3	< 2	4	< 2	2	2
Sn	1	1	1	1	1	1	1
Cs	0.2	1.1	1.1	0.3	0.1	1	1

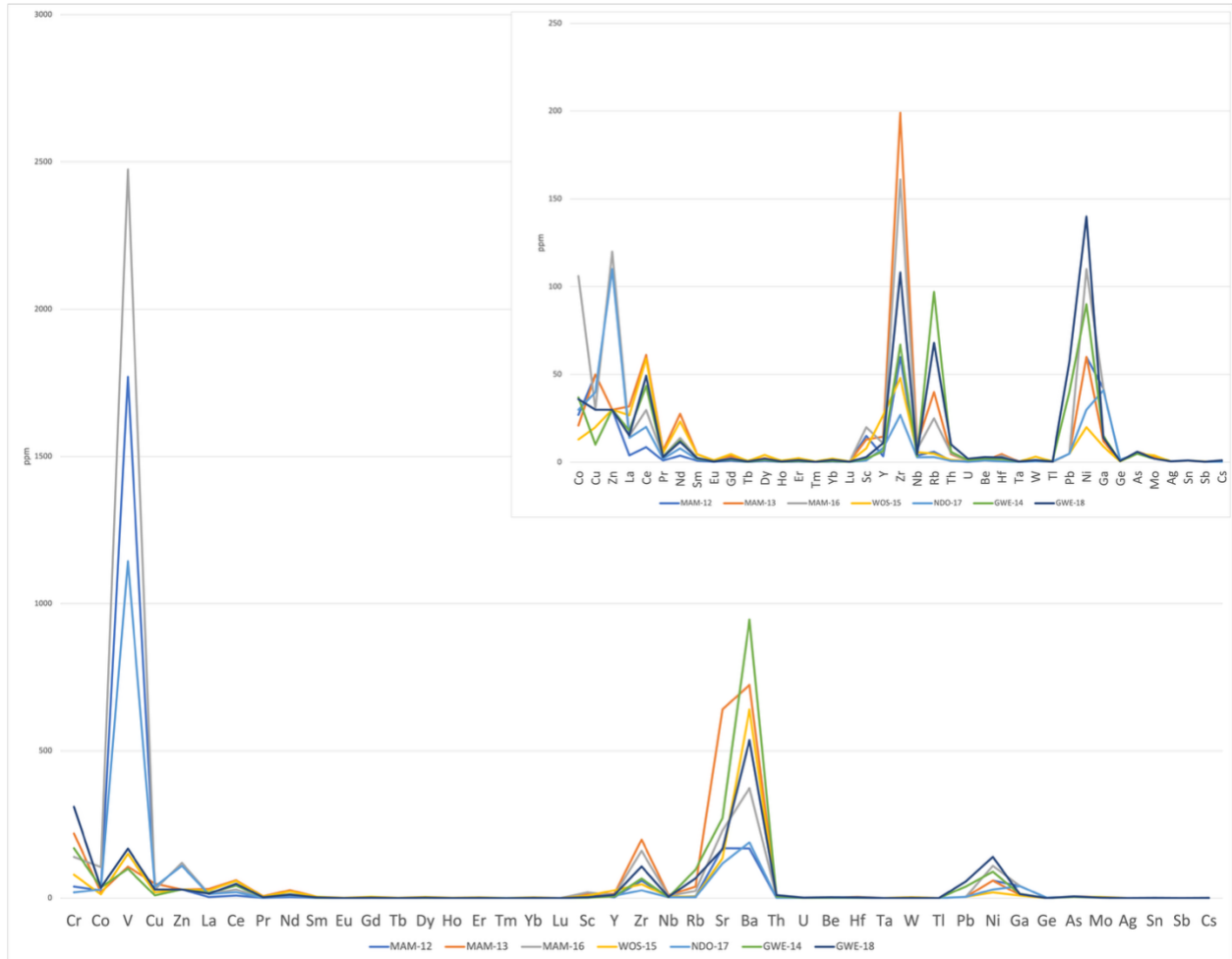


Figure 4.11: Trace element composition of slags in parts per million (ppm). Insert shows major oxide composition without V. (Source: Author)

4.3.3 Statistical Analysis

As shown in Figure 4.12, the slag samples can be distinguished based on their $\text{MgO}/\text{K}_2\text{O}$, SiO_2/MnO , MnO/TiO_2 , and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ ratios. Based on their MnO/TiO_2 ratios, the slags can be classified into four groups. The first group comprises MAM-12 and MAM-16, both of which are characterized by low MnO and high TiO_2 concentrations. The second group consists of MAM-13, which exhibits low MnO and moderate TiO_2 concentrations. The third group includes GWE-

13 and GWE-14, which are characterized by low concentrations of both MnO and TiO₂. The final group comprises WOS-13 and NDO-17, which exhibit high MnO and low TiO₂ concentrations (Figure 4.13).

The PCA results show that the ezinGwegweni slags (GWE-14 and GWE-18) plot near the centre because they contain low concentrations of both MnO and TiO₂ (Figure 4.14). In contrast, the Wosi slag (WOS-15) and Ndondondwane slag (NDO-17) are characterized primarily by low titanium dioxide (TiO₂) and high manganese oxide (MnO) concentrations. This pattern supports the conclusions of van Schalkwyk (1994) and Greenfield and Miller (2004). The Ndondondwane sample (NDO-17) is clearly distinguished by its high ferrous oxide content and very low silicate content, supporting the interpretation that the sample is an unused bloom.

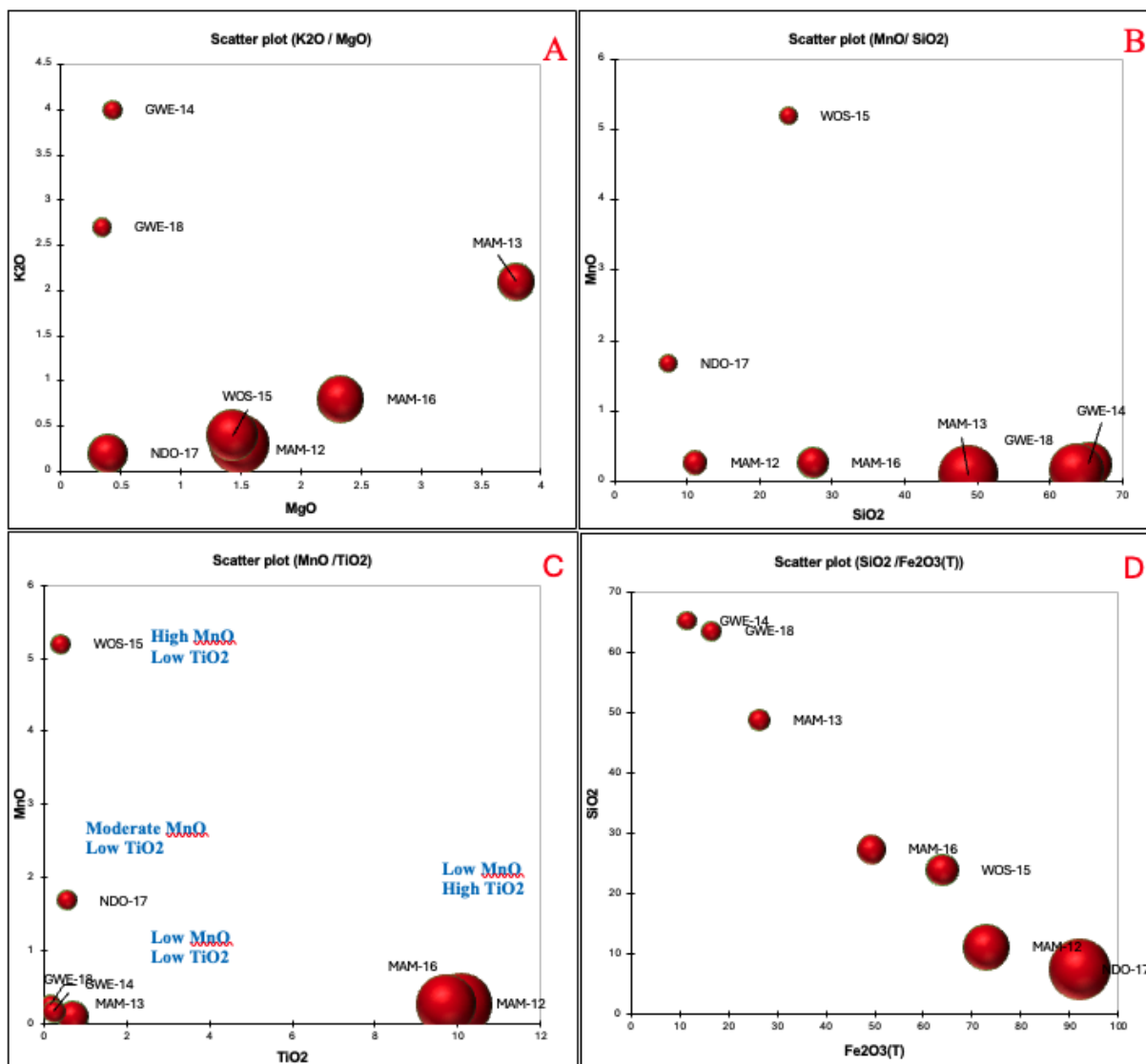


Figure 4.12: Element Ratio scatter plot of A: MgO/K₂O, B: SiO₂/MnO, C:TiO₂/MnO and D: Fe₂O₃/SiO₂. The size of the bubble indicates the concentration of the oxide on the x-axis. (Source: Author)

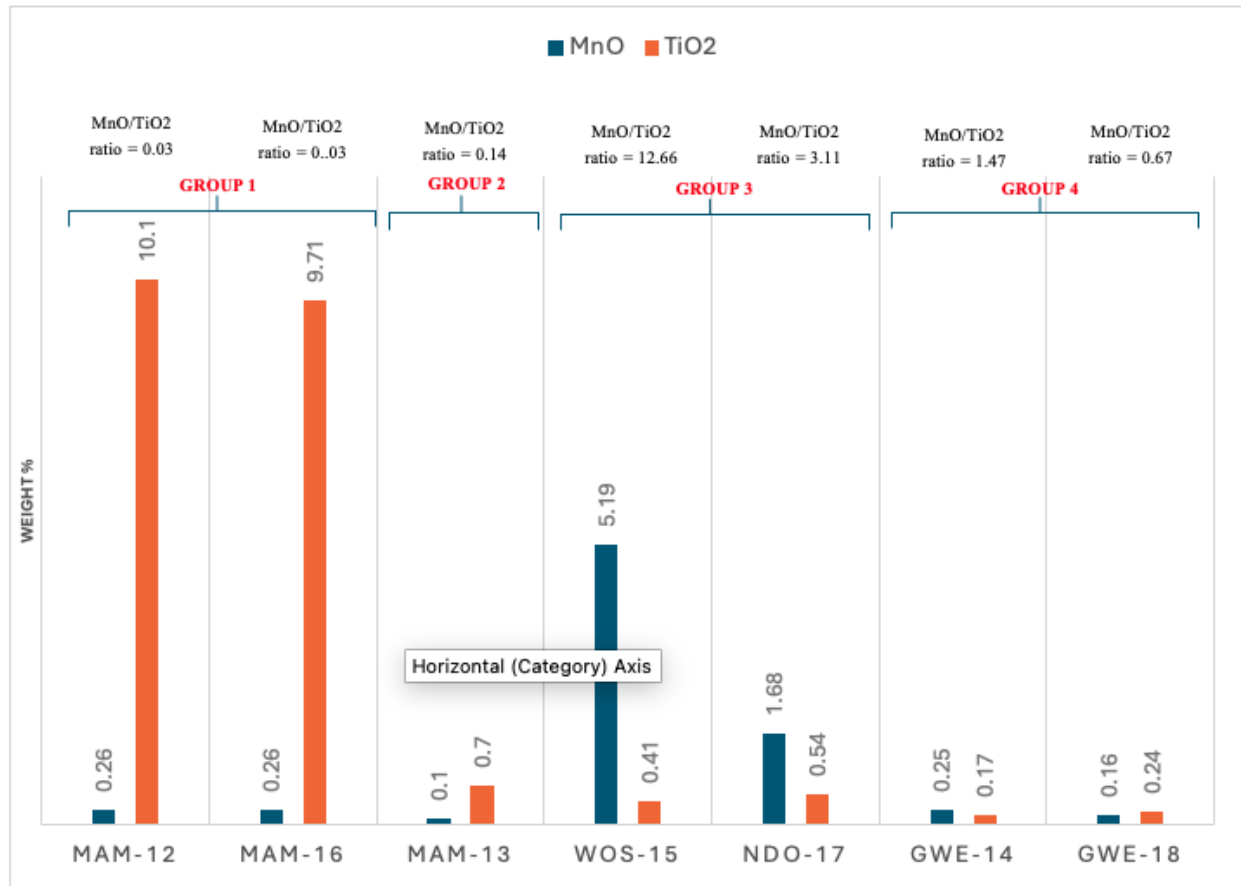


Figure 4.13: MnO and TiO₂ concentrations (ppm) of slag samples and the corresponding MnO/TiO₂ ratios. (Source: Author)

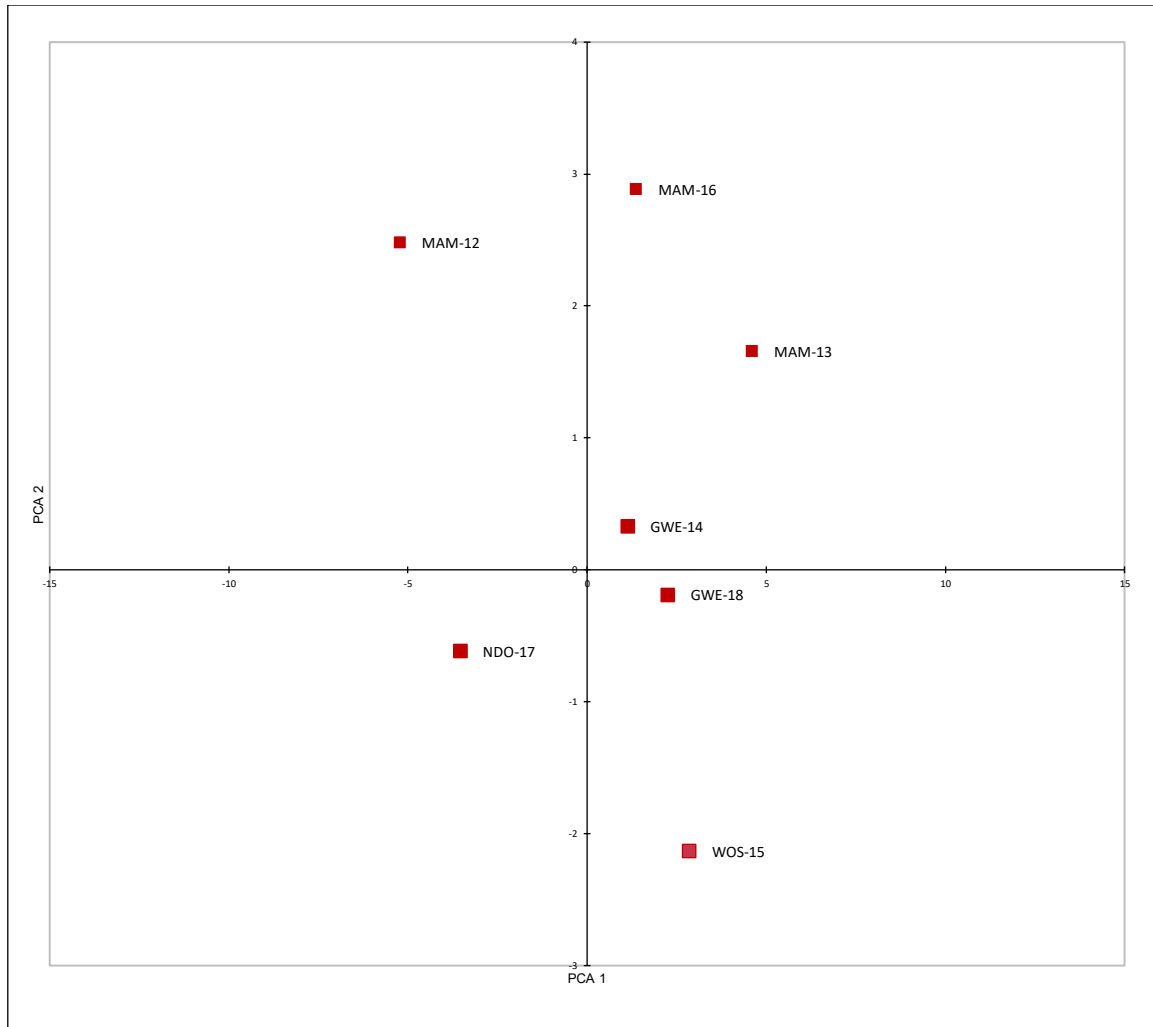


Figure 4.14: PCA scatter plot (PCA 1 vs PCA 2) showing geochemical variation among slag samples from Mamba, ezinGwegweni, Ndondondwane, and Wosi, using transformed Log10 major and trace elements. (Source: Author)

4.4 Statistical Comparison of Ores and Slags

Based on the MnO/TiO₂ ratio analysis, the ores and slags can be grouped into: low TiO₂–low MnO, low MnO–moderate TiO₂, low MnO–high TiO₂, moderate MnO–low TiO₂, and high MnO–low TiO₂ (Figures 4.15 and 4.16).

From the Principal Component Analysis (PCA) (Figure 4.17), ores and slags with low TiO_2 and MnO concentrations form a distinct cluster. WOS-15 and DEN-7 plot together due to higher MnO concentration, but DEN-7 is enriched in LILE and REE. High ferrous and vanadium concentrations of MAM-12 and NDO-17 draw them to negative PCA 1 and PCA 2. MAM-12 and MAM-13 also plot to negative PCA-2 and positive PCA-1.

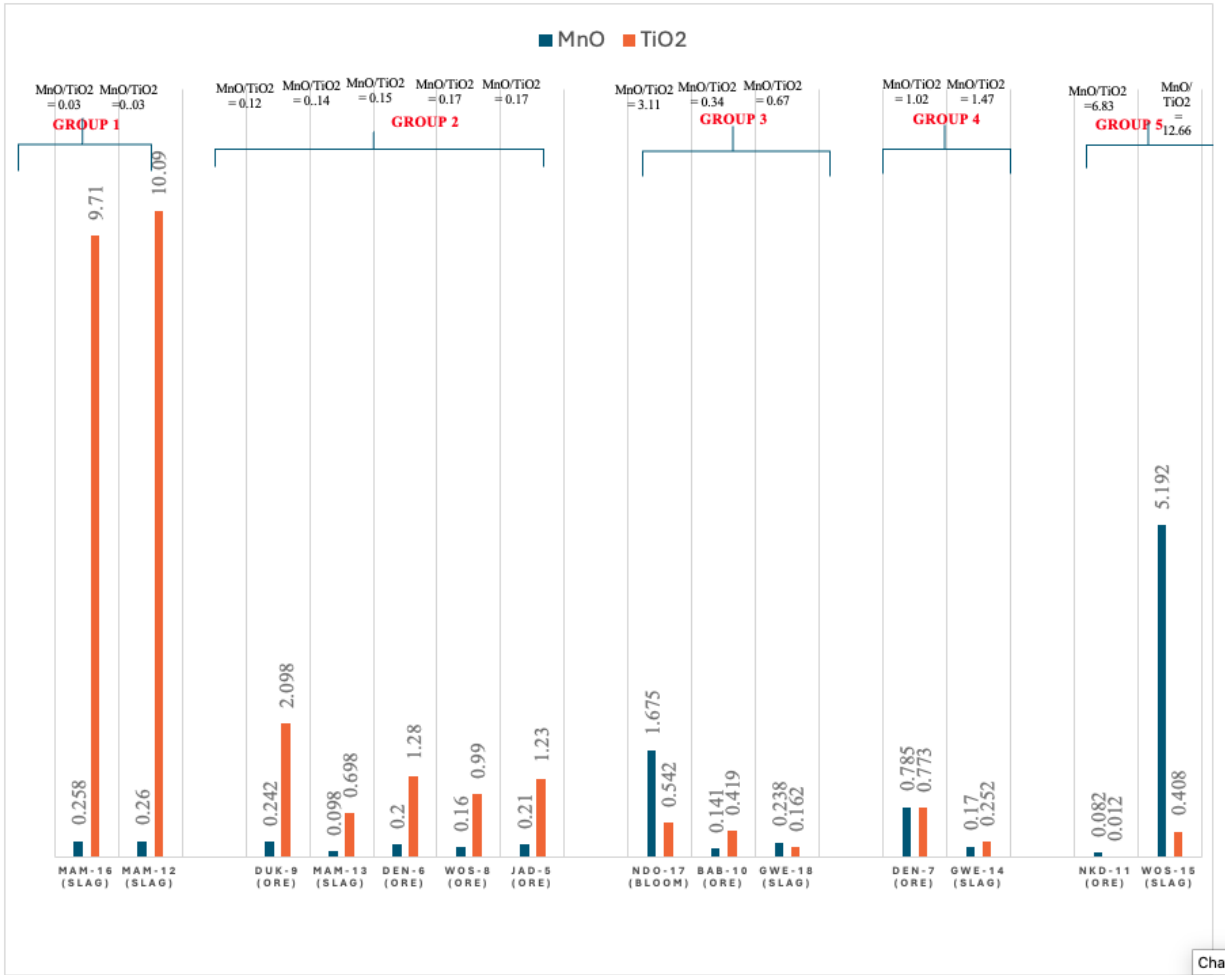


Figure 4.16: MnO and TiO₂ concentrations (in weight %) in ore and slag samples, and the corresponding MnO/TiO₂ ratios. (Source: Author)

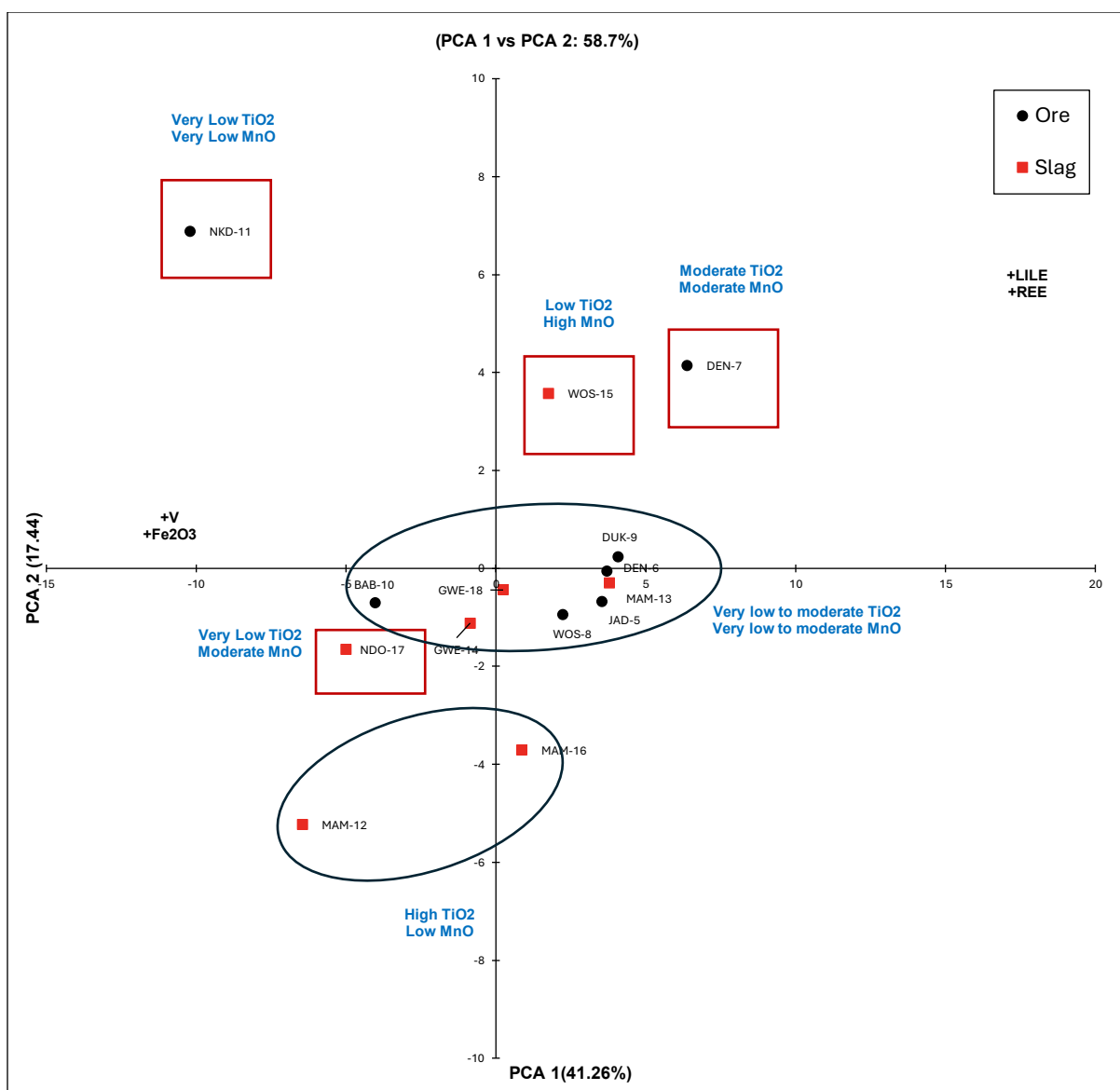


Figure 4.17: PCA scatter plot showing the geochemical correlation of slags and ore sources, using transformed Log10 major and trace elements. (Source: Author)

4.4.1 Conclusion

All ore and slag samples, except NKD-11, had high vanadium (V) concentrations, particularly the Mamba and Ndongondwane samples. This may have resulted from the use of vanadium-enriched ore sources. The MnO/TiO₂ ratio analysis distinguished the ore and slag samples into approximately four groups, a classification supported by the PCA results. The

chemical data and petrography results also suggest that NDO-17 and MAM-12 are blooms rather than slags.

4.5 Blooms

4.5.1 Thin-section petrography results

As argued in the previous section, NDO-17 and MAM-12 appear to be blooms not slags based on the chemistry and mineral phases. I have therefore included NDO-17 and MAM-12 as blooms in this section. Petrographic analysis of the bloom samples showed considerable variation in the proportions of metallic iron, iron oxides, and entrapped slag. MAM-1 and NDO-3 were dominated by ferrite or metallic iron with minor non-metallic phases, a characteristic of well-consolidated blooms.

WOS-2, MAM-4, MAM-12, and NDO-17 were more heterogeneous and retained greater proportions of non-metallic material. WOS-2 contained metallic iron phases and slag-rich phases. MAM-4 and MAM-12 contained metallic iron together with dendritic iron-oxide phases such as wüstite, within fayalitic matrices. NDO-17 was mainly dendritic iron-rich phases and elongated silicate crystals.

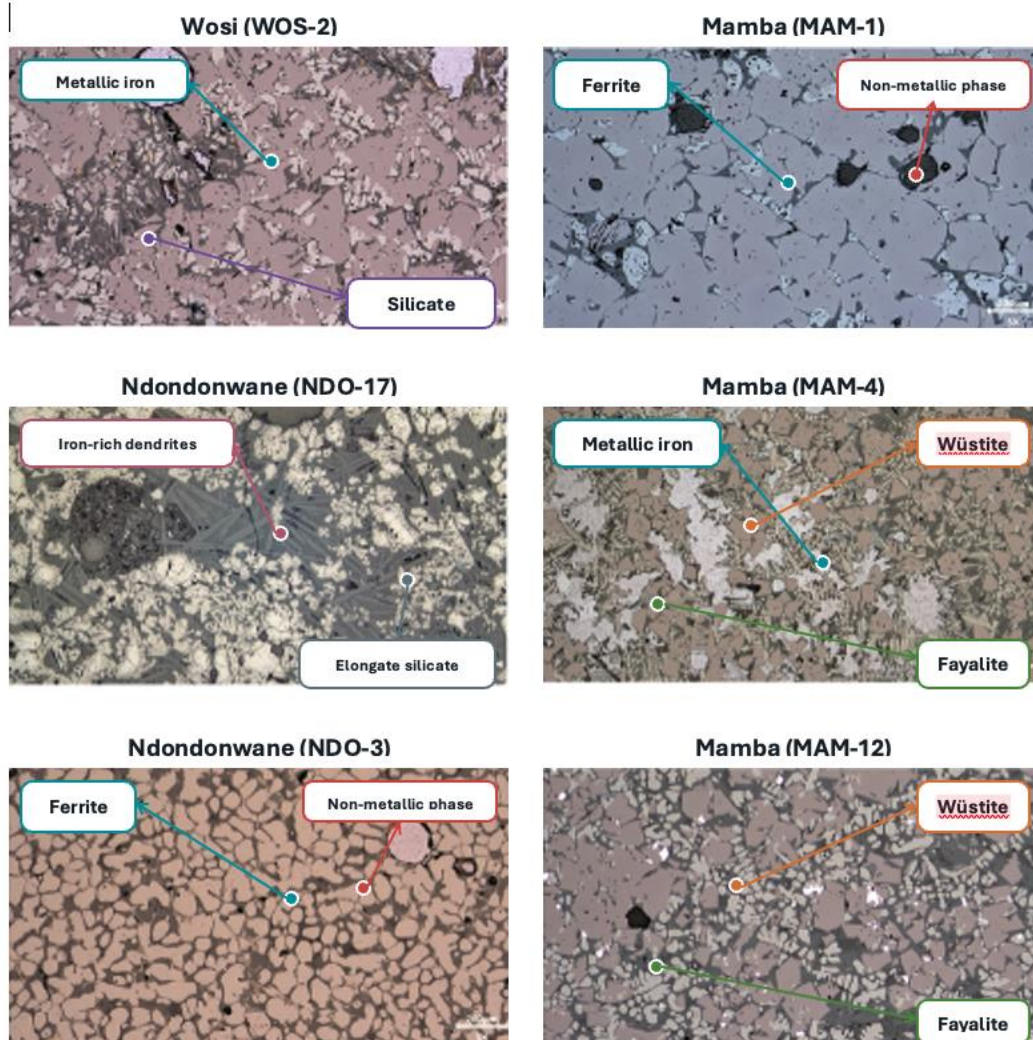


Figure 4.18: Thin-sectioned micrograph of blooms showing ferritic iron matrix. (Source: Author)

4.5.2 Chemical Composition

The bloom assemblage comprised samples from the Early Iron Age (EIA) sites of Mamba, Wosi, and Ndondondwane in the middle Thukela River Basin. The two bloom samples from Mamba (MAM-1 and MAM-3) exhibited high Fe_2O_3 concentrations of 74.86% and 73.07%, respectively, indicating iron-rich compositions (Table 4.5 and Figure 4.19). The TiO_2

concentrations across all the Mamba blooms were notably high (8.12%–15.49%). When paired with the lower MnO concentrations (0.22%–0.23%), this may indicate the presence of titanium-bearing minerals in the ore source.

The Ndondondwane bloom (NDO-3) had the highest Fe₂O₃ concentration (87.64%), making it the most iron-rich bloom (Table 4.5 and Figure 4.19). It had the lowest concentrations of SiO₂ (9.11%) and Al₂O₃ (2.63%). Unlike the other bloom samples, NDO-3 contained a significantly high MnO concentration (3.237%). The CaO content was relatively low (2.26%), the TiO₂ concentration was the lowest among all the bloom samples (0.335%), and the P₂O₅ concentration was moderate (0.21%).

The Wosi sample (WOS-2) had a comparatively lower Fe₂O₃ concentration (58.97%) than the other bloom samples but with elevated concentrations of CaO (12.3%), SiO₂ (10.62%), and MgO (2.88%) (Table 4.5 and Figure 4.19). It also had a moderate Al₂O₃ concentration (5.62%) and the highest P₂O₅ concentration (0.44%) among the blooms. The TiO₂ concentration (8.99%) was relatively high, while the Na₂O (0.20%) and K₂O (0.49%) concentrations were low.

The trace-element compositions more clearly distinguished the bloom samples (Table 4.6 and Figure 4.20). The Mamba bloom samples (MAM-1 and MAM-4) contained high concentrations of transition trace elements (TTEs), particularly V (4,298 ppm and 1,380 ppm) and Cr (90 ppm and 30 ppm). Other TTEs, such as Co (125 ppm and 61 ppm), Ni (170 ppm and 80 ppm), and Cu (50 ppm and 120 ppm), were present at moderate concentrations. Rare earth element (REE) concentrations were comparatively low, with Ce ranging from 4.09 to 11.3 ppm and Nd ranging from 2 to 5.21 ppm. Large-ion lithophile elements (LILEs) included Sr (88–374

ppm), while the high-field-strength element (HFSE) Zr ranged from 37 to 64 ppm, which was relatively low.

As with the Mamba samples, the Wosi bloom sample (WOS-2) also contained high concentrations of TTEs, including V (2,420 ppm), Ni (100 ppm), Co (91 ppm), and Cr (80 ppm). However, it was distinguished by elevated concentrations of LILEs, particularly Sr (1,102 ppm) and Ba. REE concentrations were low, with Ce at 8.74 ppm and Nd at 4.05 ppm (Table 4.6 and Figure 4.20).

The Ndondondwane bloom (NDO-3) had the lowest TTE concentrations, including V (1,148 ppm), Cr (40 ppm), Co (37 ppm), Ni (50 ppm), and Cu (40 ppm) (Table 4.6 and Figure 4.20). In contrast, it contained the highest REE concentrations, with Ce at 23.9 ppm and Nd at 10 ppm, as well as the HFSE Y at 19.9 ppm. LILE concentrations, including Sr at 84 ppm, were minimal compared with those of the other blooms.

Table 4.5: Analyses of major element oxide compositions in blooms. Unit in weight percentage (wt%). (Source: Author)

Element oxides	Mamba	Mamba	Wosi	Ndondondwane
	MAM-1	MAM-4	WOS-2	NDO-3
	In situ bloom	In situ bloom	In situ bloom	In situ bloom
SiO ₂	4.49	13.1	10.62	9.11
Al ₂ O ₃	6.41	4.93	5.62	2.63
Fe ₂ O ₃ (T)	74.86	73.1	58.97	87.6
MnO	0.228	0.23	0.207	3.24
MgO	1.47	1.1	2.88	1.19
CaO	1.12	2.95	12.3	2.26
Na ₂ O	0.08	0.2	0.2	0.08
K ₂ O	0.15	0.34	0.49	0.11
TiO ₂	15.49	8.19	8.992	0.34
P ₂ O ₅	0.07	0.16	0.44	0.21

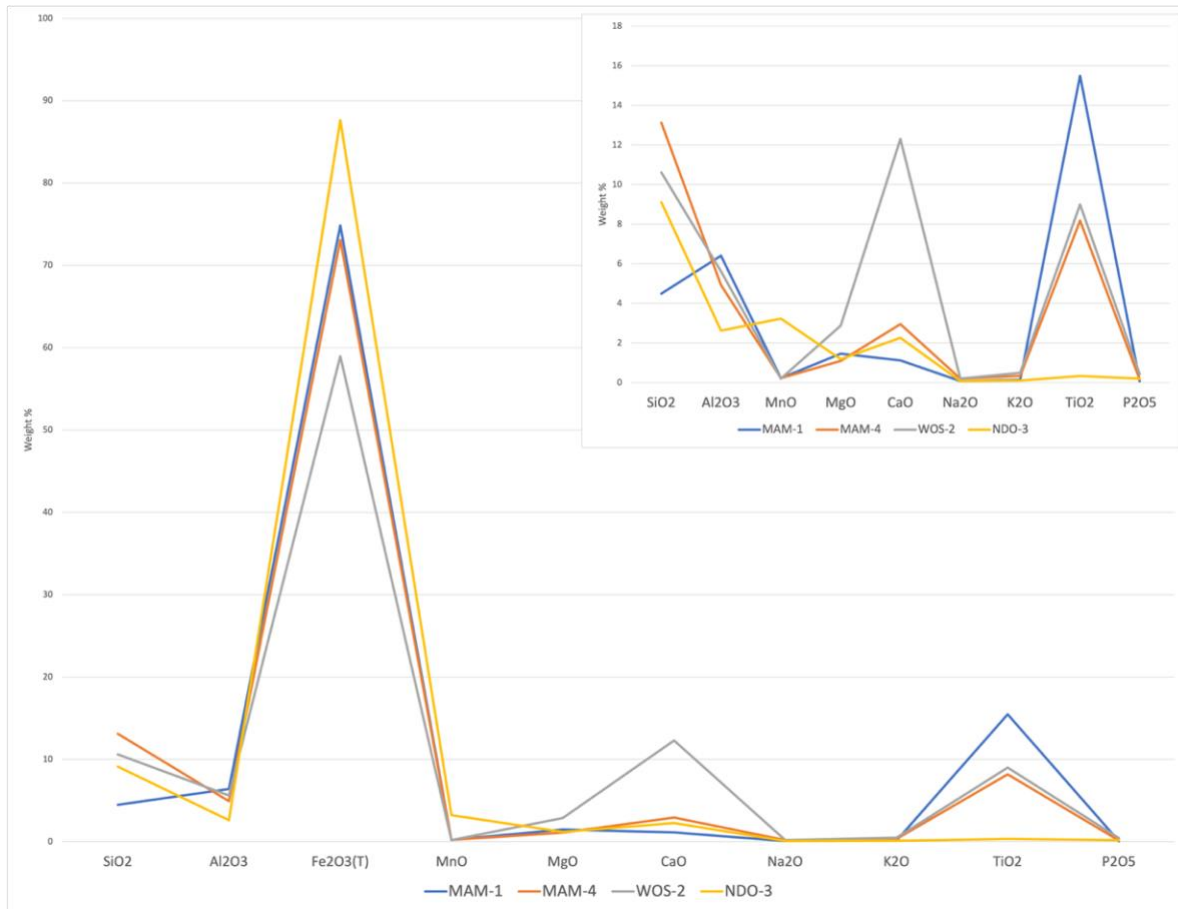


Figure 4.19: Major element oxide compositions of bloom samples (MAM-1, WOS-2, MAM-4, and NDO-3), shown in weight percent (Wt%). The insert shows major oxide compositions without Fe₂O₃. (Source: Author)

Table 4.6: Analyses of trace element compositions of bloom samples in parts per million (ppm). (Source: Author)

Element	Mamba	Mamba	Wosi	Ndondondwane
	MAM-1	MAM-4	WOS-2	NDO-3
	In situ bloom	In situ bloom	In situ bloom	In situ bloom
Rare Earth Elements (REE)				
La	2.1	13.7	5.4	4.43
Ce	4.09	23.9	11.3	8.74
Pr	0.49	2.5	1.31	1.08
Nd	2	10	5.21	4.05
Sm	0.42	2.43	1.12	0.88
Eu	0.104	0.615	0.289	0.233
Gd	0.37	2.99	1	0.78
Tb	0.06	0.48	0.15	0.12
Dy	0.32	2.86	0.88	0.72
Ho	0.06	0.59	0.17	0.15
Er	0.19	1.65	0.49	0.42
Tm	0.028	0.238	0.069	0.061
Yb	0.19	1.45	0.43	0.41
Lu	0.03	0.202	0.068	0.067
Sc	18	3	15	14
High Field Strength Elements (HFSE)				
Y	1.6	19.9	4.1	3.6
Zr	37	21	64	60
Nb	2.7	1.9	4.1	3.4
Large Ion Lithophile Elements (LILE)				
Rb	4	2	5	8
Sr	88	84	374	1102
Ba	65	134	598	923
Th	0.48	0.75	1.14	1.08
U	0.15	0.4	0.43	0.27
Transition Trace Elements (TTE)				
Cr	90	40	30	80
Co	125	37	61	91
V	4298	1148	1380	2420
Cu	50	40	120	40
Zn	< 30	100	< 30	< 30
Other Trace Elements				
Hf	1	0.4	1.6	1.5
Ta	0.13	0.06	0.2	0.18
W	< 0.5	1.3	< 0.5	0.7
Tl	< 0.05	< 0.05	< 0.05	< 0.05
Pb	< 5	< 5	< 5	< 5
Ni	170	50	80	100
Ga	55	31	35	40
Ge	< 0.5	2	< 0.5	< 0.5
As	< 5	< 5	< 5	< 5
Mo	2	2	2	6
Sn	1	1	2	1
Cs	0.2	0.1	0.2	0.2

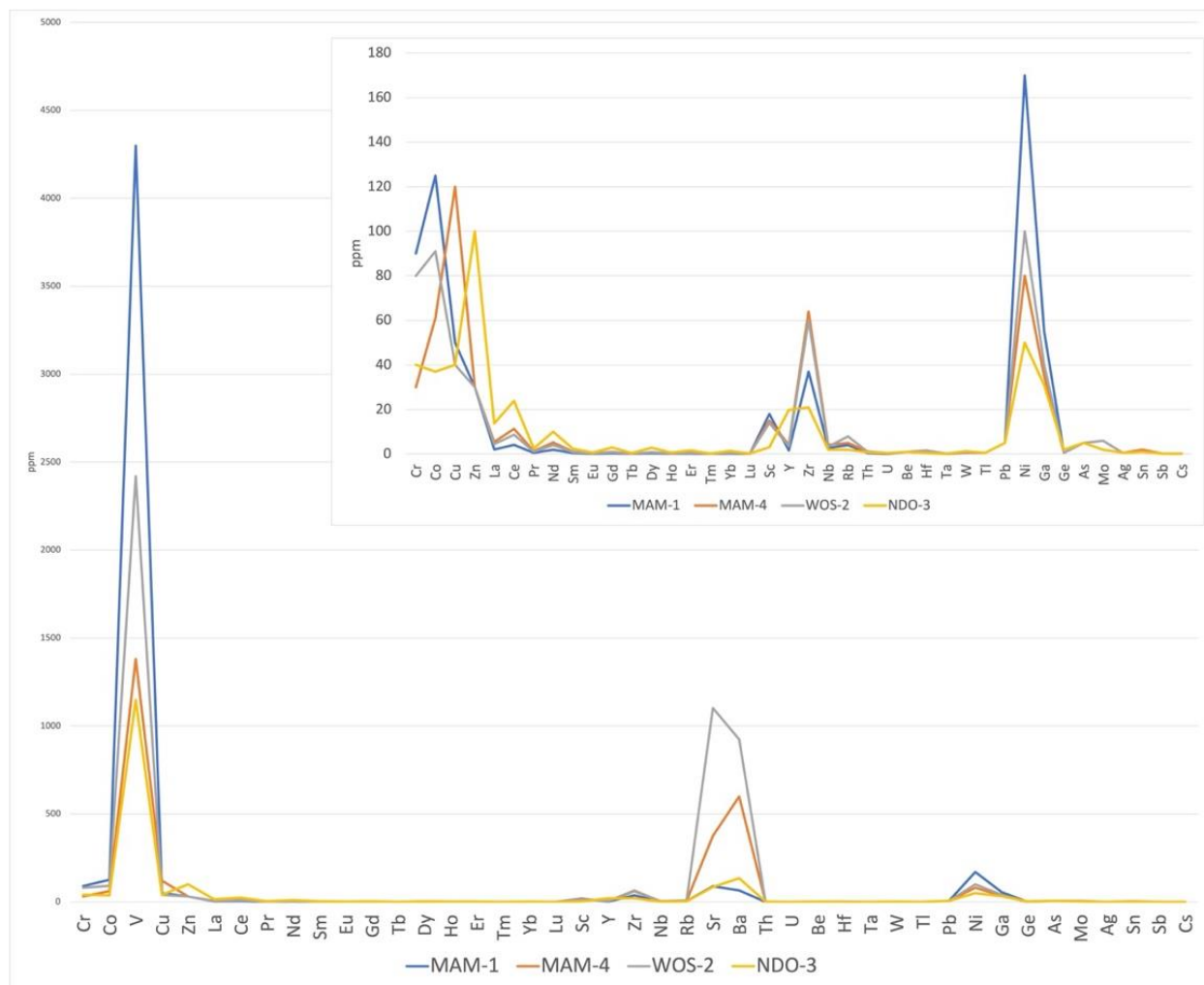


Figure 4.20: Trace element compositions of bloom samples (MAM-1, WOS-2, MAM-4, and NDO-3), shown in parts per million (ppm). The insert shows major oxide composition without V. (Source: Author)

4.5.3 Statistical Analysis

The bloom samples are separated into two main groups based on their MnO/TiO_2 ratios (Figure 4.21). The blooms from Mamba (MAM-1, MAM-4, and MAM-12) and Wosi (WOS-2)

are high in TiO_2 and low in MnO , whereas the blooms from Ndondondwane (NDO-3 and NDO-17) are very low in TiO_2 and moderate in MnO (Figure 4.21).

The PCA scatter plot further supports the MnO/TiO_2 ratio-based grouping of the archaeological bloom samples from the middle Thukela River Basin (Figure 4.22). The Mamba samples (MAM-1, MAM-4, and MAM-12) and the Wosi sample (WOS-2) plot closely together, reflecting broadly similar chemical compositions characterized by high TiO_2 and low MnO concentrations. The Ndondondwane blooms (NDO-3 and NDO-17) plot along the negative sides of PC1 and PC2. This distinct positioning suggests a homogeneous chemical signature among the Ndondondwane blooms, characterized by moderate MnO and very low TiO_2 concentrations (Figure 4.22).

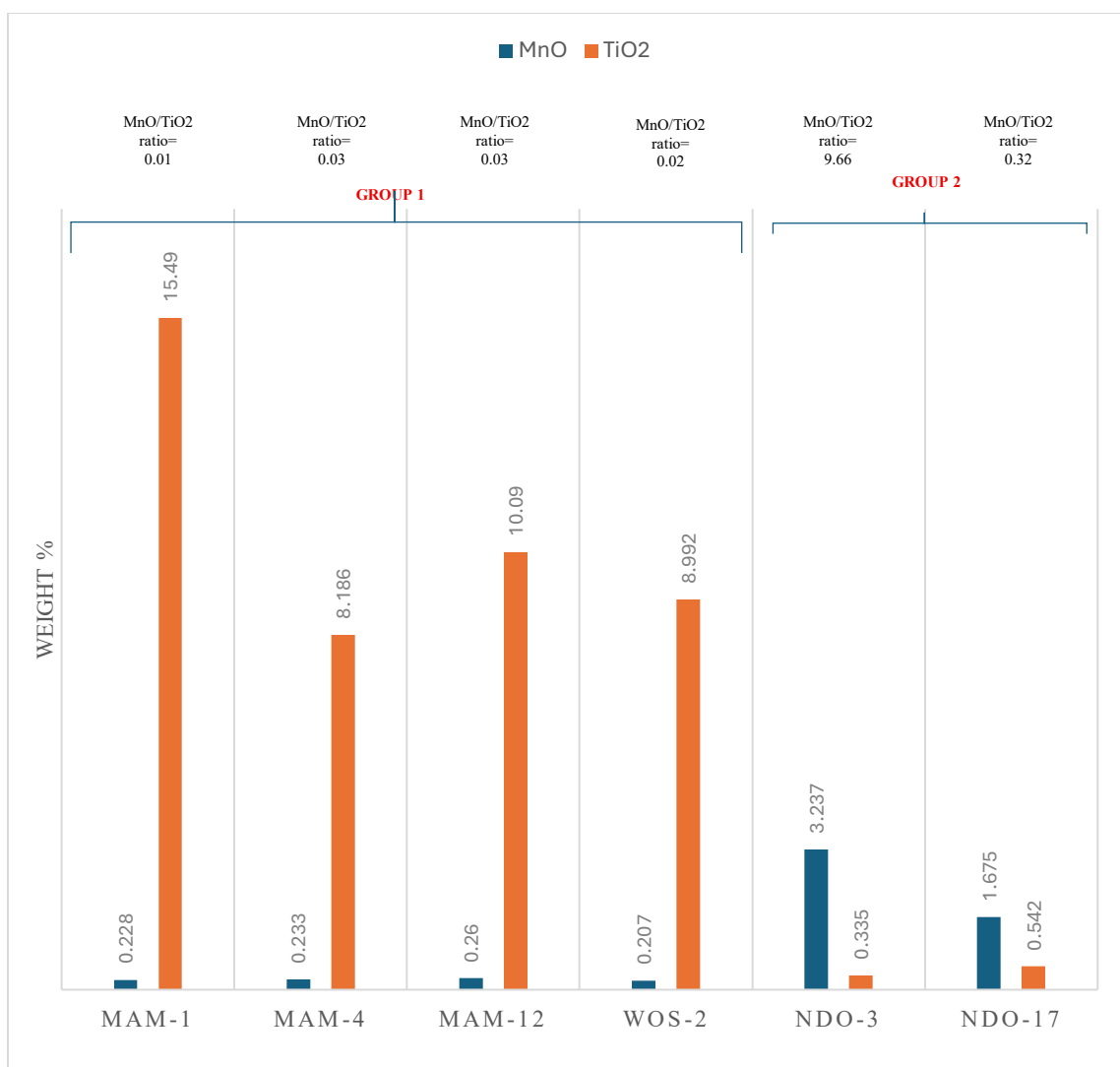


Figure 4.21: MnO and TiO₂ concentrations (in weight %) of bloom samples and the corresponding MnO/TiO₂ ratios. (Source: Author)

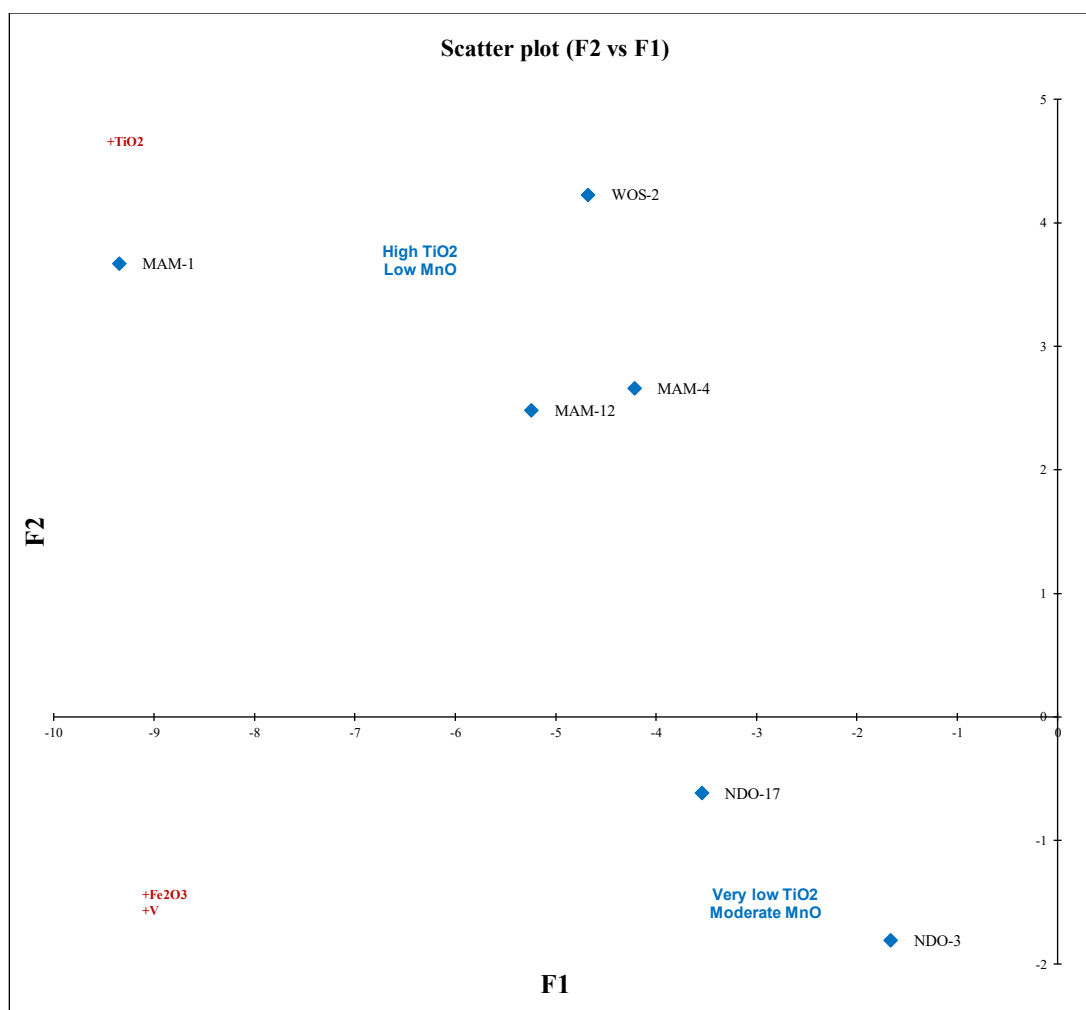


Figure 4.22: PCA scatter plot of bloom samples from Mamba, Wosi, and Ndondondwane, using transformed Log10 major and trace elements. (Source: Author)

4.5.4 Statistical Comparison of Ores, Slags and Blooms

Based on their MnO/TiO₂ ratios, the samples cluster into five major groups: low MnO–high TiO₂, low MnO–moderate TiO₂, low MnO–low TiO₂, equivalent MnO–TiO₂ ratios, and high MnO–low TiO₂ (Figure 4.23). All the Mamba samples, except MAM-13, were low in MnO but contained relatively high TiO₂ concentrations, with the MAM-1 bloom recording the highest TiO₂ concentration. The Wosi slag (WOS-15), on the other hand, was high in MnO and low in TiO₂ (Figure 4.24). The Ndondondwane materials were grouped based on their low TiO₂ and

moderate MnO concentrations. All the ore samples, the slags from ezinGwegweni (GWE-14 and GWE-18), and the Mamba slag (MAM-13) were grouped based on their low TiO₂ and low MnO concentrations.

The PCA of the ore, slag, and bloom samples supports the MnO/TiO₂ ratio analysis (Figure 4.25). The grouping of MAM-1, WOS-2, MAM-4, and MAM-12 in the upper-left quadrant agrees with the MnO/TiO₂ ratio plots shown in Figure 4.25 and reflects their geochemical similarities. The Ndondondwane blooms (NDO-3 and NDO-17) cluster with the BAB-10 ore sample, although BAB-10 plots towards the lower-right quadrant because of its high Cu loading. The Nkandla ore sample (NKD-11) remains geochemically distinct.

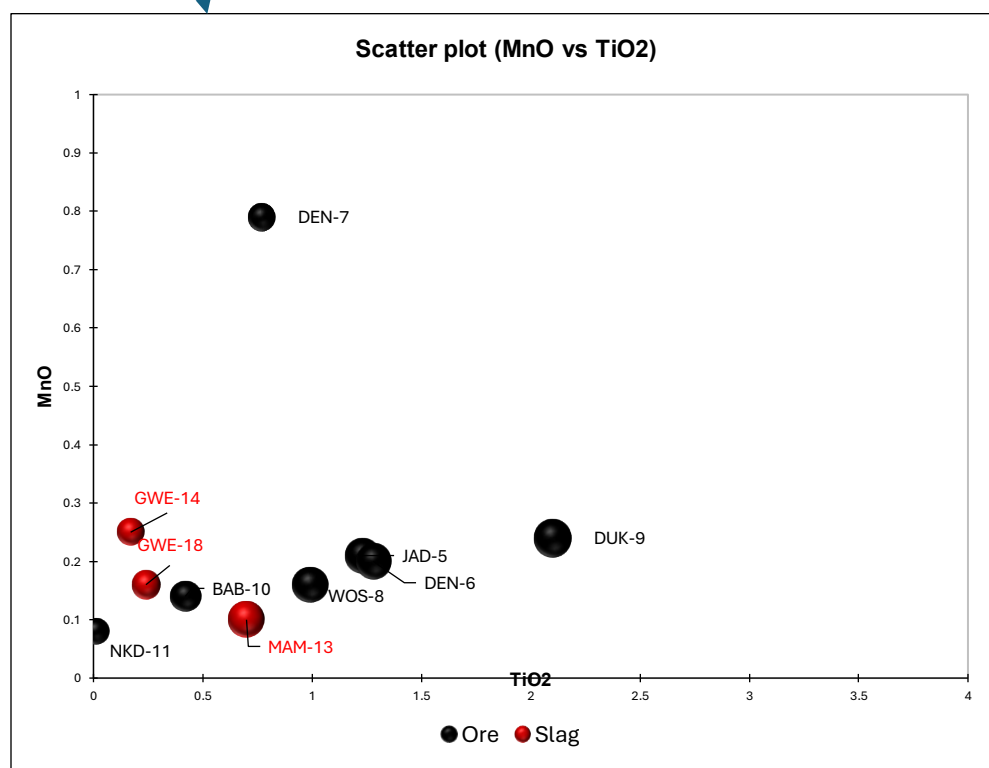
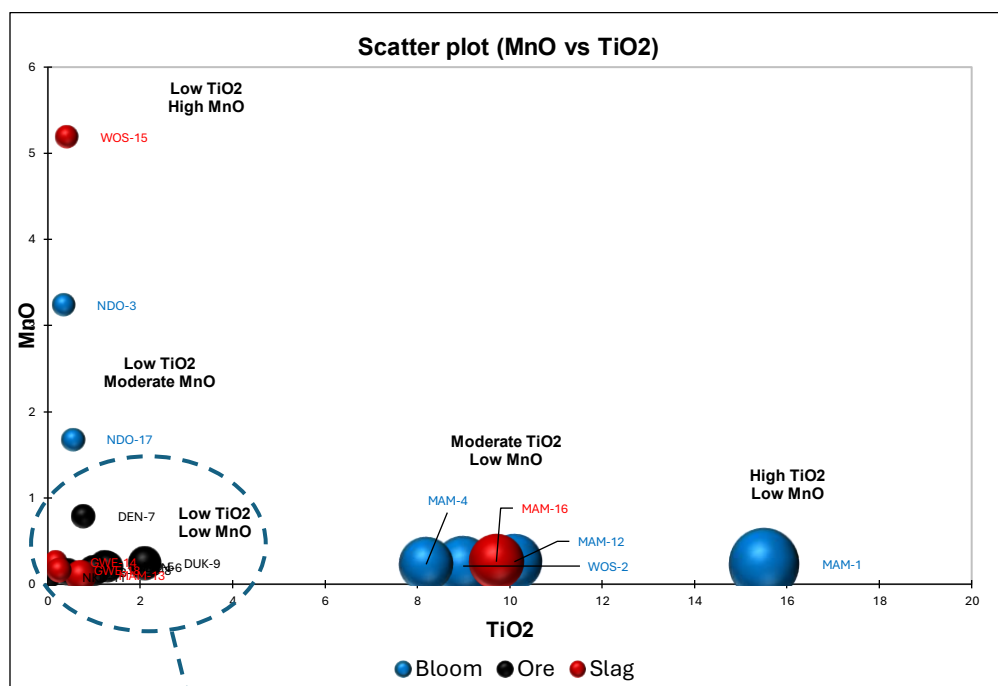


Figure 4.23: MnO/TiO₂ element ratio scatter plot of ore and slag samples. Larger bubbles indicate higher TiO₂ concentrations. (Source: Author)

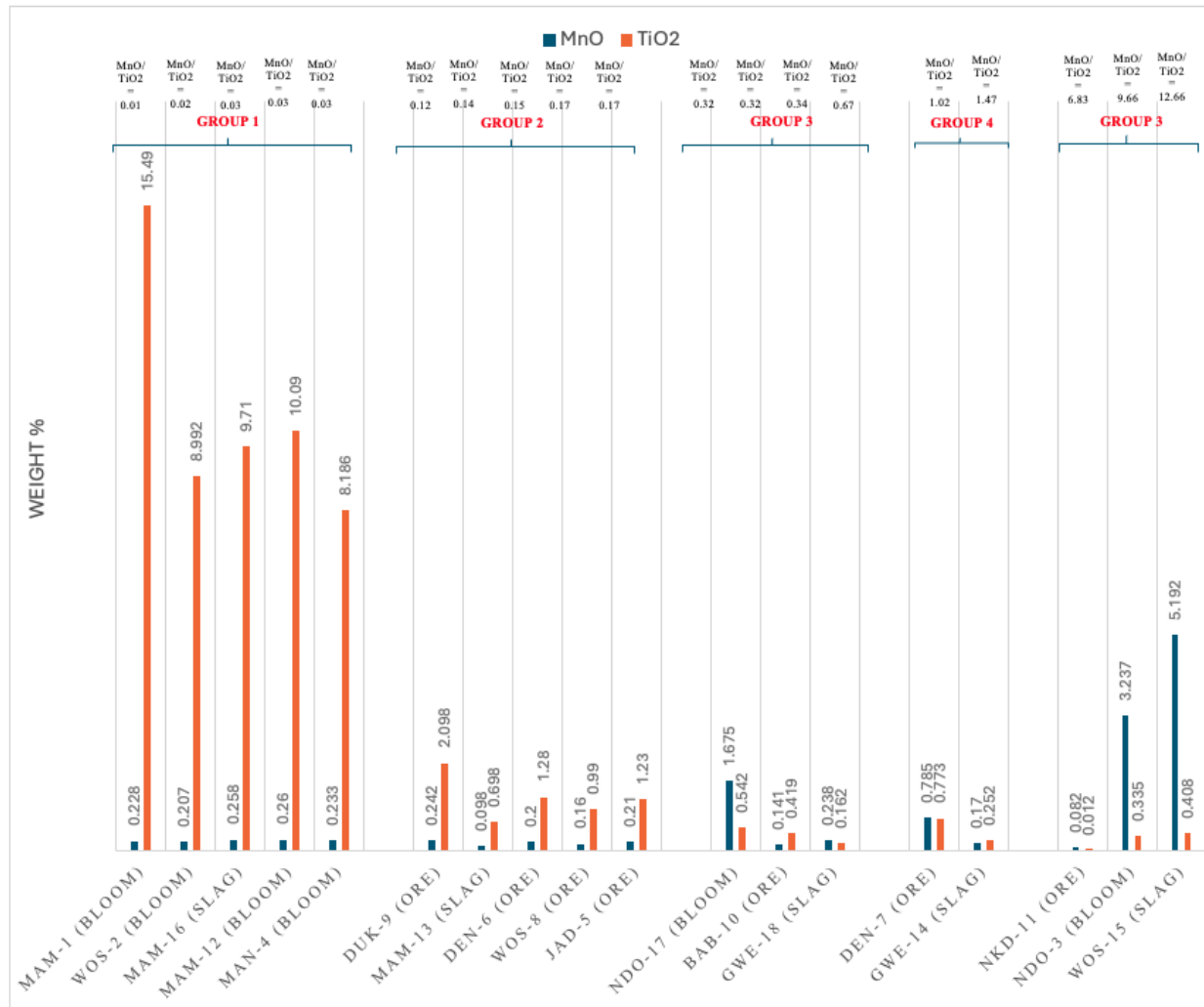


Figure 4.24: MnO and TiO₂ concentrations (in weight %) in ore and slag samples, and the corresponding MnO/TiO₂ ratios. (Source: Author)

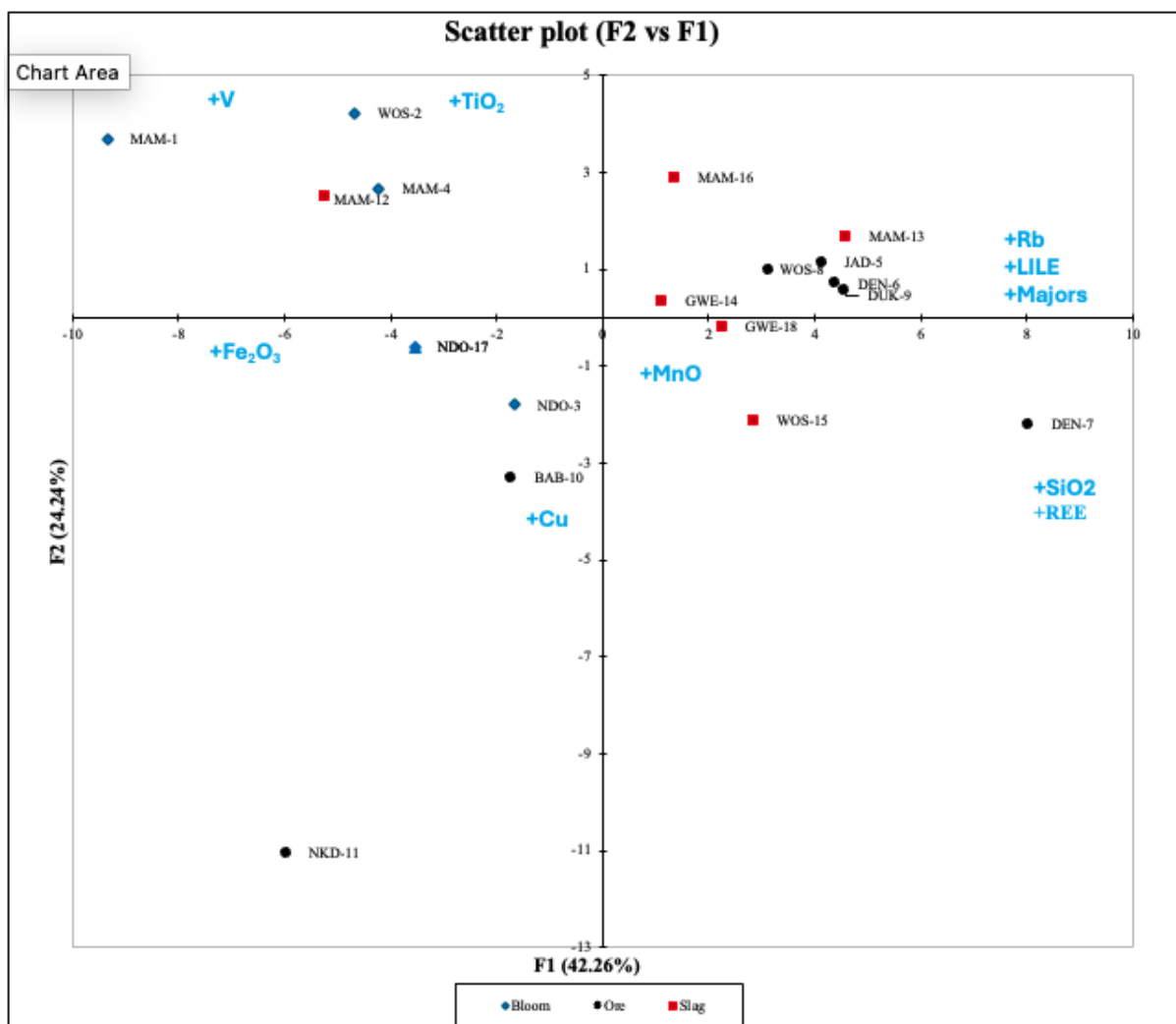


Figure 4.25: Principal Component Analysis (PCA) of ores, slags and blooms, using transformed Log10 major and trace elements using ICP-MS data. (Source: Author)

4.5.5 Conclusion

The bloom samples from the EIA sites of Wosi, Mamba, and Ndondondwane can be distinguished by their chemical compositions and MnO/TiO₂ ratios. The blooms from Mamba and Wosi are predominantly characterized by high TiO₂ and low MnO concentrations, whereas the Ndondondwane blooms are generally characterized by low TiO₂ and moderate MnO

concentrations. All the bloom samples exhibit very high vanadium concentrations, which may indicate the use of vanadium-rich ore sources.

Furthermore, when analysed alongside the ore and slag samples, the bloom samples fall within the major compositional groups identified through MnO/TiO₂ ratio analysis and principal component analysis (PCA). These groups comprise low MnO–high TiO₂, low MnO–moderate TiO₂, low MnO–low TiO₂, approximately equivalent MnO and TiO₂ concentrations, and high MnO–low TiO₂.

4.6 Iron Artifacts (Iron hoes and amulet)

4.6.1 Imaging Results

The iron artifact samples are made of two iron hoes from uMgungundlovu and a piece of “amulet” from the EIA site of Wosi. The “amulet” piece (WOS-19) had a different microstructure characterized by dendritic metallic and silicate phases (Figure 4.26). In contrast, the two iron hoe samples (MGU-20 and MGU-21) were very similar, with uniform Fe-rich phases (Figures 4.27 and 4.28). The Fe-rich phases of the iron hoes, together with pockets of slag stringers, possibly resulted from the reworking of blooms in high-temperature forges above 900 °C and hammering to reduce banding (Miller, 2002, p. 1100). This process was essential for imparting the mechanical strength required for the agricultural functions of the iron hoes.

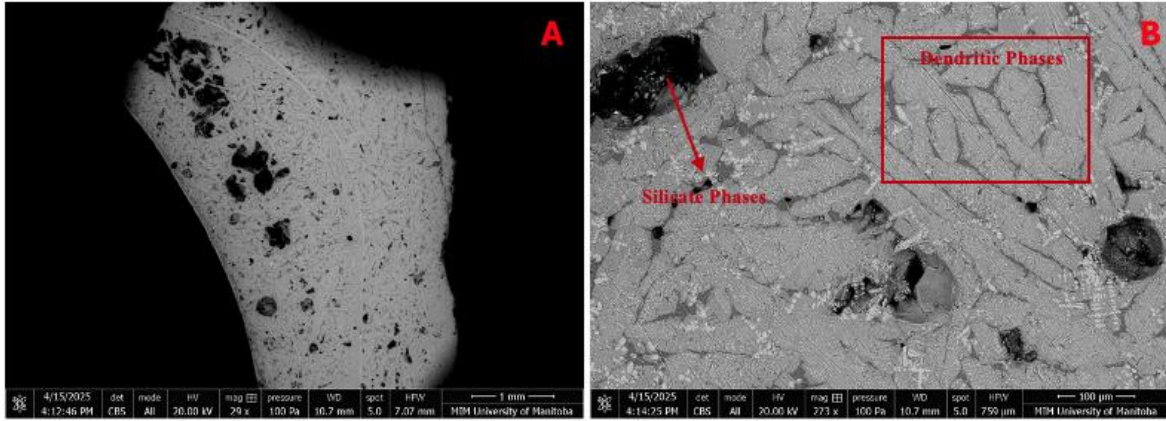


Figure 4.26: SEM image of iron “amulet” sample (WOS-19) scanned at A. 29 magnification and 1 µm B. 273 magnification and 100 µm. (Source: Author)

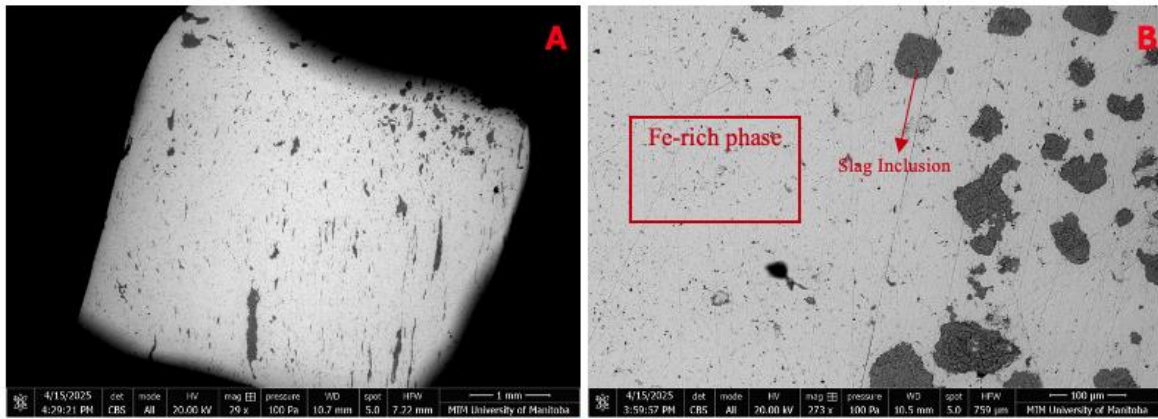


Figure 4.27: SEM image of iron hoe (MGU-20) scanned at A. 29 magnification and 1 µm B. 273 magnification and 100 µm. (Source: Author)

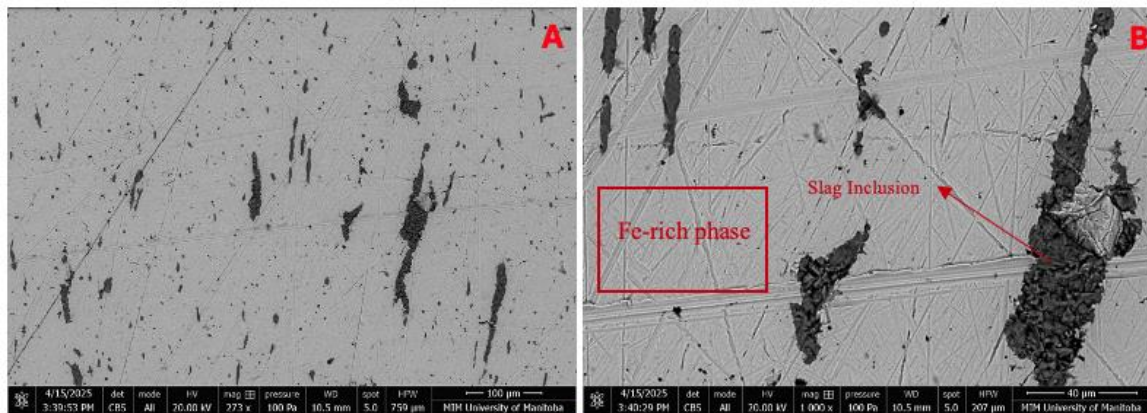


Figure 4.28: SEM image of iron hoe sample (MGU-21) scanned at A. 273 magnification and 100 µm B. 1000 magnification and 40 µm. (Source: Author)

Micrographs of the two iron hoe samples (MGU-20 and MGU-21) from uMgungundlovu revealed inclusion pockets, likely consisting of slag entrapped during the bloomery process. In sample MGU-20, the inclusions showed reduced iron (Fe) content and slightly elevated concentrations of carbon (C) and other elements, such as silicon (Si), manganese (Mn), and chlorine (Cl) (Figure 4.29 and Table 4.7). In sample MGU-21, the inclusions consisted predominantly of iron (Fe), with concentrations ranging from 75.6% to 77.8% (Figure 4.30 and Table 4.9). Other elements present included carbon (C), oxygen (O), aluminium (Al), silicon (Si), calcium (Ca), and manganese (Mn). Area 3, which contained no slag inclusions, exhibited a high iron (Fe) concentration of approximately 94.5% (Figure 4.30 and Table 4.7).

In the “amulet” sample from Wosi (WOS-19), no slag inclusions were present in the pockets, and the elements were uniformly distributed throughout the microstructure. In selected Areas 1 and 2, iron (Fe) was the dominant element, with concentrations of 56.3% and 65.7%, respectively, suggesting that these regions were composed primarily of metallic phases (Figures 4.31A and 4.31B and Table 4.7). Area 3 showed a similar elemental profile but contained slightly less Fe (59.2%) and elevated concentrations of oxygen (15.7%) and silicon (10.5%) (Figure 4.31C and Table 4.7).

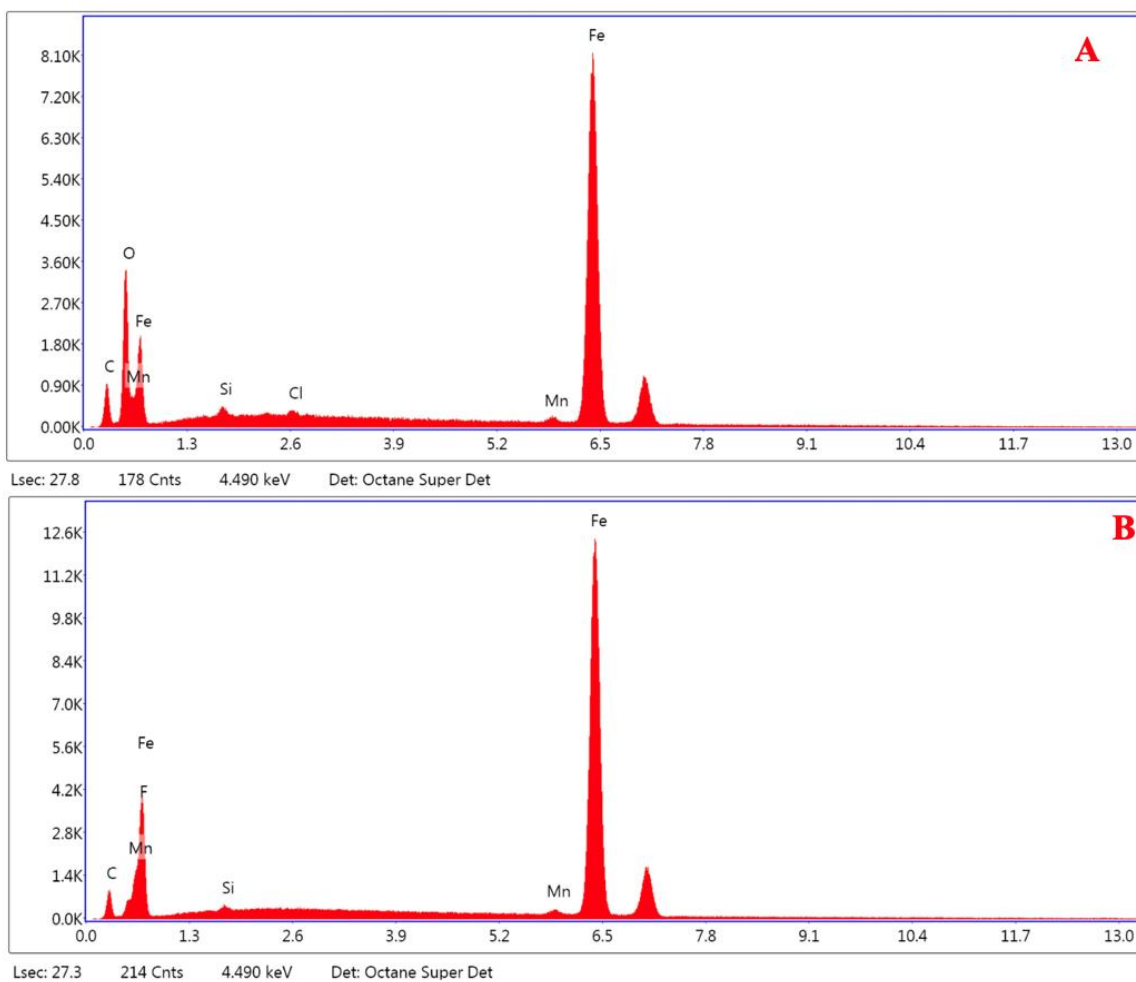
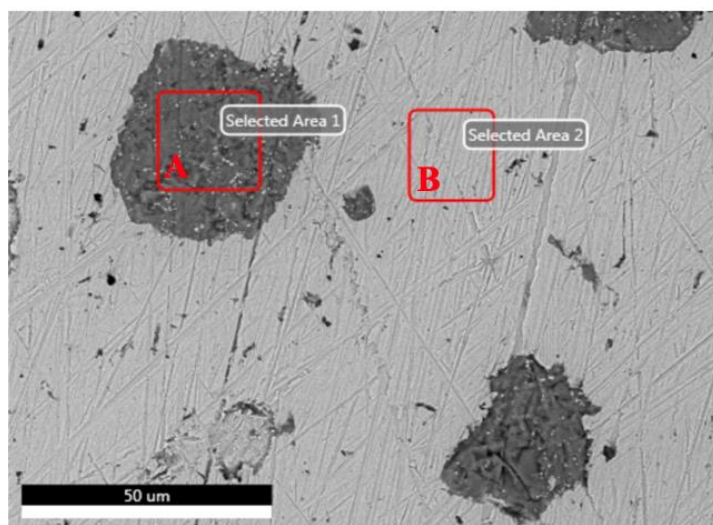


Figure 4.29: EDS spectra of iron hoe sample (MGU-20) showing elements in A. Area 1, B. Area 2. (Source: Author)

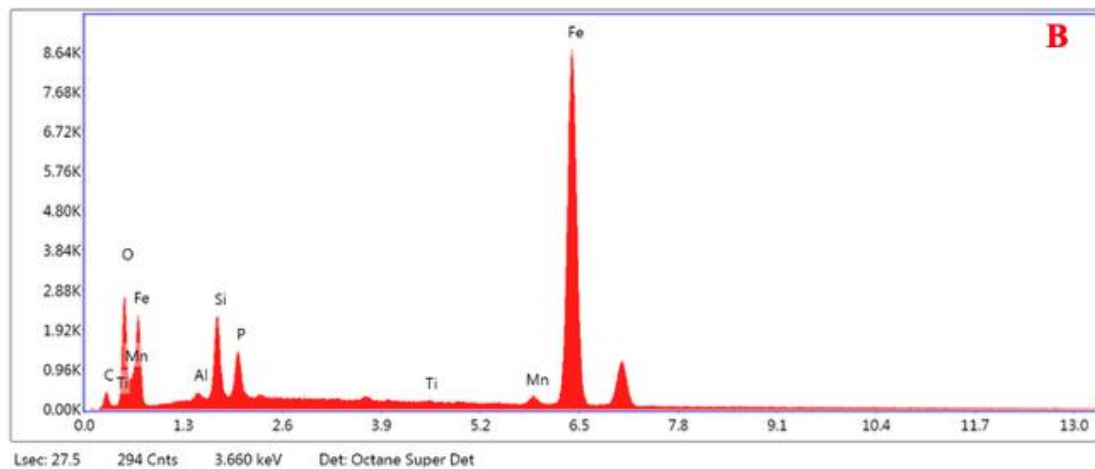
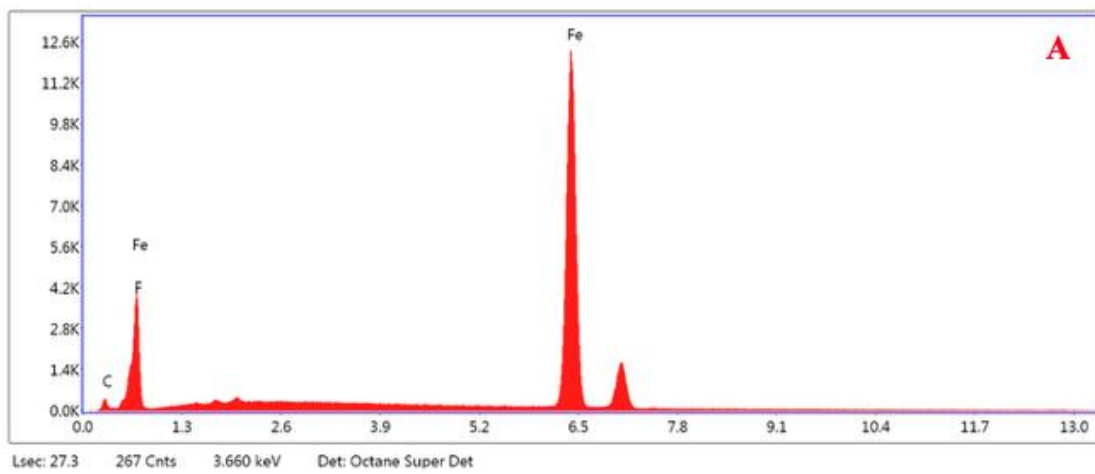
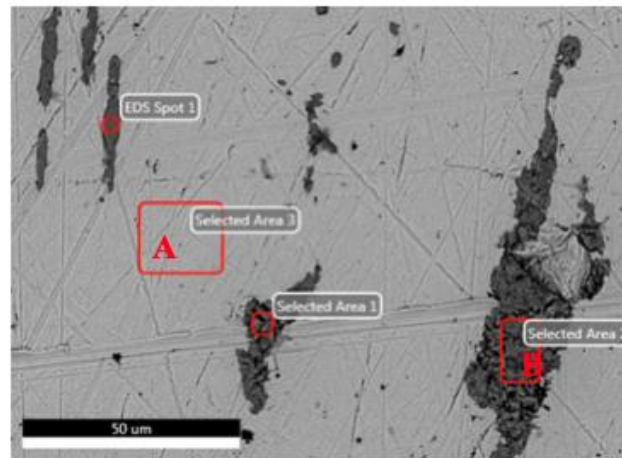


Figure 4.30: EDS spectra of iron hoe sample (MGU-21) showing elements in A. Area 3, B. Area 2. (Source: Author)

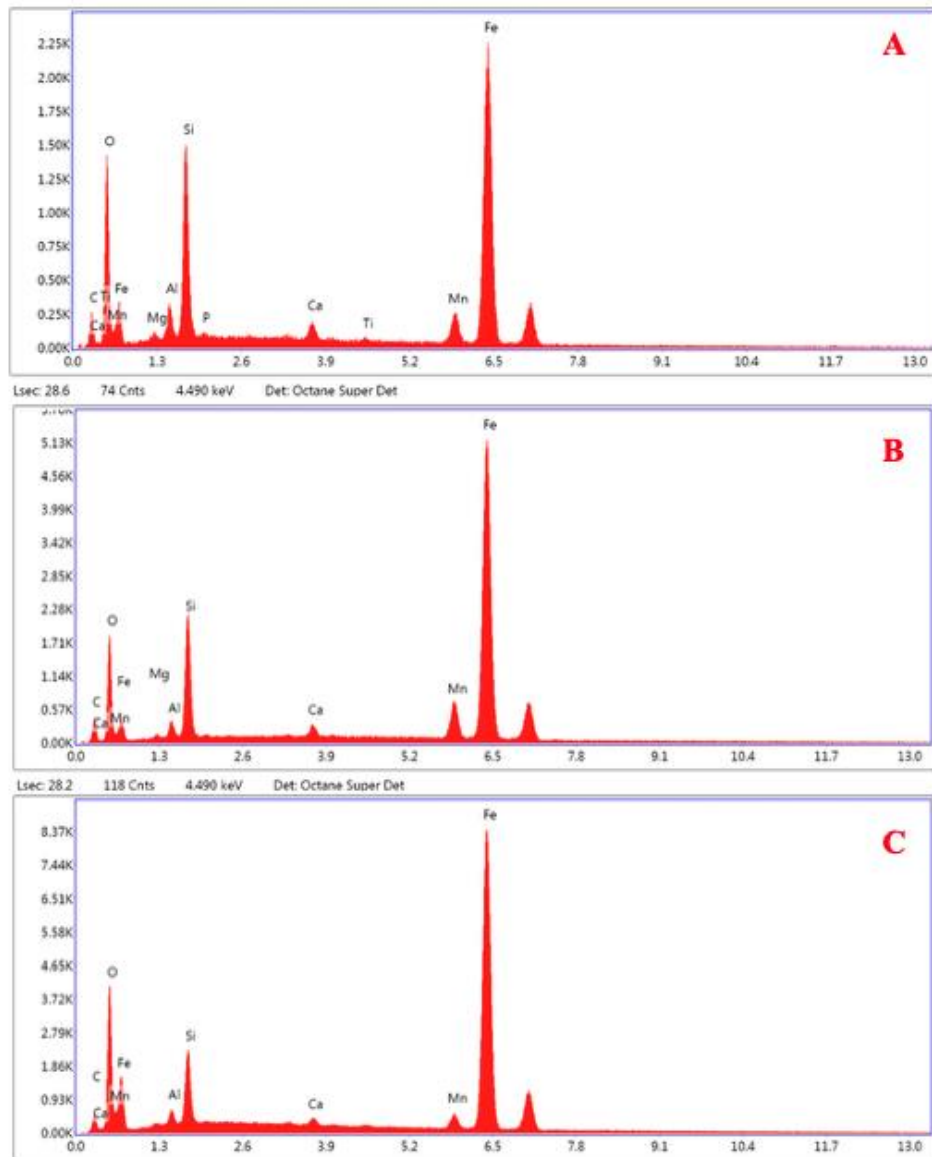
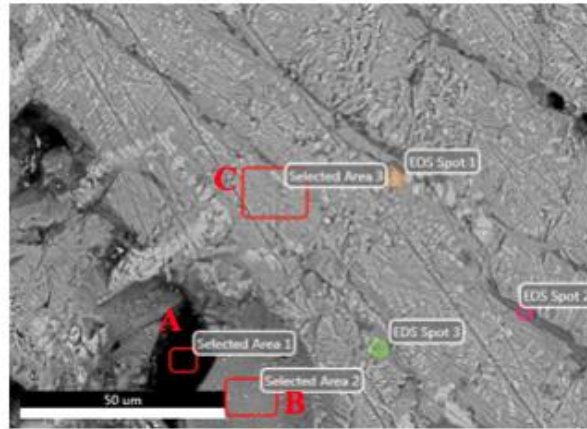


Figure 4.31: EDS spectra of iron amulet sample (WOS-19) showing elements in A. Area 1, B. Area 2, C. Area 3. (Source: Author)

Table 4.7: Summary of elements from the EDS Spot Analysis in weight percentage (Weight %). (Source: Author)

Element	mGungundlovu		mGungundlovu			Wosi			
	MGU-20		MGU-21			WOS-19			
	Iron hoe		Iron hoe			“amulet”			
	Area 1 (slag inclusion)	Area 2 (Non slag)	Area 1 (slag inclusion)	Area 2 (slag inclusion)	Area 3 (Non slag)	Area 1	Area 2	Area 3	Spot 2
C	11.0	9.1	5.8	6.0	4.7	9.7	8.1	6.6	5.7
O	12.8	-	7.9	9.4	-	15.5	9.7	15.7	21.3
Si	0.3	0.2	4.0	4.6	-	9.5	7.0	10.5	15.8
Cl	0.2	-	-	-	-	-	-	-	-
Mn	0.9	1.0	1.1	1.2	-	4.9	7.1	5.4	3.0
Fe	74.8	89.7	77.8	75.6	94.5	56.3	65.7	59.2	34.0
F	-	0.0	-	-	0.8	-	-	-	-
Al	-	-	0.3	0.3	-	1.8	1.0	1.1	6.9
P	-	-	2.7	2.8	-	0.2	-	-	1.2
Ca	-	-	0.3	-	-	1.3	1.2	0.7	8.1
Ti	-	-	-	0.1	-	0.4	-	-	0.4
Mg	-	-	-	-	-	0.5	0.2	0.8	-
Na	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	-	-	0.2
K	-	-	-	-	-	-	-	-	1.9

4.6.2 Chemical Composition

The two analysed iron hoes (MGU-20 and MGU-21) had very high FeO concentrations, recorded at 101.63% and 96.49%, respectively (Table 4.8 and Figure 4.32). Silicon dioxide (SiO₂) concentrations were particularly low in both samples, with values of 0.19% and 0.27%. Aluminium oxide (Al₂O₃) was also present at trace concentrations of 0.09% and 0.02% (Table 4.8). Manganese oxide (MnO) showed slight variation between the samples, with a concentration of 1.42% in MGU-20 and a much lower concentration of 0.05% in MGU-21, possibly reflecting differences in the manganese concentrations of the ore sources or the presence of minor slag inclusions. Other oxides, including MgO, CaO, and Na₂O, were absent, while potassium oxide (K₂O) was present only at very low concentrations (0–0.1%). Titanium dioxide (TiO₂) and phosphorus pentoxide (P₂O₅) were also low in MGU-20 (0.03%) but moderate in MGU-21 (0.76% each).

In contrast, the “amulet” from Wosi (WOS-19) had a more diverse oxide composition than the uMgungundlovu iron hoes. Although FeO was the major oxide, at a concentration of 65.07%, it was lower than that observed in the uMgungundlovu artifacts (Table 4.8 and Figure 4.32). The “amulet” from Wosi (WOS-19) had significantly higher concentrations of silicon dioxide (SiO₂), at 22.3%, and a moderate concentration of aluminium oxide (Al₂O₃), at 3.11%. Manganese oxide (MnO) was also moderately high, at 5.847%, which may reflect the use of manganese-bearing iron ore (Table 4.7 and Figure 4.26). Additional oxides present at low concentrations included MgO (0.91%), CaO (1.43%), Na₂O (0.22%), K₂O (0.25%), TiO₂ (0.182%), and P₂O₅ (0.36%). Overall, the higher concentrations of silica, alumina, and manganese in the Wosi amulet indicate a greater contribution from slag inclusions and non-metallic components than in the more iron-dominated compositions observed in the uMgungundlovu iron hoes.

The trace-element compositions more clearly distinguished the iron hoes and the “amulet.” The trace-element compositions of the iron hoes from uMgungundlovu showed broadly similar patterns between MGU-20 and MGU-21, although some variation in concentration was present. Both samples contained relatively high concentrations of copper (Cu), nickel (Ni), cobalt (Co), and chromium (Cr). Cu was the most abundant trace element, increasing from 518.43 ppm in MGU-20 to 1,030.82 ppm in MGU-21 (Table 4.9 and Figure 4.33). Ni was also high, with concentrations of 478.13 ppm in MGU-20 and 221.39 ppm in MGU-21, while Co occurred at concentrations of 155.14 ppm and 124.38 ppm, respectively. Cr was higher in MGU-20 (85.95 ppm) than in MGU-21 (29.8 ppm). Vanadium showed the opposite trend, with a low concentration in MGU-20 (4.67 ppm) and a moderate concentration in MGU-21 (38 ppm). Additional elements present in both samples included gallium (Ga), germanium (Ge), molybdenum (Mo), tungsten (W), lead (Pb), silver (Ag), tin (Sn), and antimony (Sb), although

they were generally present at very low concentrations. Other elements, such as zirconium (Zr), niobium (Nb), strontium (Sr), barium (Ba), and uranium (U), occurred only at trace concentrations, while rare earth elements (REEs) were largely absent, with only very low concentrations of yttrium (Y) and cerium (Ce) detected (Table 4.9 and Figure 4.33).

Table 4.8: Average major elements oxide compositions in iron artifacts. Unit in weight percentage (wt%). (Source: Author)

Element Oxides	Wosi	uMgungundlovu	uMgungundlovu
	WOS-19	MGU-20	MGU-21
	"amulet"	Iron hoe	Iron hoe
SiO ₂	22.3	0.19	0.27
Al ₂ O ₃	3.11	0.09	0.02
FeO	65.07	101.63	96.49
MnO	5.847	1.42	0.05
MgO	0.91	0	0
CaO	1.43	0	0
Na ₂ O	0.22	0.00	0.00
K ₂ O	0.25	0	0.1
TiO ₂	0.182	0.03	0.76
P ₂ O ₅	0.36	0.03	0.76

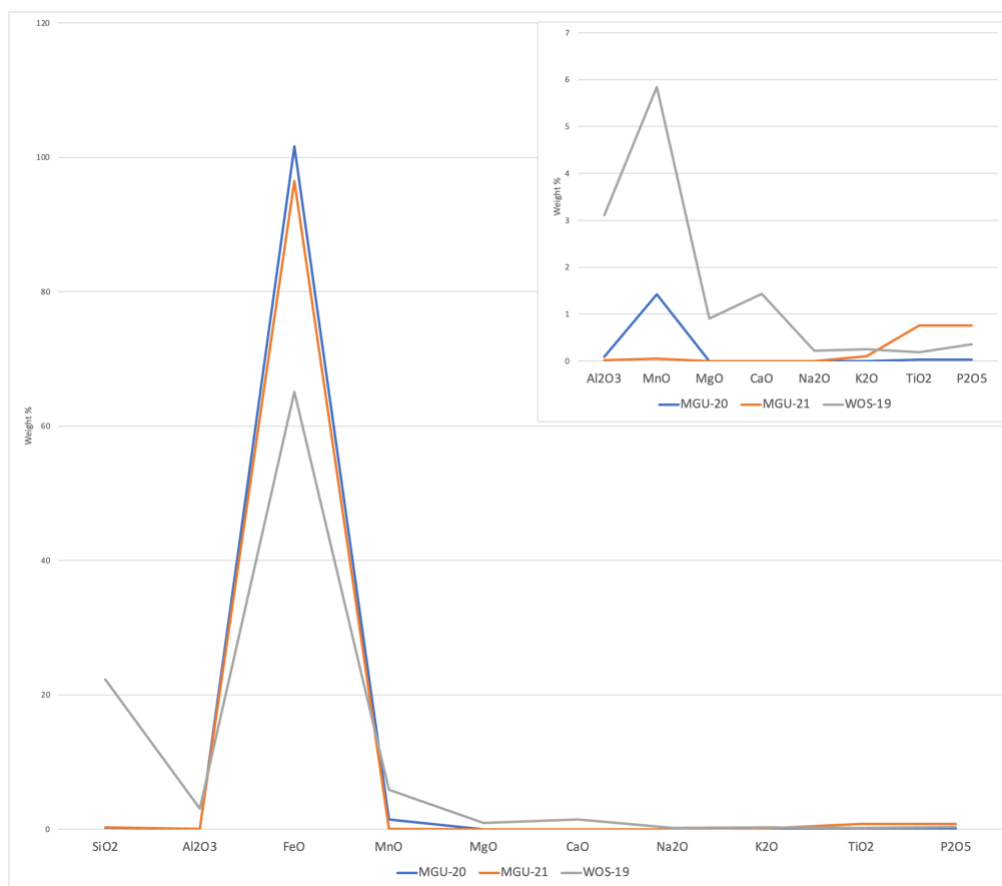


Figure 4.32: Major element oxides compositions of iron hoes (MGU-20- and MGU-21) and “amulet” (WOS-19) samples, shown in weight percent (Wt%). The insert shows major oxide composition without FeO. (Source: Author)

Table 4.9: Average trace element compositions of iron artefact samples in parts per million (ppm). All 0 figures indicate below detection limit. (Source: Author)

Element	Wosi	uMgungundlovu	uMgungundlovu
	WOS-19	MGU-20	MGU-21
	"amulet"	Iron hoe	Iron hoe
Rare Earth Element (REE)			
La	37	0	0.05
Ce	89.2	0	0.15
Pr	8.1	0	0
Nd	32.1	0	0
Sm	6.46	0	0
Eu	1.23	0	0
Gd	6.33	0	0
Tb	1.04	0	0
Dy	6.05	0	0
Ho	1.22	0	0
Er	3.38	0	0
Tm	0.393	0	0
Yb	2.7	0	0
Lu	0.372	0	0
Sc	5	0	0
High Field Strength Element (HFSE)			
Y	35.4	0	0.06
Zr	38	0.02	0.02
Nb	5.7	0.12	0.55
Large Ion Lithophile Element (LILE)			
Rb	3	0	0.04
Sr	97	0.02	0.43
Ba	559	0.17	1.45
Th	1.45	0	0
U	0.62	0.14	0.22
Transition Trace Element (TTE)			
Cr	85.95	29.8	50
Co	155.14	124.38	14
V	4.67	38	110
Cu	20	518.43	1030.82
Zn	30	8.08	1.54
Other Trace Elements			
Be	1	0	0
Hf	0.7	0	0
Ta	0.21	0	0
W	7.3	0.5	2.04
Tl	0.05	0	0
Pb	5	3.04	1.8
Ni	20	478.13	221.39
Ga	7	23.09	23.43
Ge	0.7	10.17	12.17
As	5	0	0
Mo	2	7.87	8.2
Ag	0.5	0.23	0.08
Sn	5	24.55	53.65
Sb	1.6	50.93	37.97
Cs	0.3	0	0

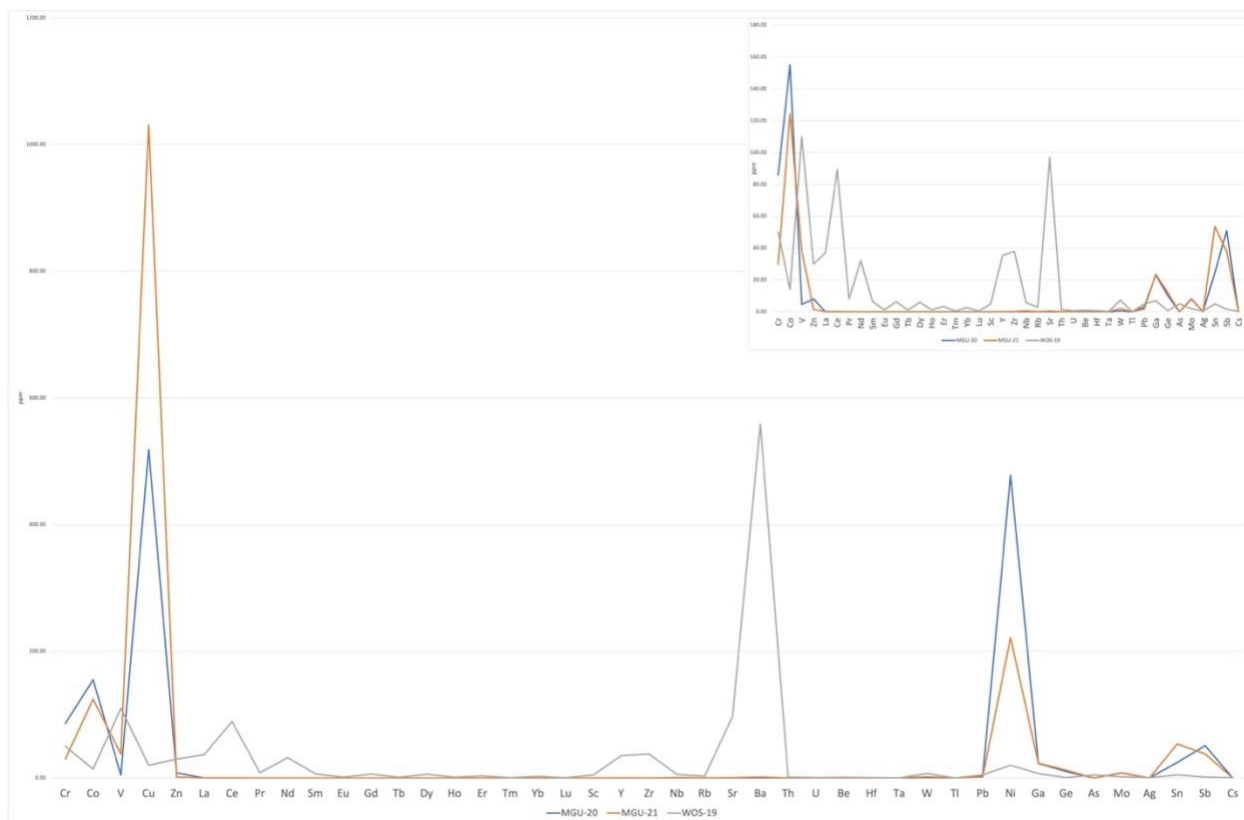


Figure 4.33: Trace element compositions of iron hoes (MGU-2- and MGU-21) and “amulet” (WOS-19) samples, shown in parts per million (ppm). The insert shows major oxide composition without Cu. (Source: Author)

4.7 Statistical Comparison of Ores, Slags, Blooms and Metal Artifacts

In the previous analyses, I demonstrated that ores, slags, and blooms can be chemically distinguished using major- and trace-element geochemistry, supported by principal component analysis (PCA) and MnO/TiO₂ ratios as an additional proxy. In this section, I integrate the metal artifacts, namely the “amulet” and the two hoes, into this interpretative framework to assess the most likely ore sources used in their production.

4.7.1 *MnO/TiO₂ Ratio Analysis*

Using manganese oxide-to-titanium dioxide (MnO/TiO₂) ratios, the two iron hoes (MGU-20 and MGU-21) have ratios of 47.33 and 0.07, respectively, and do not group on the scatter plot, suggesting that they likely originated from different geological sources (Figures 4.38 and 4.39). The “amulet” from Wosi (WSO-19) has an MnO/TiO₂ ratio of 32.13 and is distinguishable by its high manganese loading and low titanium concentration (Figures 4.34 and 4.35). The “amulet” corresponds to the Nkandla ore (NKD-11), the Wosi slag (WOS-15), and the Ndondondwane bloom (NDO-13), all of which suggest an Nkandla regional source (Figure 4.35). Similarly, MGU-20 has a high manganese concentration and groups with the Nkandla ore (NKD-11), the Wosi slag (WOS-15), and the Ndondondwane bloom (NDO-13). The other iron hoe (MGU-21) is from a high-titanium source and forms part of Group 1, which represents the broader Babanango/eMakhosini regional source (Figure 4.35).

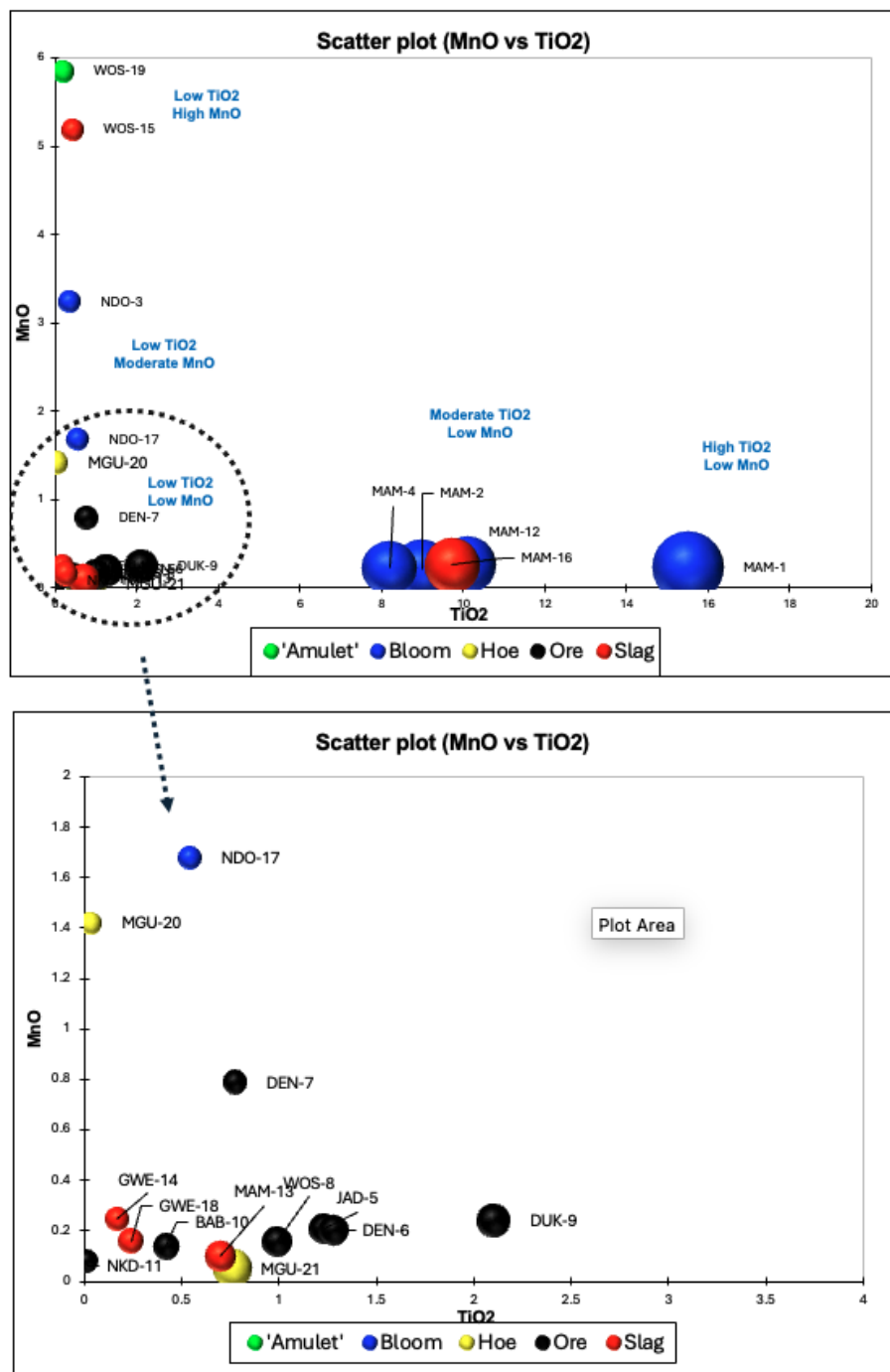


Figure 4.34: MnO/TiO₂ element ratio biplots of ore, slag, bloom, and iron artifact samples, data from ICP-MS. Larger bubbles indicate higher TiO₂ concentrations. (Source: Author)

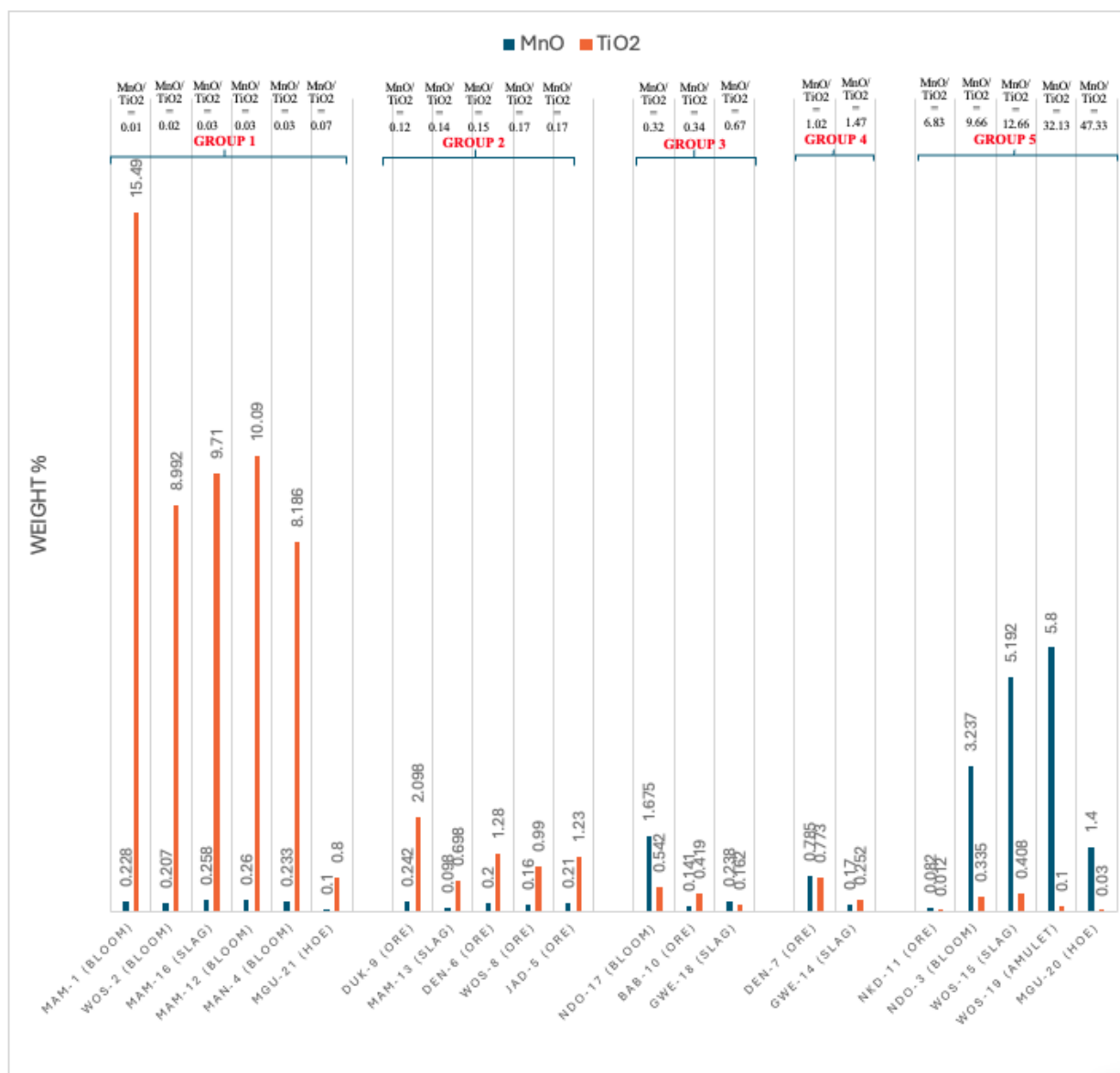


Figure 4.35: Chart showing the concentrations of Fe₂O₃(T), MnO and TiO₂ in ores, slags, blooms and iron artifacts, with corresponding MnO/TiO₂ ratios. (Source: Author)

4.7.2 Principal Component Analysis (PCA)

Using transformed log₁₀ majors and trace elements (Figure 4.40), WOS-19 plots in the lower-right quadrant with the Wosi slag (WOS-15) because of high titanium and REE loadings and separates from the others (Figure 4.36). The PCA results support the MnO/TiO₂ ratios analysis that WOS-15 and WOS-19 are likely from the same manganese-rich ore source. The two

iron hoes plot in the upper-left quadrant of the PCA indicating a different ore source from the Wosi artifact (WOS-19).

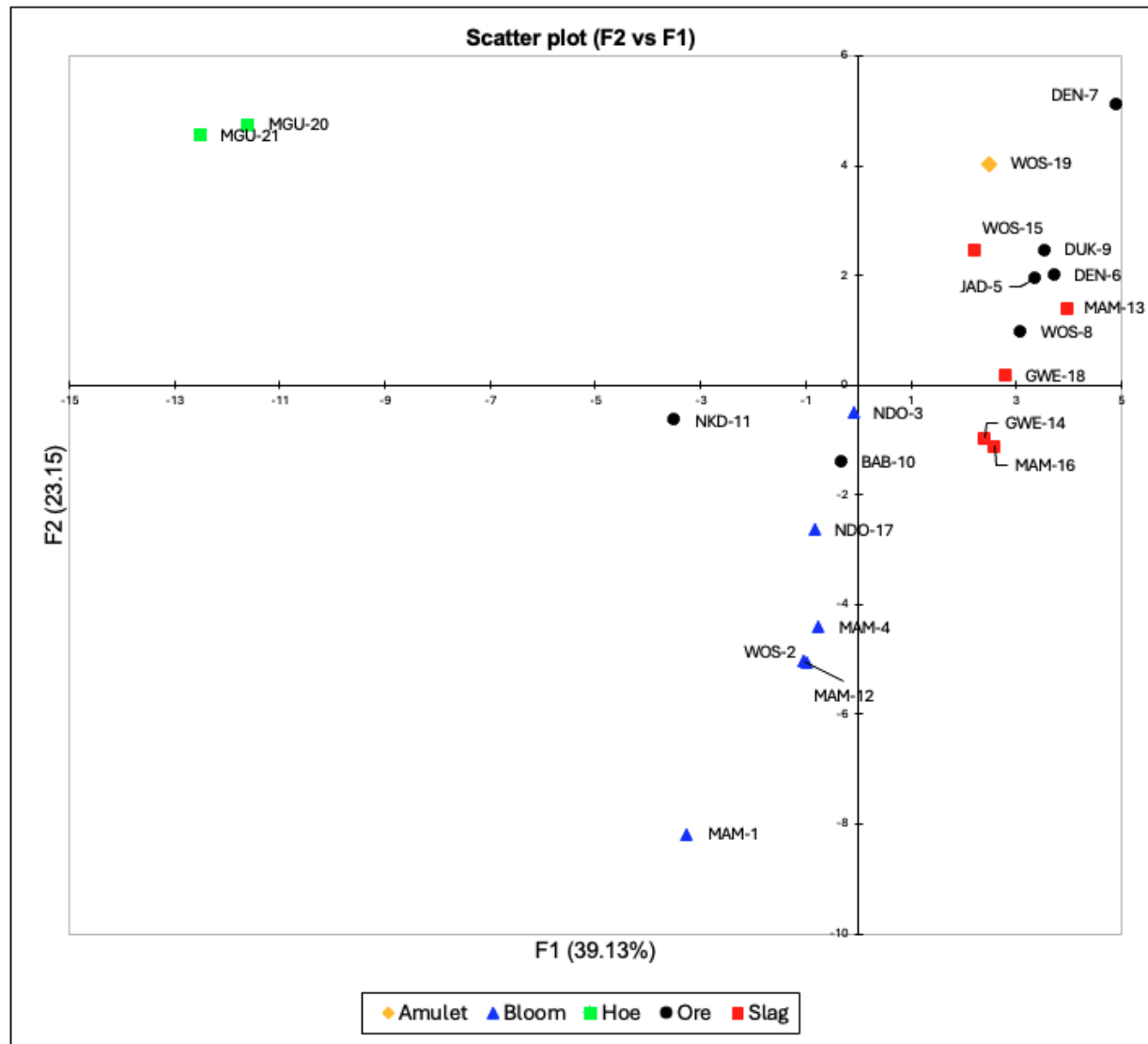


Figure 4.36: Principal Component Analysis (PCA) of ores, slags, blooms and metal artifacts using transformed Log10 major and trace elements of ICP-MS. (Source: Author)

4.8 Chemical Signature of the *Chaînes Opératoire* from Ore to Artifact

Using the raw ICP–MS data generated for all material categories, I examined whether the bloomery process alters chemical compositions across the *chaîne opératoire*, from ore through intermediate products, to the finished object. To evaluate compositional shifts along this operational sequence, I selected the most variable elements and oxides identified in the analytical results, specifically Fe₂O₃, V, Rb, Sr, and Ni. These were analyzed to determine whether their concentrations increase or decrease throughout the *chaîne opératoire*, thereby providing insight into elemental behaviour, patterns, and the impact of bloomery smelting on the final metallurgical signature.

Using Wosi samples as a reference (orange-coloured bars), there is an increasing concentration of iron (III) oxide (Fe₂O₃) through the bloomery process, whereas Vanadium (V), Rubidium (Rb), Strontium (Sr) and Nickel (Ni) decreased through the bloomery process (Figure 4.37 and Table 4.10). The observed sequence across the *chaîne opératoire* reflects the chemical partitioning that occurs during bloomery and subsequent forging (Zhang et al., 2022, p. 4523; Heo et al., 2021). As iron ores are reduced in the bloomery furnace, iron oxides are progressively converted into metallic iron, resulting in an enrichment of Fe in the bloom and final artifacts (Stepanov *et al.*, 2022b, p. 80). It must also be noted that vanadium (V) was slightly higher in the Wosi slag. Also, strontium (Sr) was very high in the Wosi slag (WOS-2) because, though these trace elements sometimes transition into the molten iron, a greater concentration can still be in the smelting slags (Navasaitis, Selskienė and Žaldarys, 2010, p. 115).

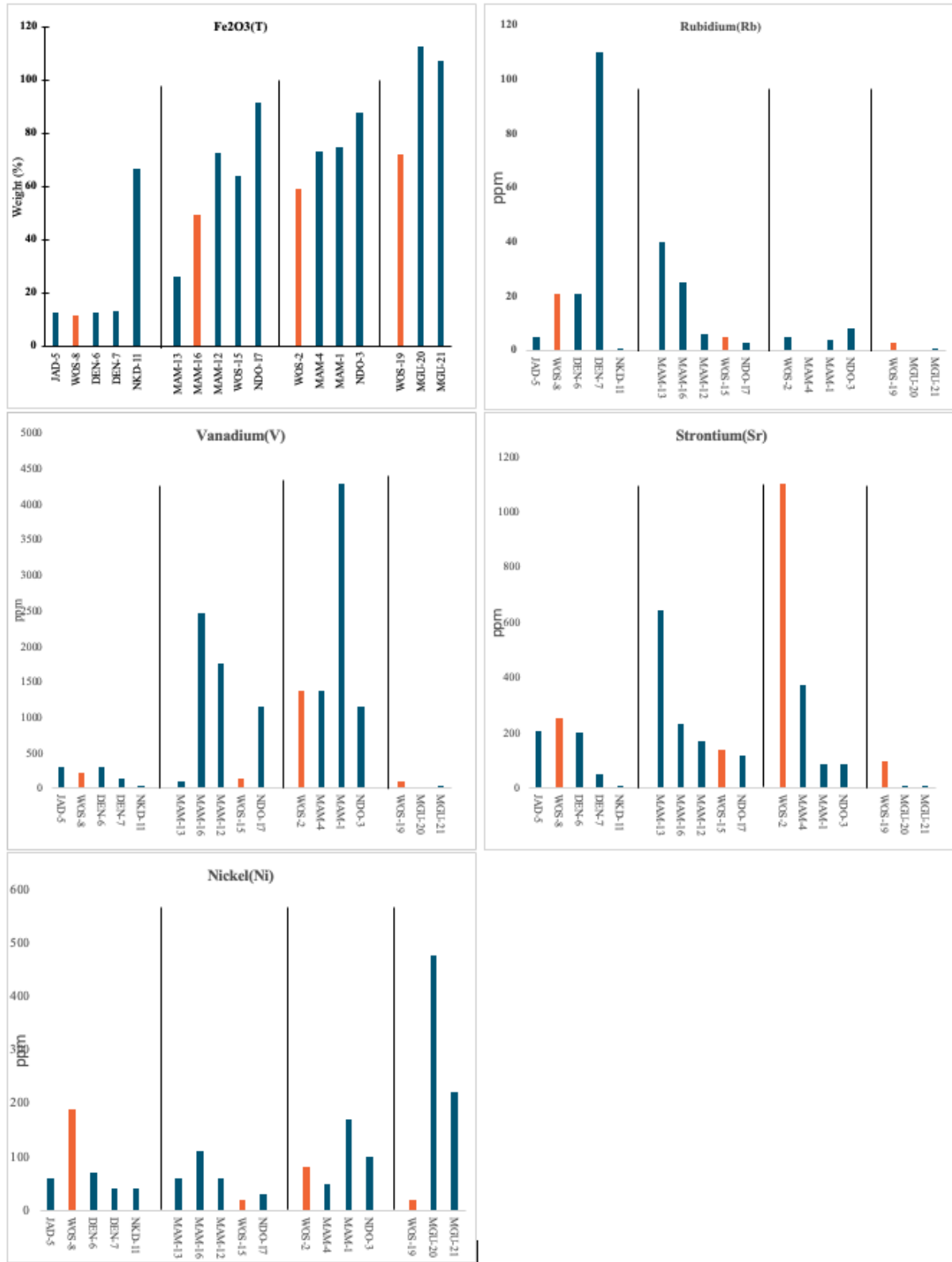


Figure 4.37: Charts showing an increase or decrease of Fe₂O₃, V, Rb, Sr and Ni through the bloomery process. The orange bars represent Wosi materials. (Source: Author)

Table 4.10: Table summarizing the general chemical signature of Fe₂O₃, V, Rb, Sr and Ni through the bloomery process from ore to finished artifact. (Source: Author)

Element/Oxide	Ore	Slag	Bloom	Metal Artefact	Trend / Interpretation
V (Vanadium)	Low (Average 199.8 ppm)	Very High (Average 1129.2 ppm)	High (Average 2211 ppm)	Very Low (<110 ppm)	Enrichment in slags and blooms reflects V association with Fe phases, partial loss during smelting.
Rb (Rubidium)	Very High (Average 158 ppm)	High (Average 15.8ppm)	Low (Average 4 ppm)	Very Low (<3 ppm)	Rb behaved as a lithophile element; retained in silicate slag and lost during process. DEN-7 is Rb source specific.
Sr (Strontium)	Low (Average 143 ppm)	High (Average 259 ppm)	Very High (Average 412 ppm)	Very Low (<average 97 ppm)	Sr concentrated in slag phases, indicating its affinity for Ca-bearing silicates and fluxes. Sr content is source for Mamba samples (MAM-13 and MAM-2).
Ni (Nickel)	High (Average 80 ppm)	Low (Average 56 ppm)	High (100 ppm)	Very High (up to 20 ppm)	High Ni content is particular to the two iron hoes but very low in the “amulet”
Fe₂O₃ (iron (III) oxide)	Very low (20–45%)	Low (40–90%)	High (60–88%)	Very high (>72%)	Indicates progressive iron enrichment through the smelting process.

4.9 Conclusion

I started by discriminating the ore sources, which established that the geological ore samples from BAB-10, NKD-11 and DEN-7 were unrelated, but JAD-5, DEN-6, and WOS-8 consistently cluster together based on their geochemistry and MnO/TiO₂ ratios. The unknown archaeological ore sample (DUK-9) is associated with JAD-5, DEN-6, and WOS-8 groups, suggesting similar geochemistry. Most ore and slag samples, except NKD-11, had high vanadium (V) concentrations, particularly those from Mamba and Ndongondwane, prompting possible use of vanadium-rich ore sources.

The bloom samples from the Early Iron Age (EIA) sites of Wosi, Mamba and Ndondondwane are also clearly differentiated by their geochemistry. Mamba and Wosi blooms are characterized by relatively high TiO_2 and low MnO concentrations, whereas Ndondondwane blooms are low in TiO_2 and moderate MnO concentrations. Like slags, all bloom samples were also high in vanadium concentrations, further linking to a possible vanadium-rich ore source.

After distinguishing the ores, slags, and blooms using major and trace element geochemistry and MnO/ TiO_2 ratios, I then incorporated the iron hoes and “amulet” into the analytical framework to establish a possible association. The two iron hoes from uMgungundlovu share broadly similar geochemistry and microstructural characteristics, differing only slightly in trace element composition. In contrast, the Wosi “amulet” (WOS-19) is chemically and microstructurally distinct, with relatively higher manganese concentration and low titanium.

Finally, I explored the effects of smelting on Fe_2O_3 , V, Rb, Sr, and Ni through the *chaîne opératoire*. The Wosi samples, which had a complete material sequence, have Fe_2O_3 increasing but V, Rb, Sr, and Ni decreasing through the *chaîne opératoire*. This was not consistent across all samples, as V and Sr were higher in some blooms. Some slags have substantial ferrous content, and this may indicate ineffective smelting or that the slags were collected from different parts of the furnace. Another possibility is that they may have been removed at different stages of the smelting process, or possibly that they represent unused blooms.

CHAPTER 5: DISCUSSIONS AND CONCLUSION

5.1 Introduction

This chapter discusses the technological and geochemical insights into iron production during the Zulu Kingdom era, resulting from the application of multiple analytical techniques that provided detailed geochemical data of ore, slag, bloom samples, and three iron artifacts. Multivariate statistical analysis explored the geochemical relationships among these materials, enabling the identification of potential ore sources and the chemical signature of the *chaîne opératoire*.

This study aimed to improve the current understanding of the production of iron technology within the Zulu Kingdom in southeastern Africa. This focused-on iron ore sourcing and the effects of smelting on the chemical composition through the bloomery process. The three main objectives of this study were to:

1. establish the ore sources used by Zulu iron workers in manufacturing iron implements;
2. determine the chemical composition of sampled pre-industrial iron artifacts (hoes and amulet), smelting by-products (slags and blooms) and iron ores, which comprised archaeological and comparative sources used for smelting by Zulu ironworkers; and
3. understand the changes in the chemical composition of materials through the manufacturing sequence.

To achieve these research objectives, I tested three main hypotheses derived from previous archaeological research and documented oral history:

1. Slag samples from smelting sites have been treated as valuable materials for understanding ore sourcing and smelting technology (Chirikure and Bandama, 2014b; Daoust, 2014; Hauptmann, 2020). However, less attention has been paid to how the bloomery process may alter the chemistry of ores, which could complicate the association slags, blooms, and finished products with different ore sources. If the bloomery process alters the chemical compositions of ores to the extent that there is no direct, traceable relationship between the composition of ores and finished iron objects, then this severely hampers the ability of archaeometallurgists to identify the ore sources for finished iron objects. Alternatively, if the bloomery process does not alter the chemical composition of ores to the extent that there is no direct relationship between the chemical composition of ores, manufacturing by-products and finished objects, then it should be possible to associate both by-products and finished objects with ore sources.

Sites dating to the Zulu Kingdom period do not have a full range of materials that represent the bloomery iron smelting process, namely ore, slag, bloom, and finished objects. To test this hypothesis, I analysed samples of ores, slags, blooms and an iron object from three Early Iron Age sites in the middle Thukela River Basin to monitor differences in the chemical composition of manufacturing by-products and finished objects produced during bloomery iron smelting.

2. Previous research on Zulu metallurgy has emphasized the importance of iron-banded formations in Pietermaritzburg Formation shales as ore sources (Whitelaw, 1991, pp. 33-34). It is not known if whether these were the only or preferred ore sources used by Zulu ironworkers. If Zulu ironworkers exploited a range of iron ore deposits for smelting activities, then there would be differences in the chemical compositions of

slags, blooms, and iron artifacts from archaeological sites. Alternatively, homogeneity in the chemical compositions of iron-making by-products and objects would result from the use of ore from the same source.

To test this hypothesis, I analysed iron ore from three different deposits and compared its chemical composition with those of ore, slag and iron object samples from three sites dating to the Zulu Kingdom period: kwaDukuza, ezinGwegweni and uMgungundlovu.

3. Maggs's (1992) research pointed to oral historical accounts that emphasized the dominant role of *amaCube* smiths in producing iron implements and weapons during the Zulu Kingdom period. If iron objects from royal *amakhanda* were made exclusively by *amaCube* smiths in the Nkandla area, then the iron objects would exhibit only a chemical composition of the source ore material used by *amaCube* smiths. Alternatively, if iron-making by-products and finished objects do not match the chemical composition of the source materials used by *amaCube* smiths, then other smiths provisioned the Zulu capitals with iron implements and weapons.

To test this hypothesis, I analysed two iron hoes from King Dingane's capital of uMgungundlovu and compare their composition to ores from the Nkandla area, as well as ores from Babanango Plateau, Mhlatuze River catchment near kwaBulawayo-2 and Tugela Group amphibolite.

5.2 Discussion

5.2.1 Chemical Composition of Ores, Slags, Blooms and Iron Artifacts

The chemical compositions of the analysed samples, including ores, slags, blooms, and metal artifacts, provided preliminary insights into the technological processes and material transformations associated with iron production during the Iron Age in the eastern lowlands.

Determining the chemical compositions of these materials was important to understanding how the materials can be distinguished and correlated.

5.2.1.1 Ore Samples

Iron metallurgy is largely influenced by the availability and suitability of ore resources (Hauptmann, 2020, p. 11; Van Schalkwyk, 1994, p. 141). Previous studies have established that that Zulu ironworker exploited varying ore types for smelting (Miller and Whitelaw, 1994; Whitelaw, 1991; Mathoho, Nyamushosho and Chirikure, 2023; Bandama, Chirikure and Hall, 2013; Greenfield and Miller, 2004; Hall *et al.*, 2006; Humphris, 2010). The chemical analysis showed that the unknown archaeological ore and geological ores had varying concentrations of major element oxides but predominantly SiO₂, Al₂O₃ and Fe₂O₃. The major oxides and TiO₂/MnO ratios were used to discriminate the ore samples.

The geological samples based on the TiO₂/MnO ratios, Principal Component Analysis (PCA) and Agglomerative Hierarchical Clustering (AHC) were discriminated into four groups. The unknown archaeological ore from kwaDukuza (DUK-9) was titaniferous but grouped with the geological ores from Jameson's Drift (JAD-5), Wosi (WOS-8) and Denny Dalton (DEN-6), which were low in MnO and high in TiO₂. In the AHC, the kwaDukuza ore sub-groups with Jameson's Drift (JAD-5), Wosi (WOS-8), Denny Dalton (DEN-6), and plotted with Jameson's Drift (JAD-5) and Denny Dalton (DEN-6) in the PCA. Based on the geological contexts, Jameson's Drift (JAD-5) is associated with Pietermaritzburg shale, Denny Dalton (DEN-6) with Mozaan shale, and Wosi (WOS-8) with the Mambulu Complex of the Tugela Group amphibolite (Geoscience, 1988; Council for Geoscience, 1988). Based on these results, the unknown archaeological ore from kwaDukuza (DUK-9) was most likely sourced from the Mozaan Shales group or another source with similar chemistry.

Major element chemical analysis of the ore from the Early Iron Age site of Wosi concluded that iron workers used ore from a high manganese source (van Schalkwyk, 1994, p. 94). This conclusion was supported by the chemical analysis of the ore sample from Wosi (WOS-8) and was consistent with the composition of ore sample from Jameson's Drift, which had low titanium oxide (TiO_2) and high manganese oxide (MnO).

5.2.1.2 Slag Samples

Slags are silicate-based by-products of smelting (Miller and Killick, 2004), and are considered one of the most important materials to analyse due to their common occurrence at smelting sites and their geochemical value in understanding ore sourcing and smelting technology (Chirikure and Bandama, 2014b; Daoust, 2014; Hauptmann, 2020). The slags contained high silica and alumina, as well as substantial traces of vanadium (V). The elevated alumina (Al_2O_3) content observed in the slags likely derives from aluminosilicate gangue minerals in the ore or hercynite formation during smelting (Miller and Whitelaw, 1994, p. 82). Other major oxides identified in the samples (MgO , MnO , TiO_2 , P_2O_5 , K_2O , CaO) were present at relatively minor concentrations.

The slag samples were grouped into four based on the MnO/TiO_2 ratios. Mamba slags (MAM-12, MAM-13 and MAM-16) were low in MnO and very low in TiO_2 . MAM-12 and MAM-16 form one grouping with low MnO concentrations and very high TiO_2 concentrations, but MAM-13 was very low in MnO and moderate in TiO_2 . The Wosi slag (WOS-15) and Ndondondwane slag (NDO-17) forms another group due to high MnO and low TiO_2 . Mamba slags (MAM-12, MAM-13 and MAM-16) can be associated with titanium-rich ores, whereas Wosi slags (WOS-15) are from manganese-rich ores. This chemical observation aligns with findings from Mamba and Wosi by van Schalkwyk (1994; 1994). The ezinGwngweni slags

(GWE-14 and GWE-18) also form another group due to very low MnO and TiO₂, and plots with Pietermaritzburg Shales in the MnO/TiO₂ ratios and PCA.

It was observed that slag samples from Mamba (MAM-12) and Ndondondwane (NDO-17) contained a substantial weight percentage of ferrous content (73% and 92%, respectively) and plotted with the blooms as seen in the Fe₂O- Al₂O₃-SiO₂ ternary plot (Figure 5.1). The rationale for using Fe₂O- Al₂O₃-SiO₂ is that Al₂O₃ and SiO₂ allow differentiation based on the silicate composition of slags. Similarly, MAM-16 and WOS-15 also contained high ferrous content but plots with the slags from ezinGewgewni (GWE-14 and GWE-18). The high iron content could be attributed to inefficiency in the bloomery process to separate ferrous content from ore, or the slag could be from different parts of the internal furnace and removed at different stages of the smelting process (Miller and Killick, 2004, p. 24; Mathoho, Nyamushosho and Chirikure, 2023, p. 9). Another possibility accounting for this could be unused bloom mislabelled as slag during bagging of the samples because identifying slags based on visual inspection alone can be misleading (Miller and Killick, 2004, p. 34).

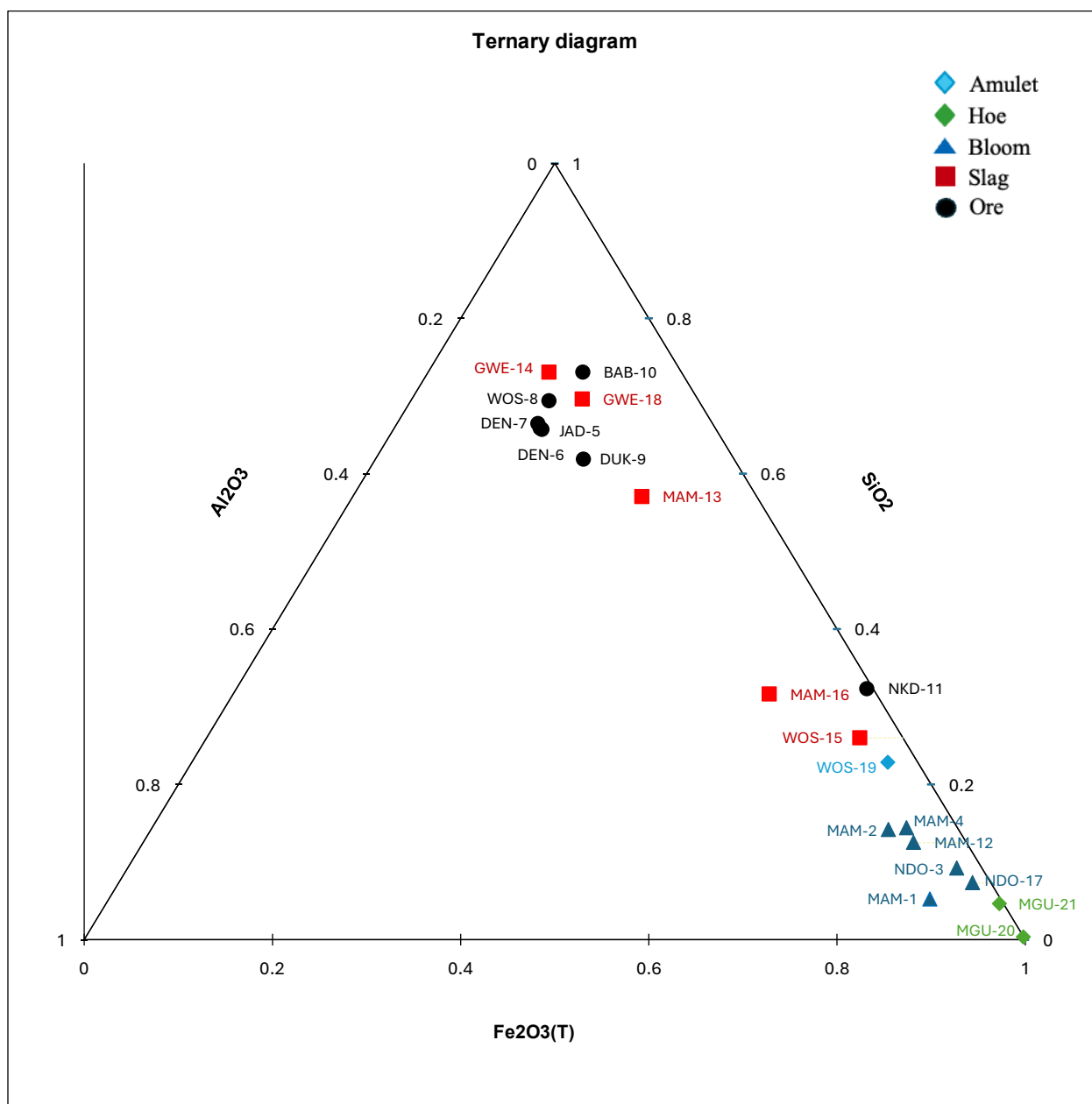


Figure 5.1: Ternary plot showing Fe₂O₃-SiO₂ -Al₂O₃ system of all materials (ores, slags, blooms and iron objects) using data from ICP-MS. Data normalized to equal 1. Al₂O₃ and SiO₂ allow differentiation based on the silicate framework of the slags. (Source: Author)

5.2.1.3 *Bloom Samples*

I analysed in-situ blooms from the EIA sites of Wosi, Mamba and Ndondonwane. The blooms contained primarily iron (58.97%-87.6%), with other minor concentrations of other oxides such as SiO₂, Al₂O₃, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, and P₂O₅. All bloom samples had high vanadium (V) concentration. The bloom samples from Mamba (MAM-1, MAM-4 and MAM-12) and Wosi (WOS-2) were geochemically similar and are likely derived from the same titaniferous ore source (Greenfield and Miller, 2004, p. 1525; Van Schalkwyk, 1994, p. 135). In contrast, the bloom samples from Ndondondwane (NDO-3 and NDO-17) did not correlate with the others and are likely sourced from a low-titanium ore source with higher manganese concentration (Greenfield and Miller, 2004, p. 1525; Van Schalkwyk, 1994, p. 135).

5.2.1.4 *Iron Artifacts*

The analysed iron artifacts comprised two iron hoes from uMgungundlovu and an “amulet” fragment from the EIA site at Wosi. The two iron hoes (MGU-20 and MGU-21) were chemically similar in major oxide concentrations but were discriminated by trace element compositions. In both the qualitative LA-ICP-MS and semi-quantitative SEM-EDS results, the hoes contained high ferrous content with low silicates. This compositional uniformity, including the observed slag inclusions, may be attributed to the operation of an efficient and well-controlled bloomery smelting process. In contrast, the iron “amulet” sample from Wosi (WOS-19) was chemically different. The “amulet” had lower ferrous content and higher silicates compared to the hoes. Although there are no records indicating that Zulu ironworkers used poorly smelted blooms to produce jewellery, poorly consolidated blooms could have formed when the ores contain insufficient iron oxides during the bloomery process (Stepanov, Borodianskiy and Eliyahu Behar, 2019).

5.2.2 *Ore Source(s) Used by Zulu Ironworkers*

The geochemical results summarized in the previous sections demonstrate significant chemical variation among the analysed ores, slags, blooms, and iron artifacts from different archaeological sites across the study area. These variations are reflected in the differing concentrations of major oxides and trace elements, which sets the foundational data to establish possible ore sourcing by linking the iron artifacts to sampled ores. To determine the potential ore sources exploited by iron smelters during the Zulu Kingdom period, both archaeological and geological ore samples were geochemically correlated with smelting by-products (slag and bloom) and finished objects, including iron hoes.

5.2.2.1 *Nkandla Ore Sources*

Ore samples from the area between the Mhlatuze and Thukela Rivers were analysed to represent the geological variations across the Nkandla area. This sample included JAD-5 (Pietermaritzburg shale with thin siltstones and sandstones), WOS-8 (Tugela Group, Dondondwane Formation, hornblende-biotite and biotite gneiss with Mambulu Complex intrusive medium-grained gabbro and subordinate norite) and NKD-11 (Dywka Group diamictite).

Within the Middle Thukela Basin, Mamba materials (slags and blooms) were sourced from titaniferous ores, which, according to van Schalkwyk (1994, p. 135), are about 1 km south and southwest of the site. This is evident in the elevated concentration of TiO_2 in all Mamba slags and blooms. On the other hand, Wosi materials (slags, blooms and iron “amulet) and Ndondondwane materials (blooms) are from high manganese ores within the Tugela Group Amphibolite with low titanium (van Schalkwyk, 1994, p. 1525; Greenfield and Miller, 2004). Vanadium concentrations were notably high in slags (MAM-12: 1770 ppm; MAM-16: 2474

ppm; NDO: 1144 ppm) and blooms (MAM-1: 4298 ppm; MAM-4: 1148 ppm; WOS-2: 1380 ppm; NDO-17: 2420 ppm). This could also be a potential ore source for ironworkers since there are vanadiferous magnetite outcrops nearby (Greenfield and Miller, 2004, p. 1525).

Archaeological and historical sources identify the *amaCube* as a significant supplier of iron during the Zulu Kingdom period (Maggs, 1992; Gardiner, 1836). To explore potential ore sources, magnetite banded iron ores were collected from the Middle Thukela River near Nkandla for geochemical correlation with the iron hoes. The ore sample from Nkandla (NKD-11) exhibited a notably high ferrous oxide content (66.95%) and low silicate proportion (32.27%), a characteristic of a high-grade iron ore and a potential ore source.

From the Principal Component Analysis (PCA), the iron hoes group in the PCA biplot. However, they can be discriminated by their trace element composition and MnO/TiO₂ ratios (MGU-20: 0.07 and MGU-21: 47.33). This disparity suggests that the hoes were likely smelted from different ore sources rather than a single source.

Again, the MnO/TiO₂ ratios analysis indicates that one of the iron hoes (MGU-20) is likely from the Nkandla regional source, but the other iron hoe (MGU-21) is not. This analysis shows that the iron objects from mGungundlovu were not exclusively made using Nkandla ore sources. Maggs (1992, p. 85) acknowledged the important role of the *amaCube* as one of the principal iron suppliers to the Zulu Kingdom, but argued that “by no means, however, did they have a monopoly” and that other groups played significant roles. Consequently, iron objects used at Royal *amakhanda* were not made exclusively by the *amaCube* iron workers. This pattern may have changed during the rule of different kings. However, the ore sample from kwaDukuza (DUK-9) was occupied at least during the 1830s and the slag samples from ezinGwegweni

(GWE 14 and GWE-18), last occupied in the 1870s, show a stronger association with shale ore sources available within 30 km of the sites.

This implies that iron workers exploited a range of ore deposits with varying geochemical compositions, leading to observable compositional differences in their metallurgical by-products and that the Zulu Kingdom benefited from other iron suppliers or clans (1992, p. 85). This aligns with regional archaeometallurgical patterns observed elsewhere in southern Africa, where diverse geological sources were often utilized in iron production due to differences in ore quality, accessibility, and technological preference (Chirikure et al., 2013; Mathoho & Chirikure, 2023; Friede et al., 1982).

5.2.3 Chemical Signature of Elements Through the Bloomery Process

The transformation of iron ore into finished products necessitates technical knowledge and skills (Chirikure and Bandama, 2014b; Bandama, Chirikure and Hall, 2013; Stepanov *et al.*, 2022a). Within archaeometallurgical contexts, this process encompasses both chemical and physical transformations that enable the effective reduction of ferrous oxides from associated gangue materials (Bauvais and Fluzin, 2009). Successful smelting operations require careful control of fuel types, furnace atmospheres and oxidizing or reducing agents to achieve the desired metallurgical outcomes, reflecting an understanding of pyrotechnological principles among ironworkers (Fluzin, 2014).

Based on the available samples for this research, not all sites yielded a complete set of materials necessary to fully reconstruct chemical behaviour during the bloomery process. Wosi, however, was chosen to examine this process because it yielded a complete assemblage of materials, including ore, slag, blooms and a finished artifact. The presence of this complete

chaîne opératoire at Wosi allows for a more comprehensive assessment of metallurgical processes and elemental behaviour during iron production.

The chemical analysis showed that the ferrous content progressively increased and becomes more refined throughout the *chaîne opératoire*. This trend suggests effective separation and concentration of iron during smelting (Rehren *et al.*, 2017; Miller, Killick and Van der Merwe, 2001; Charlton *et al.*, 2010). In contrast, the concentrations of trace elements such as V, Rb, Sr, and Ni decreased through the different stages of the process, although Sr and V exhibited elevated concentrations in the bloom.

5.3 Conclusion

This research investigated iron technology within the Zulu Kingdom (c. 1818–1879), with a specific focus on iron ore sourcing, which involved analysis of a range of geological ores, slags and iron artifacts. I also established whether other sources for EIA materials agree with previous archaeological and ethnographic research. Furthermore, I investigated the chemical transformations that occurred during the EIA bloomery process, which involved comparable technologies and procedures. The study used geochemical and imaging techniques, together with advanced statistical tools, to examine ores, slags, blooms, and iron artifacts.

First hypothesis: Geochemical analysis in archaeometallurgy is important to understanding the bloomery process and determining whether it alters the chemical composition of ores to the extent that correlations with finished objects are lost (Rehren *et al.*, 2017; Chirikure and Bandama, 2014b; Bandama, Chirikure and Hall, 2013; Desautly *et al.*, 2009). From the results, the geochemical signatures still allow for the direct correlation between the chemical composition of ores, manufacturing by-products and finished objects.

Second hypothesis: As part of this study, I explored the possible ore sources used by Zulu ironworkers. From the analysis, the chemical variations in the iron-making by-products and objects are because of smelting ores from varying sources. Zulu metalworkers smelted ores from a range of geological sources, likely guided by considerations of accessibility and ore quality (Moffett, 2020, p. 4; Roodt, 1996, p. 94; Maggs, 1992, pp. 73-74).

Third hypothesis: Lastly, I tested the hypothesis that if iron objects from Royal *amakhanda* were made exclusively by *amaCube* smiths, then iron objects would only exhibit the chemical composition of the source ore material used by *amaCube* smiths. The geochemical analysis suggests that while the *amaCube* were significant producers (Webb and Wright, 1986, p. 96), one of the two hoes analyzed in this study did not geochemically correlate with the high ferrous iron banded ore sample (NKD-11) north of Nkandla, nor with ore samples from outcrops around the middle Tugela River in the south. This may suggest other ore sources also played an important role in the Zulu iron industry.

5.4 Recommendations

5.4.1 Scope and Materials

The local geology of KwaZulu-Natal is complex and has potential for future archaeometallurgy studies with a focus on iron ore sourcing. For this thesis, three regional sets of comparative samples were used to establish the geochemical signature for potential ore sources. This included Mozaan shales at Denny Dalton, Pietermaritzburg shales from the Babanango Plateau, Pietermaritzburg shales in the Mhlathuze River catchment near kwaBulawayo-2, Tugela Group amphibolite within the Thukela River Basin catchment and Banded Iron Formation near

the Middle Thukela River close to Nkandla. In this regard, the comparative scope can be expanded to cover other regional sets and geological formations as well as other potential ore sources known to archaeological records (Maggs, 1992, p. 79; Maggs, 1986; Greenfield and Miller, 2004; Whitelaw, 1991; Van Schalkwyk, 1994) and historical records (Gardiner, 1836, pp. 105-217; Webb and Wright, 1986; Delegorgue, 1997, pp. 16-17).

5.4.2 *Techniques and Instrumentation Options*

Geochemical methods and techniques continue to advance, and other iron sourcing techniques are attracting equal attention (Chirikure, 2023). Although conducting geochemical studies on materials is expensive, it is worth exploring other new techniques, such as isotopes, to source iron objects. Isotope analysis in archaeometallurgy that show considerable potential include transition metals, such as iron (Fe) isotopes (Braun *et al.*, 2013; Milot *et al.*, 2016; Milot *et al.*, 2020), heavier metallic elements such as lead (Pb) isotopes (Molofsky *et al.*, 2014; Rademakers *et al.*, 2019; Ciarlo *et al.*, 2022; Degryse, Schneider and Muchez, 2009; Radivojević *et al.*, 2010; Schwab *et al.*, 2006; Gentelli *et al.*, 2021) and tin (Sn) isotopes (Haustein, 2010), and alkaline earth metals such as strontium (Sr) isotopes (Braun *et al.*, 2013; Degryse *et al.*, 2007; Dufour *et al.*, 2007; Degryse, Schneider and Muchez, 2009).

Osmium isotope ratio analysis has proven effective in other studies because osmium has isotope composition, which ideally allows for differentiation between various sources and processes in archaeometallurgy studies (Braun *et al.*, 2013; Junk, 2003; Liss, Levy and Day, 2020; Dillmann *et al.*, 2017). Additionally, osmium is a heavy element with resistance to fractionation and is highly siderophile, ensuring that the isotopic signature is preserved in the resulting metal (Braun *et al.*, 2013; Pernicka, 2014; Hauptmann, 2020). Future studies in this region would benefit from osmium isotope analysis or a combination of Pb-Sr isotope analysis

using Thermal Ionization Mass Spectrometry (TIMS), a technique that enables the separation and precise measurement of isotopes based on their mass-to-charge ratios (Ciarlo *et al.*, 2022; Hauptmann, 2020; Degryse, Schneider and Muchez, 2009).

5.4.3 *Experimental Bloomery*

As part of my research, I examined the effect of smelting on the chemical composition of iron artifacts through the production sequence. Future research could build on this work through controlled experimental bloomery. This would provide a more systematic understanding of how major and trace elements behave at different stages of iron production and help determine which geochemical signatures are retained, altered, or lost during smelting. Such experiments would also strengthen interpretations of the relationships among ores, slags, blooms, and finished iron artifacts.

5.5 **Research Challenges**

For this thesis, one major challenge was working with materials such as slags and blooms that had been identified based on macroscopic characteristics rather than through laboratory analysis. This is because slags and blooms are sometimes difficult to distinguish solely through visual inspection without further petrographic, metallographic, and chemical analyses (Miller and Killick, 2004). Additionally, slags can be distinguished according to the part of the furnace from which they originated. One outcome of my analysis was the differentiation of slag and bloom samples, which significantly assists in understanding the iron-manufacturing *chaîne opératoire*. To mitigate this, I used both chemical and petrographic analyses to identify and confirm the materials as either slag or bloom.

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