

**GEOCHEMICAL CHARACTERISATION AND FEASIBILITY
OF WINNING AND PRODUCTION OF PLASTER-OF-PARIS
FROM DOWA WEST GYPSUM DEPOSITS**

Rodney Sywell Mwachifumya MSHALI
BSc(Malawi), PG Dip. (ITC-Netherlands)

A thesis submitted to the University
of Malawi in partial fulfillment of the requirements for the award of a degree of
Master of Science in Applied Chemistry

Chancellor College
University of Malawi

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DECLARATION

I declare that this thesis is my original work, and that it has not been submitted for a degree award in any university. Acknowledgement has been made where work from other authorities has been used.

Signature: _____



Date: 3rd February, 200

Full Names: Rodney Sywell Mwachifumya MSHALI

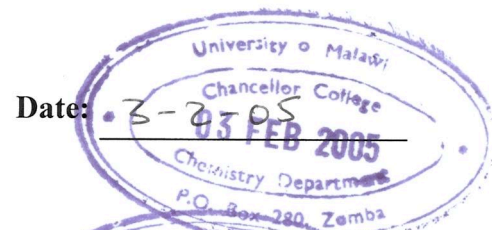
DECLARATION AND APPROVAL OF SUPERVISORS

We hereby declare that this thesis is the student's original work; and where assistance has been sought, it has been duly acknowledged. This thesis is therefore submitted with our approval to the University of Malawi as partial fulfilment of the requirements for the degree of Master of Science in Applied Chemistry.

Signature: _____

PP Dr W.R.L. Masamba
Main Supervisor

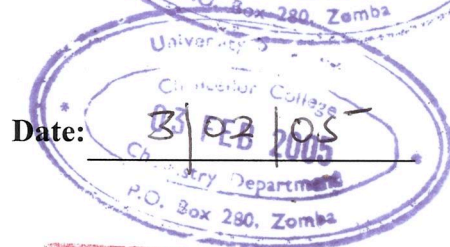
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Prof. J.D.K. Saka
Supervisor

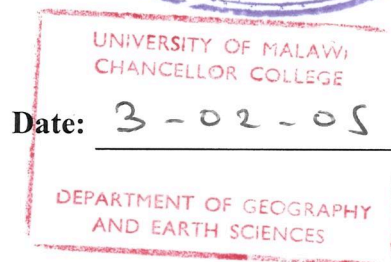
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PP Late Dr M. B. Dolozi
Supervisor

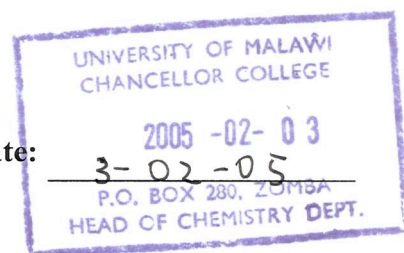
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Signature: _____

Dr E. M. T. Henry
Deputy Head, Chemistry Department

Date: _____



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ABBREVIATIONS AND DEFINITIONS OF SPECIFIC TERMS

AAS	Atomic Absorption Spectrophotometer
BGR	Bundesanstalt für Geowissenschaften und Rohstoffe
BS	British Standard
Calcination	thermal treatment of an ore to effect its decomposition and the elimination of a volatile product, usually carbon dioxide or water
CCAP	Church of Central Africa Presbyterian
cps	counts per second
<i>Dambo</i>	a shallow, seasonally or permanently waterlogged, grass-covered depression (<i>chichewa</i> term, known in other languages as <i>mbuga</i> , <i>molapo</i> or <i>naka</i>)
DS	<i>Divergence Slit</i>
EDTA	Ethyl Diamine Tetra-acetic Acid
EIA	Environmental Impact Assessment
Geosol	soil or sediment profiles showing similar stratigraphic relationship
ICCD	International Training Centre for Diffraction Data
ITC	International Institute for Aerospace Survey and Earth Sciences
JCPDS	Joint Committee Powder Diffraction Standard
MBS	Malawi Bureau of Standard
MOR	Modulus of Rupture
my	million years
PCPDF	Personal Computer Powder Diffraction File
PCPDFWIN	Personal Computer Powder Diffraction File Windows
PHA	Pulse Height Analyser
POP	Plaster of Paris
RS	Recovery Slit
TA	Traditional Authority
UV	Ultraviolet
w/v	weight/ volume

DEDICATION

This thesis is dedicated to parents, Mr Sywell Robert and Mrs Ethel Nyaukandawire Mshali, who have always morally supported my academic undertakings, my wife Glory and my children Florence, Rodney Masuzgo and Ethel Kwangu for their patience and support during the study leave.

ABSTRACT

This study concerns the determination of the geochemistry of gypsum resources as calcium sulphate dihydrate in the *dambos* of Dowa West, comparisons of methods for winning gypsum from the ore at laboratory scale, and production of plaster-of-Paris (POP) products. Calcination of gypsum to POP at temperatures of 100 °C, 130 °C, 160 °C and 175 °C was made to compare quality of local POP products between them and also with those on the markets. *Dambo* gypsum deposits in the Dowa West area are typified as precipitated calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) based on low solubility product (K_{sp}) for calcium and sulphate in borehole water. Most borehole water sites had high solubility products ($\log_{10}$ values > -5.52) and were identified as favourable localities for gypsum occurrences. High solubility products were experienced at Kabata (MS002), Mandala (DW62), James Madise (R34), Kachisa (RJ79), Mpatsa (P47), Mphimbi (Z82), Kabwinja (KB130), Kashangula (X183), Kayembe Health Centre, GSD Mponela and Sendeza (JG 145) borehole sites. The study reveals that calcium ions were released from calcic-feldspars (plagioclase) and calcic-amphiboles in gneiss rocks whereas sulphate ions formed from pyrite (FeS_2) by oxidation of sulphur in hornblende-kyanite-muscovite schist rocks. The ions were released from the rock-forming minerals into groundwater and translated into precipitation of gypsum in the *dambos*. The solubility products of calcium and sulphate ions ranged from $\log_{10}$ -8.48 to -4.34 for the dry season and -8.51 to -4.07 for the rainy season. Gypsum precipitation occurred at localities where $\log_{10}$ values of solubility product exceeded -5.52; thus, most near *dambo* sites exhibited high solubility product values and reflected high local concentrations of calcium and sulphate ions. These localities showed very high positive correlation co-efficients between the two ions; thus, $r = +0.82$ for the rainy season and $r = +0.92$ for the dry season respectively. These conditions being favourable make gypsum precipitation likely to occur in the *dambos*.

The calcium oxide content in sediments of Kasangadzi, Livuna, and Machentche *dambos* indicated range of $0.08\% \pm 0.09\%$ to $3.75\% \pm 5.98$ and the sulphate content ranged from $0.33\% \pm 0.13$ to $4.37\% \pm 1.06$. The other oxides showed ranges of $0.04\% \pm 0.02$ to $0.54\% \pm 0.28$ for magnesium oxide; $0.05\% \pm 0.02$ to $0.65\% \pm 0.07$ for sodium oxide; $0.02\% \pm 0.01$ to $0.32\% \pm 0.38$ for potassium oxide; $23.16\% \pm 11.55$ to 65.67 ± 4.35 for silicon dioxide; $7.23\% \pm 3.52$

to $15.97\% \pm 2.69$ for aluminium dioxide; $1.65\% \pm 0.98$ to 5.25 ± 1.05 for carbonate; and $2.23\% \pm 0.03$ to $9.60\% \pm 3.96$ for iron oxides. The concentrations of calcium oxide and sulphate were higher than the normal concentrations of 1.4% for calcium oxide and 0.36% for sulphate in the Dowa West sediments. Sufficient abundance of essential ions within the sediments also indicated favourable conditions for gypsum formation. The quality of Dowa West gypsum was characterised by major oxide contents ranging from $30.75\% \pm 0.98$ to $34.75\% \pm 1.05$ for calcium oxide, $46.51\% \pm 0.36$ to $54.58\% \pm 0.23$ for sulphite, and other oxides such as magnesium and iron oxides were within acceptable limits ($<1\%$).

Mineral grain quantification showed that gypsum occurs in association with lateritic clay in Kasangadzi *dambo* and with quartz in Livuna and Machentche *dambos* respectively. Gypsum can easily be separated from the gangue at $>2.8\text{mm}$ diameter aperture above which size fractions are enriched in gypsum crystals. It is also shown that gypsum in clay is easily removed by washing through sieves; and Kasangadzi and Livuna ores with clay showed very high head assay values being much greater than 10%. Gypsum recovery is therefore very high in the *dambos* with high gypsum crystal content and very fine clay. Gypsum separation using the dry shaking table and ball-milling proved partly successful with 30% gangue separated from gypsum with particles $>500\mu\text{m}$ in diameter.

Microscopic examinations exhibited that gypsum crystallised around the tiny quartz grains as naturally seeded material; and this is evident from the X-ray diffraction pattern for POP-product and calcium sulphate hemihydrate (synthetic bassanite) in which synthetic quartz is included as a trace. Dowa West gypsum was identified with a major peak at a 2θ -angle of 11.67° and two other peaks at 23.40° and 29.11° on the X-ray diffraction spectrograms. Similar X-ray peaks were also identified on the spectrogram for Zimbabwe gypsum.

Plaster-of-Paris (POP) calcined^s at $>160^\circ\text{C}$ from the local gypsum was typified by X-ray diffraction patterns with peaks at 2θ -angles of 29.65° , 14.65° and 25.59° . The hydrated POP gave almost the same X-ray diffraction patterns as the calcined gypsum (POP). The co-existence of the hemihydrate and the gypsum phases were earmarked at calcining

temperatures below 160 °C by the X-ray spectrograms showing the three X-ray diffraction peaks for gypsum phase combined with little hemihydrate phase ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). Setting time for POP products was found to increase with increased temperature of calcination from 3.5 minutes for 100 °C -POP to 11.25 minutes for 175 °C-POP. The heat of formation evolved from POP hydration increased in magnitude from 1182.39 J/mole for 100 °C-POP product to 3993.84 J/mole for 175 °C-POP product. The 175 °C-POP product reacted with water more than the 100 °C-POP and 130 °C-POP products during the hydration process. POP products from the laboratory and proto-type ovens at 160 °C gave heat of hydration capacities of 3915.01 J/mole and 3047.93J/ mole respectively. This showed that the proto-type oven requires improvement by oven-wall insulation to give effective calcination conditions. This study also shows that the chemical characteristics of the Dowa West POP material are compatible with the BS 1191 standard with SO_3 content >35%, and MgO content <0.2%. The Dowa West chalk-sticks conform to the chemical specifications of "Alabaster brilliant white" as a superfine water resisting calcium sulphate. Chalk sticks of the Dowa West batch showed high strength with an average Modulus of Rupture (MOR) of $22.98 \pm 2.50 \text{ kg/cm}^2$ almost similar to the imported dusty chalk sticks. Production of the local chalk sticks at 160 °C with POP/ water ratio of 1:1 shows that strong chalk sticks can be locally fabricated.

CHAPTER 1: INTRODUCTION

1.1 Gypsum exploration and exploitation in Malawi

Gypsum was first explored in some *dambos* around Lake Malombe in Mangochi and Chitedze in Lilongwe by the Geological Survey Department in the 1980s (Mamu, 1983). Stratigraphic studies were made in seven *dambos* of central Malawi containing visually abundant gypsum in the soil profiles (Freshney, 1985). These studies identified gypsum-rich *dambos* such as Katete, Kaula, Chimimbe, Machentche, Livuna, Kasangadzi, and Chikhobwe in the Dedza-Lilongwe-Dowa plain. To exploit gypsum in Dowa West, a trial gypsum small-scale mine was made at Katete *dambo* west of Chisepo 1986 (Daniel, 1986). Later in 1995, Interep Malawi Limited mined gypsum on a small-scale at Kasangadzi *dambo* and produced 195 tonnes in eight months for the manufacture of fertiliser. The company operated at a reasonable profit then (Mines Department, 1995). With small-scale mine development at Kasangadzi *dambo*, exploration work was further made in the Dowa West area over Livuna, Mtiti and Linthembwe *dambos*. The Livuna deposit showed 500,000 tonnes of estimated reserves with an average ore grade of 12% gypsum. Calcination of gypsum to plaster-of-Paris (POP) over a wide temperature range of 120 °C to 230 °C showed that POP would be produced from the local gypsum, but the optimum calcination temperature was not determined by Chikusa (1987).

However, these earlier studies showed that the origin of gypsum in *dambos* within the land environment was not established to support gypsum exploration work (Mamu, 1983; Freshney, 1985). The relationship between concentrations of the gypsum-forming ions and precipitation of gypsum as calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was not established.

1.2 Scope of present study

Metal oxides contents were determined in sediments to ascertain geochemical characteristics of *dambo* sediments in which gypsum occurs. As gypsum precipitates from groundwater, solubility

products for calcium and sulphate ions were also calculated to gauge the likelihood of gypsum precipitation. The solubility product and metal contents were used as geochemicals tool for gypsum exploration. Hence, they gave a scientific basis of inference for gypsum occurrences in this study.

Gypsum profiles for Kasangadzi, Livuna, and Machentche *dambos* were mapped and graphically represented to provide the depositional characteristics of gypsum occurrence in sediments. Gypsum profile mapping was done over these *dambos* reflecting varied gypsum content and gangue mineral association. Separation of gypsum crystals from the gangue minerals was investigated based on the cheap and affordable winning methods; thus, the wet-sieving and ball-milling methods involved use of simple pieces of equipment at a laboratory scale.

Gypsum calcination to plaster-of-Paris (POP) and POP hydration to set-POP were chemical processes that provided POP products for various industrial uses. Gypsum was calcined at various temperatures to typify the quality of POP produced. POP-water ratios in the hydration process were partly taken as a measure in producing set-POP with definite quality.

POP hydration varied with the extent to which POP reacted with water as reflected by the amount of heat energy evolved. Crystallography of gypsum, POP, set-POP were determined using X-ray diffractometer; and definite crystalline phases were identified against the right material. This gave an understanding of gypsum and POP crystal structures. Quality of POP and gypsum was inferred from physico-chemical properties; therefore, suitability of POP and gypsum for specific industrial uses was determined from the properties.

The present study examined gypsum exploration based on chemical parameters, winning methods of gypsum from *dambo* sediments, physico-chemical properties of gypsum and plaster-of-Paris (POP) as its product used in various industries. This work provides some solutions to problems of locating *dambo* gypsum deposits and process of winning and conversion of gypsum to industrial products. Basic physico-chemical data on gypsum and POP is also included for use by mining and manufacturing industries in Malawi.

1.3 Aim of the study

The aim of the research work was to investigate the geochemistry of gypsum resources in the *dambo* environment of Dowa West and establish the physico-chemical properties of gypsum and opportunities for the production of plaster-of-Paris. The specific objectives of the study were to:

- (i) determine the geochemistry of gypsum resources in relation to precipitation of calcium sulphate in the *dambo* environment of Dowa West;
- (ii) identify methods of winning gypsum from the ore; and
- (iii) determine calcination process of gypsum to plaster-of-Paris and comparing the product with similar commodities available on the market.

1.4 Outline of thesis

With these objectives, the second chapter concerns the literature review on previous studies about gypsum based on physico-chemical parameters and environmental concepts on the geochemistry of gypsum deposits. The third chapter covers all the methods used in carrying out various investigations of the research work. The fourth chapter looks at the results of the research work and discusses the findings with regard to the concepts portrayed in chapter two. The fifth chapter presents conclusions and recommendations for further investigations to the present work.

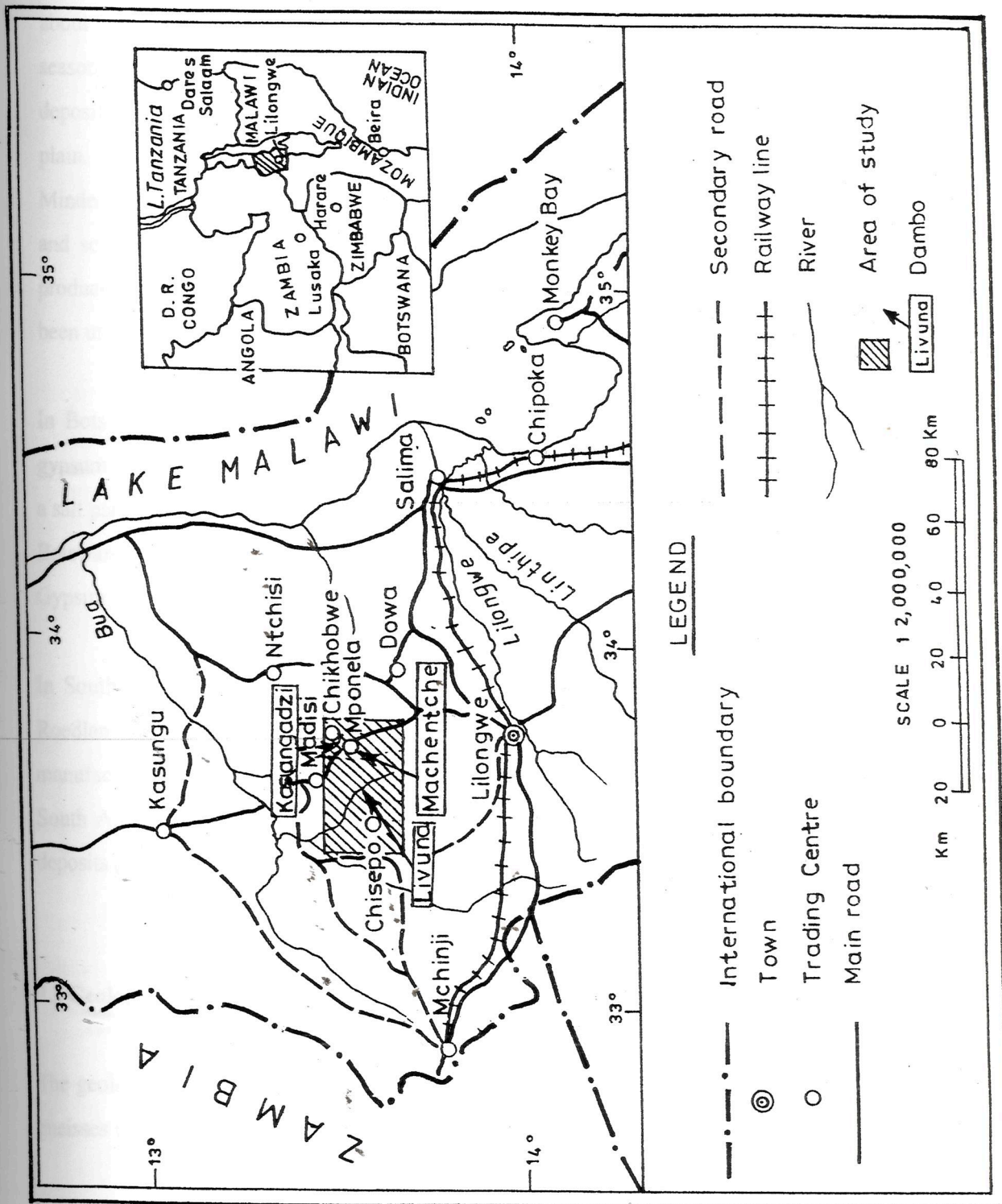
CHAPTER 2: LITERATURE REVIEW

2.1 Location and physiography of study area

The study area lies between latitudes $13^{\circ} 27\frac{2}{3}'$ and $13^{\circ} 39\frac{1}{2}'$ south; and longitudes $33^{\circ} 28'$ and $33^{\circ} 44\frac{1}{2}'$ east in Dowa West of central Malawi (Fig. 2.1). Its topography is characterised by *dambos* as wet flat-lying river valleys covered with short grass. The area covers about 930 km^2 (31 km by 30 km) partly falling in Traditional Authority (TA) areas of Dzoole, Kayembe and Chakhadza with a population of 114, 814 persons of whom 57, 382 are women (National Statistical Office, 1998). The population of the area takes up 24, 252 households; and the population distribution is characterised by a calculated population density of 123 persons per km^2 .

The area is accessible by the tarmac road (M1) and dirt feeder roads linked to Chisepo, Mdika, Kayembe and Chikhobwe (Fig.2.1). Apart from the roads, motorable tracks and footpaths also provide access to most villages and the *dambos* with high potential for the occurrence of gypsum. This area has also been utilised for intensive mixed farming system (Land Husbandry Training College, 1983). The interfluvial areas with gentle slopes ranging between 2° and 5° is being cultivated to tobacco, groundnuts and maize; and *dambos* are mainly used for livestock grazing. Natural vegetation in the area consist of open woodland savanna grading into woodland of drier uplands (Land Husbandry Training College, 1983). Short grass and reeds cover the constantly wet river channels as *dambos*.

The Dowa West area falls within the catchment of the Bua River Basin. As tributaries of the Bua, the major rivers flowing through the area are Mtiti, Livuna, and Kasangadzi rivers. The river basins are covered by *dambos*. These are flooded from end December to May during the rainy season. Livestock grazing and winter cropping cease for a while until the water-table subsides resulting in the *dambos* becoming dry. The rainfall received in the area ranges from 400 to 800 mm per year for a rainy season of four months from December to April (Department of Meteorological Services, 1983).



2.2 Gypsum deposits and mining in Southern Africa

Deposits similar to the Dowa West gypsum occur in Zambia, Botswana and South Africa. Gypsum in Zambia is mined from the Kafue flood plain at the Lochinvar Gypsum Mine situated about 50 km north-west of Monze Town. Mining at the Lochinvar mine is carried out in the dry-season to avoid floods in the rainy-season (Chanda and Lob, 1995). The Lochinvar gypsum deposit contains thin (0.5-1m) gypsum clay layers covering about 200km² in the Kafue flood plain. The grade of the gypsum ore lies between 18% and 23% gypsum; and gypsum mining by Mindeco in the 1990s yielded 5 tonnes per day. Gypsum is recovered from the ore by washing and screening over 2mm-sieves. Small-scale mining is preferred for such a deposit to keep production costs low (Chanda and Lob, 1995). The gypsum from the Lochinvar mine has mainly been utilised by the cement factory and the ceramics industry.

In Botswana, gypsum was located at Shashe north west of Gaborone. The deposit comprises gypsum crystals with particle sizes ranging from 0.2 to 10mm and appears to have developed in a salt pan characterised by arid to semi-arid climatic conditions (Bain, 1965). The gypsum ore in Botswana contains quartz pebbles and clay as a matrix. The average ore grade is 30% gypsum. Gypsum, mined from salt pan areas, is used in the manufacture of cement.

In South Africa, the gypsum deposits occur in many places that include Kimberley-Boshof, Roedlan and West Coast deposits. Most of these deposits have been exploited for cement manufacture and other gypsum consuming industries. Like in Botswana, gypsum deposits in South Africa formed over salt pans; and the average ore grades exceed 25% gypsum in most deposits (Oosterhuis, 1998).

2.3 Geology of the Dowa West area

The geological sequence of the rocks in the Dowa West area comprises the basement complex gneisses of Precambrian age (approx. 450my) as paragneisses and orthogneisses (Walter, 1972).

The basement complex gneisses are scantily encountered as small circular outcrops as shown in Fig. 2.2. From these outcrops of basement rocks, it may be inferred that metapelitic gneisses and schists are dominated by kyanite-bearing biotite-muscovite schists (Xsm) which is very pyritiferous around Chisepo (Piper, 1996). The biotite-muscovite schists grade into the graphite-muscovite schist (Xsmr) north and east of Chisepo. Quartzo-feldspathic gneiss and granulite (Xgg) apparently predominate from Mndolera extending to Mponela. The metagabbros (Xb) appear to have intruded into the pelitic schist and gneisses; and they are encountered as a belt of small isolated bodies in the area around Madisi. Pegmatitic gneisses (Xp) forming a small mountain range east of Kayembe prominently stand out as later intrusive bodies with NW-SE trending faults. Pegmatites (p) with calcic-feldspars and quartz reefs (q) appear exposed along the river courses (Bloomfield, 1968).

The superficial deposits in the form of soils predominantly cover the surface geology of the Dowa West area. These deposits are Miocene (approx. 26my) to Recent (0.01my) in age (Walter, 1972). Sandy soils (Qs) mostly overlie the quartzo-feldspathic rocks and pegmatites, and occur on the margins of dambos. Lateritic horizons also form the regolith in some slopes between the interfluves and dambo margins. The *dambo* soils and alluvium take up the network of *dambo* depressions in the Dowa West area.

The *dambo* soils are characterised by very fine sand deposits, grey soils and alluvium. Paragneisses predominantly underlie the Dowa West area. These paragneisses are defined by mineral assemblages in rocks that include biotite-hornblende gneisses; muscovite-graphite, locally pyritiferous, pelitic schists; and pegmatitic gneisses mixed with granulitic gneisses (Piper, 1996). Metamorphism over the pelites yielded pyritiferous hornblende-kyanite-muscovite schist (Xsm) (Piper *et al*, 1989). The pyritiferous rocks at Kadamsana and Khanyu hill near Chisepo indicate that sulphur content is high with an average grade of 8% sulphur (S) (Mamu and Kayira, 1975).

Orthogneisses occur as granitoid gneisses in small exposures north east of Livuna river. These gneisses are apparently interbanded with biotite gneisses that trend in the north northwest direction (Walter, 1972). The rocks appear as small outcrops scattered within residual soils of the area. According to Walter (1972), the *dambo* environment also provides sediments of Miocene to Quaternary age (Approx. 26 to 0.01my); and the sediments host the deposited gypsum.

2.4 Dambo sediments and types of gypsum deposits

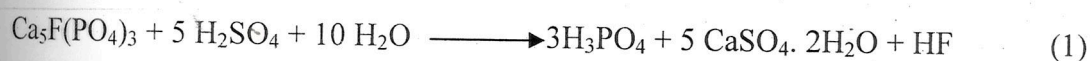
Superficial deposits in the *dambos* in Dowa and the rest of central Malawi are inferred to be Miocene (approx. 26my) in age (Walter, 1972). The deposits consist of the dark grey, greyish brown silty clay or sandy horizon with a thickness range of 0.5 to 1m from the top. The undulating yellowish or orange silty clay horizon with gypsum crystals covers a thickness between 0.2 and 1m in the middle. The weathered bedrock of quartz-feldspar-mica gneiss lies at the bottom with a thickness of greater than 1.5m (Daniel, 1985). The horizons display unclear boundaries, but do indicate episodic depositions of ferric oxides that reflect seasonal groundwater fluctuations (Chapuma, 1987). The *dambo* sediments are examined based on layers defined as 'Geosols' that are assemblages of soil or sediment profiles showing similar characteristics of lithostratigraphy, morphology and other evidence (Botha, 1996).

In case of deposits that formed in a sea environment, gypsum precipitated from high concentrations of salts in solution under an arid climate with a solubility of $K_{sp} = 3 \times 10^{-6}$ (Meites, 1981). The formation of gypsum deposits in marine conditions is extensively studied to typify calcium sulphate as gypsum and anhydrite (Jorgensen, 1978). In a land environment, gypsum precipitates from groundwater with relatively low concentrations of calcium and sulphate, but having solubility products above the solubility constant (Water Department, 1985; Table 2.1).

Table 2.1: Chemical composition of water samples from Dowa West (Water Department, 1985)

Borehole No.	Ca ²⁺ ppm	Mg ²⁺ ppm	SO ₄ ²⁻ ppm	HCO ₃ ⁻ ppm	pH (25 °C)
Goma B P3	176	100	362	243	7.6
Mlima RP3	132	38	221	348	7.9
Kapondo Dw 38	5.5	2.7	88	230	7.7
Kamkanda P4	225	224	1413	190	8.2
Nyonyo RP2	69	26	254	94	5.1
Wazili RP 24	13	2.1	9.5	49	6.3
Soko P30	186	55	550	296	7.6
Mbobo P29	69	28	182	288	7.6
Chaliwa P14	219	88	984	129	7.8

The third type of gypsum is chemically produced as a by-product of manufacturing industries. For instance, gypsum produced from the manufacture of phosphoric acid emerges from the reaction between sulphuric acid and rock phosphate as shown in equation (1) below (Kinamambo, 1988).



2.5 Mineralogy and uses of gypsum

Gypsum is crystalline calcium sulphate combined with two molecules of water and chemically defined as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It crystallises into a monoclinic system with a hardness of 2 on the Mohs scale and a specific gravity of 2.3 (Deer *et al.*, 1965).

Gypsum changes to plaster-of-Paris upon heating to temperatures above 120 °C (Equation-2); and the dihydrate form is regained upon hydration. This change finds a lot of applications in industry as shown in Table 2.2.



The industrial applications of gypsum include portland cement production, gypsum plaster board, paint manufacture, chalk production, filler in industrial products as shown in Table 2.2 (Oosterhuis, 1998).

In Malawi, gypsum used by Portland in Blantyre and Shayona in Kasungu to produce cement respectively. Gypsum has been used in the manufacture of fertiliser as a source of calcium and sulphur by Press Agriculture Limited in Lilongwe (Mines Department, 1995). Calcined gypsum is currently being utilised in the manufacture of chalk-sticks by some factories in Blantyre. Potential industries in which gypsum would be used in Malawi include ceramic and building material production, manufacture of insecticides as a filler or carrier, paint industry, production of plaster-of-Paris (POP) bandages, and dentistry.

2.6 Baseline concentrations of calcium and sulphate ions

According to Goldshmidt (1954), concentration of calcium is normally more than 1% (1.4% CaO) in residual sediments rich in silicate minerals. Abundance of sulphate ions ranges between 50 and 100 ppm in podzolic soils. Goldshmidt (1954) also indicated that black mud normally contains 0.12% sulphur that is equivalent to 0.36% sulphate after oxidation. The sulphate ions emerge from oxidation of pyrite, a sulphide mineral (Walder and Chavez, 1995); thus, the oxidation process proceeds as in reaction (3):

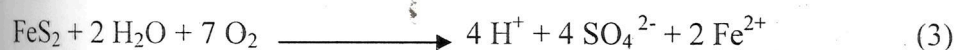


Table 2.2: Main uses of gypsum (Oosterhuis, 1998)

Gypsum products	Uses
Gypsum cement	Added as a retarder to Portland cement to control the setting time
Gypsum plaster boards	Provides dry linings to masonry walls, ceilings, partitions and where fire protection or sound and thermal insulation are required
Building plasters	'Plaster of Paris' and wall-plaster are made using gypsum
Gypsum blocks	Used for internal partitioning of walls. Blocks consist of gypsum with or without aggregate
Gypsum cove cornices	Used in buildings, these consist of core of set plaster enclosed in paper
'Plaster of Paris' bandages	Used for splinting fractures, rest splints and body supports
Dental gypsum products	Composed of finely powdered gypsum and modifiers to yield a homogeneous material for moulding and castings
Fertilisers	Low-grade gypsum improves soil quality. Dissolves more quickly than lime
Paint manufacture	Good quality finely-ground gypsum is used as a base for cold-water paints
Paper making	Terra alba and pearl filler are used as fillers in certain writing papers and boards
Insecticides/ Pesticides	Calcined granular gypsum is used as a carrier for toxic substances
Textiles	Ground gypsum used as a filler in cotton and cloth when a lustrous or glossy surface is required
Foodstuff, such as bread and beer	Very high purity required is used as a filler and source of calcium
Match heads and chalks	Gypsum used as a filler in match-head and plaster-of-Paris as raw material for chalk production

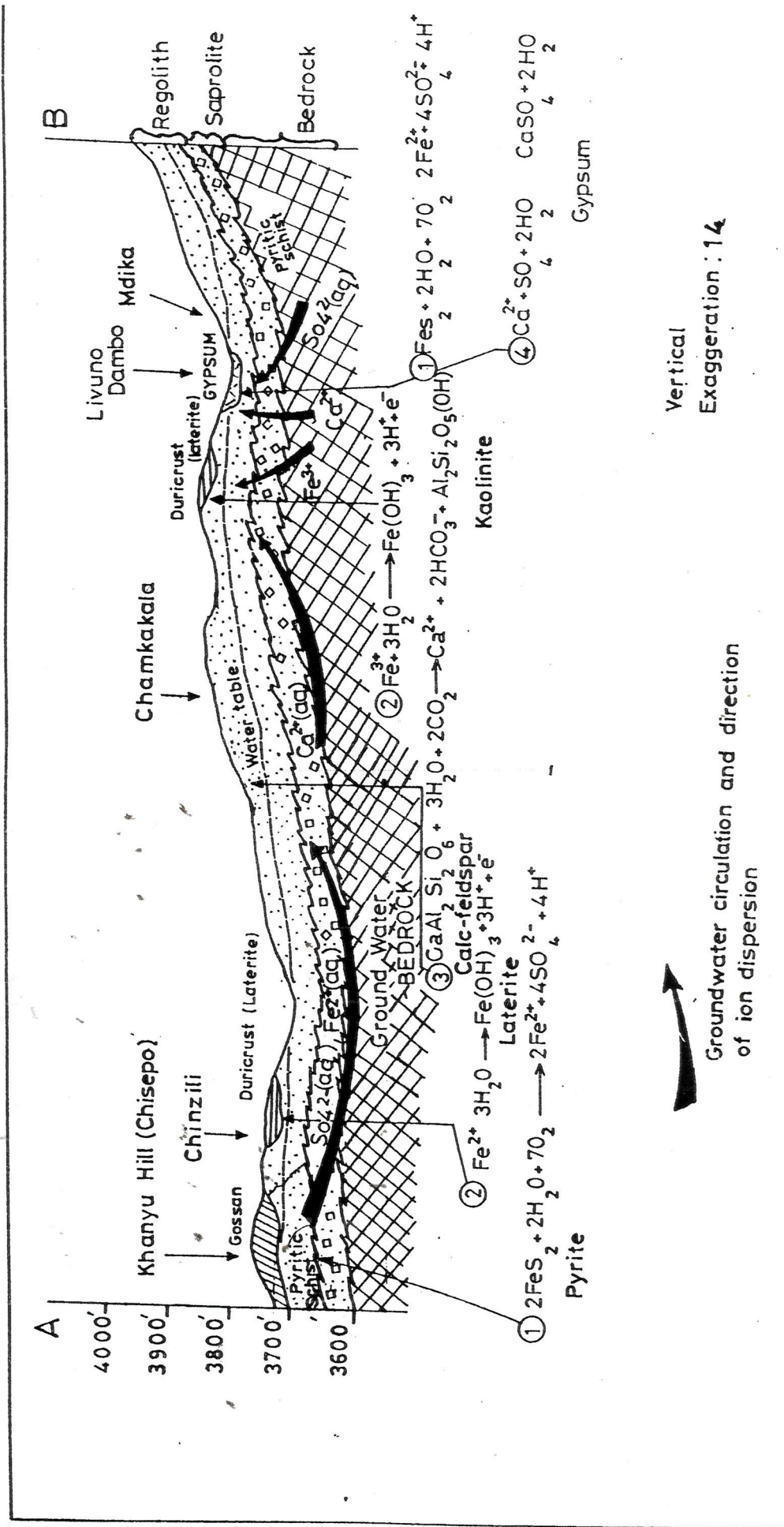
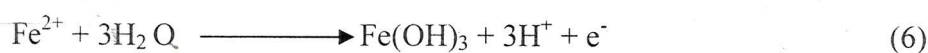


Figure 2.3 Gypsum deposit model and underground geochemical processes (modified after McFarlane, 1992)

transported by upward and downward groundwater movement to *dambo* areas such as Livuna (Thomas, 1974).

In the Dowa West area, the groundwater is known to move up and down based on increase in volume owing to recharge from the rainwater as illustrated in Figure 2.3. According to Braber (1965), gypsum deposits formed under environmentally favourable conditions that included the presence of rocks capable of providing calcium and sulphur in the zones of weathering. The calci-feldspar in the bedrock gets hydrolysed (Ii and Misawa, 1994; equation (4)). Sulphur is released from pyrite as it is oxidised by dissolved oxygen in groundwater through the formation of sulphate ions (Walder and Chazev, 1995; equation (3)). The clay layer encountered in the Dowa West *dambos* acted as the host of the two types of ions when groundwater flowed into *dambo* sediments. The layer absorbed and released the ions through cation and anion exchange mechanisms in the clay minerals as the water-table rose during the rainy-season and drew down during the hot dry-season (Bloodworth, 1990). The long dry periods also promoted precipitation of gypsum as concentrations of ions increase with evaporation over the *dambo* sediments. Livuna, Matchentche and Kasangadzi *dambos* have fine, compact clay layers as described by Bloodworth (1990).

As indicated in Figure 2.3, iron (II) was oxidised to iron (III) following equation (6).



Iron hydroxide ($\text{Fe}(\text{OH})_3$) formed laterite where water table was in contact with the interfluvial slope extending towards a river valley or *dambo*. Groundwater flowing from the highland towards the *dambos* deposited laterite. Lateritic layers or duricrusts were observed in places like Chinzili, Chatanga and south east of Matola C.C.A.P (Mc Farlane, 1992).

The high relief profile that is indicated in Figure 2.3 is likely to favour water seepage through the weathered zone towards the *dambo* at a high underground gradient around Livuna *dambo*. This provided mobilisation of sulphate and calcium ions towards the *dambo* areas to a depth of more

than 30 metres within the weathered gneiss (Water Department, 1958). This is evident from borehole information that showed the water table to be maintained at about 30 metres in the dry-season (Water Department, 1958). The development of gypsum deposits progressed with precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystals in *dambo* areas perched on the undulating landform as shown in Figure 2.3. As gypsum formed, groundwater was in constant circulation with dissolved oxygen and the diagenetic processes led to gypsum forming within the *dambo* sediments. During the rainy season when the water table advanced away from the bedrock towards the surface, calcium and sulphate ions were carried up into the clay-laden *dambo* sediments within the depth of two (2) metres from the surface. In the dry-season, *dambo* sediment layers ($\approx 2\text{m}$ thick) became desiccated under high solar heat influx with maximum temperatures around 28°C (Surveys Department, 1981). The water table therefore went down due to high evaporation rate while calcium and sulphate ions precipitated out as gypsum crystals in the 'Geosols' of the *dambo* sediments.

In this case, Ca^{2+} and SO_4^{2-} ionic species crystallised into gypsum above their solubility product. According to Stranks *et al* (1974), the ions dissolved independent of their respective concentrations and their total concentration in solution remained low ($<0.01\text{M}$). Furthermore, other ions did not have influence on the solubility product of the two ions. $\text{CaSO}_4(\text{s})$ as a compound in the form of Ca^{2+} and SO_4^{2-} was also influenced by the solubility of the calcium sulphate precipitate remaining in equilibrium with its ion species in solution. The precipitation of calcium sulphate was interfered with the common ion effect resulting in formation of carbonate nodules in the same *dambo* sediments (Skoog and West, 1976; Chang, 1991).

2.8 Use of multivariate data analysis

The multivariate data analysis can be used based on the partial correlation that is used to statistically quantify the strength of the relationship between one element and several other elements or chemical species as dependent variables. The single element or chemical species is considered the basis of change for the other elements. The occurrence of one element is gauged

relative to the occurrence of the others based on the same medium and conditions. The relationship between one element or chemical species and the others has also specific dispersion trends that show their abundance in groundwater. Two elements or chemical species may increase or decrease together in abundance forming a definite relationship. The trend of variability of one element (variable X) against the other (variable Y) is independently expressed as a ratio to the product of their respective variances. Thus, the relationship between chemical parameters or ions is defined by the correlation ratio in equation 7 below (Davis, 1986):

$$r = \text{Covariance}[xy] / \sqrt{\{\text{variance}[x] \text{ variance}[y]\}} \quad (7)$$

where **r** denotes correlation ratio; **x** denotes concentration of chemical species or parameter assumed to be an independent variable; and **y** denotes concentration of chemical species or parameters assumed to be a dependent variable.

Multivariate analysis is in this case typified by correlation co-efficients between concentrations of ions and chemical parameters; and the interrelationship of co-existence among them may be reflected by the change in climatic seasons for calcium, sulphate and other ions in *dambos* (Ratha and Sahu, 1995). Pairs of chemical parameters or ionic species indicate multiple-covariations quantified as correlation ratios. These ratios normally range from -1 and +1. The ratio of +1 or close to +1 would signify best correlated chemical parameters or ionic species. The ratio close to +0.7 would represent good correlation whereas +0.5 and less may be considered poor correlation. The value of zero (0) or close to it means the chemical species do not occur together. The ratio value of -1 or close to it denotes extreme negative correlation in which abundance of one chemical species increases and the other being correlated with decreases. The correlation ratio of -0.7 would represent good negative correlation; and -0.5 or more would tend to poor negative correlation.

2.9 Grain size distribution analysis and wet screening

The grain size distribution in sediment ore provides the size fractions that are rich in gypsum and gangue minerals. It is from apportioning by sieving that the dominant gypsum-rich size fractions are established. The sediment samples are sieved through a stack of sieves in the series 2mm,

1mm, 630 μ m, 500 μ m, 355 μ m, 200 μ m, 112 μ m, and 63 μ m to ensure that the mineral sediments are reasonably sized in terms of their approximate spherical diameters. The grains are classified on the sieves relative to gravel, sand, silt and clay. Mineral grains may be separated based on mineral types and their individual abundance quantified as weight percent. This assists in establishing amounts of gypsum in each size fraction as trapped on the sieves. Statistical parameters may also be worked out to relate gypsum occurrence with grain size fractions in which it occurs in abundance. Gangue minerals would also be quantified through sieving. The use of sieves or screens enables the classification of sediments rapidly from fine gravel (2mm) to silt (63 μ m) grades. Sieves with apertures less than 63 μ m are inefficient to trap the fine particles (Bloodworth, 1990). The Dowa West *dambo* sediments contain various grain sizes of minerals including gypsum crystals that can be separated by wet sieving (Daniel, 1986). The shape and diameter of mineral particles are determined through data analysis and computation of sorting co-efficients. Sorting co-efficients are quite varied in typifying grading of grain sizes; thus, a sorting co-efficient of < 2.5 gives very well sorted sediments, >2.5 to 4.0 denotes moderately sorted sediments, and >4.0 corresponds to badly sorted grain sizes (Leeder, 1982). Percent sediment-lot passed through each sieve is expressed through equation 8 below (Bloodworth, 1990):

$$\% \text{Sediment-lot (<mesh size)} = 100\% - (a/b \times 100\%) \quad (8)$$

where **a** denotes the weight of the sediments retained on the sieve

b denotes the weight of the sample sieved

However, winning of gypsum by wet screening from sediment ore may best be done with a combination of screens according to the Rittinger method with the aperture ratio of $\sqrt{2}$ (1.414); thus, the aperture of one screen is 1.414 times greater than the next below it in a stack. The theoretical sequence of six sieves with the largest aperture being 6.3mm would be in the series 6.3mm, 4.45mm, 3.15mm, 2.22mm, 1.58mm, and 1.11mm (Richard and Locke, 1953).

With the gypsum crystals separated from sediments by wet screening, the head grade assay can be calculated according to the method used by Mitchell and Briggs (1991). Thus, the gypsum

content (%) is multiplied by the weight size fraction (%) to give the gypsum ore grade (%) as analysed through sieving over a stack sieves.

2.10 Thermodynamics of gypsum formation

The formation of calcium sulphate dihydrate from groundwater proceeds with the inclusion of water as part of the crystals. This is preferred with the enthalpy change (ΔH) of the reaction drawing to a low energy level thereby making the reaction exothermic. This process provides the difference between the standard enthalpy changes of formation for the products from reactants at 25°C (Stark *et al*, 1982; Fletcher, 1993) as shown in chemical equation (9a) below:



The reaction of calcium sulphate with water in equation (9a) proceeds to form calcium sulphate dihydrate (gypsum) to a state of lower energy level. The formation of gypsum depends on the disorder of reactants and products making up the reaction system and the surrounding. Energy changes are due to the breaking and forming of chemical bonds coupled with the change in temperature as reaction in equation (9a) proceeds to the right (Krauskopf, 1967; Chang, 1991). In this case, entropy of the surrounding ($\Delta S^\circ_{\text{surrounding}} = -\Delta H^\circ/T^\circ$); thus, $\Delta S^\circ_{\text{surrounding}} = -(-1018 \text{ kJ/mole} \times 1000 \text{ J})/(298\text{K}) = 3416.1 \text{ J/K/mole}$. The entropy of chemical system in equation (9a) proceeds with regard to the second law of thermodynamics (Chang, 1991; Stark *et al*, 1982); and the standard entropy change (ΔS°) for the formation of gypsum can therefore be interpreted as follows:

$$\Delta S^\circ_f(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) = \sum v S^\circ(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) - \sum v S^\circ(\text{CaSO}_4 + 2\text{H}_2\text{O}). \quad (9b)$$

v denotes number of moles of substance in the reaction.

$\Delta S^\circ_f(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) = (194 - 107 - 2 \times 69.9) \text{ J/K} = -52.8 \text{ J/K/mole}$; this represents the entropy of the gypsum formation. However, groundwater and *dambo* sediments including gypsum deposits can be expressed as standard entropy of the universe; thus,

$$\Delta S^\circ_{\text{universe}} = \Delta S^\circ_f(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + \Delta S^\circ_{(\text{surrounding})} \quad (9c)$$

$$\Delta S^{\circ}_{\text{universe}} = -52.8 \text{ J/K/mole} + 3416.1 \text{ J/K/mole} = 3363.3 \text{ J/K/mole}.$$

With $\Delta S^{\circ}_{\text{universe}} > 0$, gypsum formation in the *dambos* of the Dowa West area certainly proceeded with a spontaneous reaction according to the second law of thermodynamics (Chang, 1991; Stark *et al*, 1982).

2.11 Crystallography and X-ray diffraction analysis of gypsum

Gypsum crystals are twinned giving the swallow-tail shape (Cox *et al*, 1974). Its grains exhibit the monoclinic crystal system characterised by a combined crystal shape of clinopinacoid, prism and hemipyramid (Deer *etal*, 1965). Gypsum grains are also characterised by a microscopic 'flash figure' with a biaxial angle estimated at 53° (Kerr, 1954).

Powdered gypsum is placed at the centre of the goniometer; and X-rays are emitted from the X-ray tube bombard it as they go through the divergence slit (DS). The X-rays diffracted from the gypsum powder converge on the receiving slit (RS) symmetrically positioned to the X-ray tube (ICDD, 1997). The diffracted X-rays are captured by the scintillation detector and converted into electric signals.

The signals from the gypsum-diffracted X-rays go through the pulse height analyser (PHA). They are quantified after the noise components have been removed. X-ray intensity is then expressed in the magnitude of a counted value in counts per second (cps). The X-ray intensity of gypsum-diffracted rays and the diffraction angles are gauged by the goniometer. The X-ray detector is in this case rotated twice as fast as the gypsum powder to allow the incident and reflection angles (θ) of X-rays to be the same. The detector position is placed at angle 2θ . As the X-rays bombard the gypsum powder, the path length of diffracting X-rays is increased by an integral number of wavelengths ($n\lambda$) diffracted from parallel planes. This phenomenon is recorded as signals in the form of diffraction peaks with intensities on the spectrogram plotted as X-ray intensities fixed against the diffraction angles at 2θ (Navrotsky, 1994). The intensities (I)

of the peaks are plotted relative to the first order diffracted X-rays and are expressed as percentages. The gypsum powder is analysed by continuous scanning.

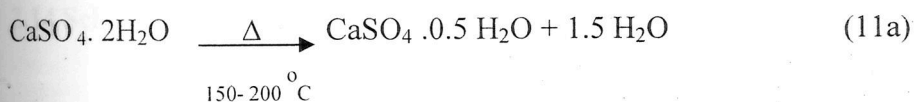
The distance between the atomic planes in the powdered gypsum samples where X-rays are diffracted is obtained from the Bragg equation below; thus

$$2d \sin \theta = n\lambda \quad (10)$$

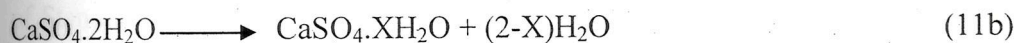
where d = distance between the atoms, θ = peak angle position of diffracted X-rays, λ = X-ray wavelength, and $n = 1, 2, 3, \dots$ (series of the emerging X-rays). From this equation, the distance between the atoms (d) may be put as the subject; thus $d = n\lambda / 2 \sin \theta$. This distance between atoms varies regularly based on the types of atoms or ions. Therefore, the type of atoms or ions constituting the sample of gypsum and plaster-of-Paris is identified from the diffraction peaks and the two-theta angle portrayed on the spectrograms.

2.12 Calcination of gypsum to plaster-of-Paris

The Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is transformed into bassanite or plaster-of-Paris ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) by heating to temperatures between 150°C to 200°C (Groves, 1958). The bassanite is produced with the loss of three-quarters of the molecular water as portrayed in equation (11a). Bassanite is convertible to the dihydrate form, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by rehydration as shown below:



Products of dehydration for gypsum heated at various temperature points is defined by equation (11b):



where $0 \leq X \leq 2$

The value of X is dependent on the amount of water of crystallisation retained in calcium sulphate hemihydrate (POP) produced at temperatures of calcination (Groves, 1958). The X-ray spectrograms with energy intensity peaks typifying the POP products obtained at various temperatures of calcination can be used as a basis for defining the quality of the POP (ICDD, 1997).

2.13 Hydration of calcined gypsum to form dihydrate

The reaction between the plaster-of-Paris and water to form the dihydrate product is an exothermic reaction which depends on the level of calcination (Groves, 1958). The chemical equation (12) below explains the change of plaster-of-Paris to the dihydrate product.



From the equation, it may be established that the heat is evolved as the calcium dihydrate forms ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The heat energy is given off as the reaction between plaster-of-Paris and water proceeds to the right in equation (12). The energy evolved in equation (12) can be quantified using a simple calorimetric method (Kelly, 1941; Franz and Malm, 1960).

2.14 School chalk-sticks

School chalk-sticks are produced from hydration and hardening of the plaster-of-Paris (POP). POP is mixed with water to form calcium sulphate hydrate that is allowed to set in a mould and to be extruded as chalk-sticks (Börgardts, 1991). Metal oxides are determined in the POP products to check its compatibility with standard specifications according to the Malawi Bureau of Standards (Standard MBS 187, 1999). The major oxides analysed included calcium oxide (CaO), sulphite (SO_3), magnesium oxide (MgO), iron oxide (Fe_2O_3), sodium oxide (Na_2O), potassium oxide (K_2O). Cadmium (Cd) and lead (Pb) are determined to monitor toxicity levels.

The chalk-sticks from local and commercial POP materials are analysed to compare quality of the two types of POP (MBS 187, 1999). According to Borgardtts (1991), the chemical composition for POP used in chalk-making should have average contents of 32.3% CaO, 46.0% SO₃, 0.5% SiO₂, 0.4 MgO, 0.9% (Al₂O₃ + Fe₂O₃). However, the British standard (BS 1191) requires that the POP should have a minimum of 35.0% SO₃, %CaO be at least 2/3 of SO₃, and a minimum of 0.2% MgO.

The varied calcining temperatures and POP/water mixture ratios are used as parameters to characterise chalk-sticks (Lach, 1985). The hydration of calcium sulphate gives rise to gypsum crystals that are often idiomorphic. Platy, needle, prismatic or fibrous shapes emerge to form aggregates. This varies from one POP type to another based on temperature of calcination that influenced the calcium hemihydrate to form. The Modulus of Rupture (MOR) values are used to typify the chalk sticks based on the diameter and the load they sustain upon breaking across the transverse area (Ryan and Radford, 1987).

The calcination temperatures and POP/water mixture ratios influence the quality of chalk-sticks. The strength of chalk-sticks is determined using Modulus of Rupture (MOR) (Ryan and Radford, 1987). Chemical composition and abrasion properties of the sticks are also determined (Malawi Bureau of Standard, 1999).

CHAPTER 3: MATERIAL AND METHODS

3.1 *Dambo* selection and gypsum profile assessment

Three *dambos* were selected for the study in the Dowa West area based on morphology in terms of broadness and relief (Walker and Lyall, 1960). The *dambos* selected were Kasangadzi, Livuna and Machentche. Kasangadzi *dambo* was selected to provide an example of a large river valley with an active river course and having a lot of alluvial sediments. Livuna *dambo* gave an example of a locally tilted *dambo* in which gypsum profiles would display different characteristics of deposition from Kasangadzi *dambo* with a large perennial river channel. Machentche *dambo* was selected as a *dambo* in which the alluvial deposits broadly extend for a very wide area at depth (<1m). Evidence of development of the *dambos* was featured in the correlatable lithostratigraphic units as gypsum profiles; and the occurrence of gypsum was ascertained by defining 'Geosols' as lithologic units hosting gypsum crystals (Botha, 1996).

Pit-sites were levelled using a laser-beam automatic level to mark the morphology of the *dambo* in a cross-sectional perspective. Lithostratigraphic sections were also drawn from profile descriptions made from pits dug along the horizontal profiles. Gypsum-bearing lithologic units were zoned in sediment profiles and correlated with the others in the next adjacent profile.

3.2 Sediment sampling

Forty-two (42) samples were collected from the pits at about 0.5m spacing for various analyses at site shown in Fig 3.1, 3.2 and 3.3. The samples were taken at distinct points along the profiles as a way of ascertaining the possible changes in grain size of the *dambo* sediments. Some of these gypsum profiles from which samples were taken did not contain gypsum crystals. These,

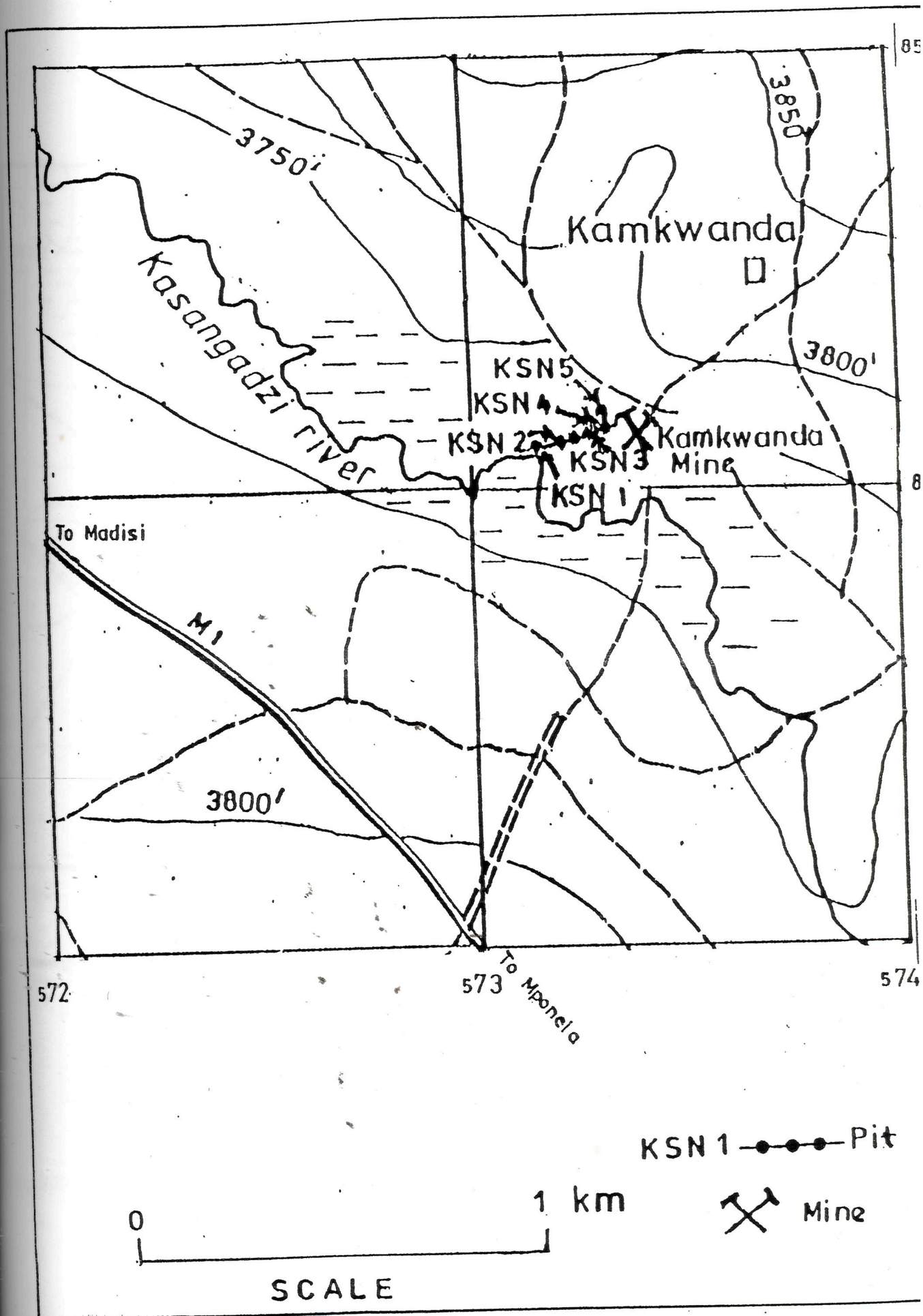


Figure 3.1 Location of pit profiles across Kasangadzi dambo

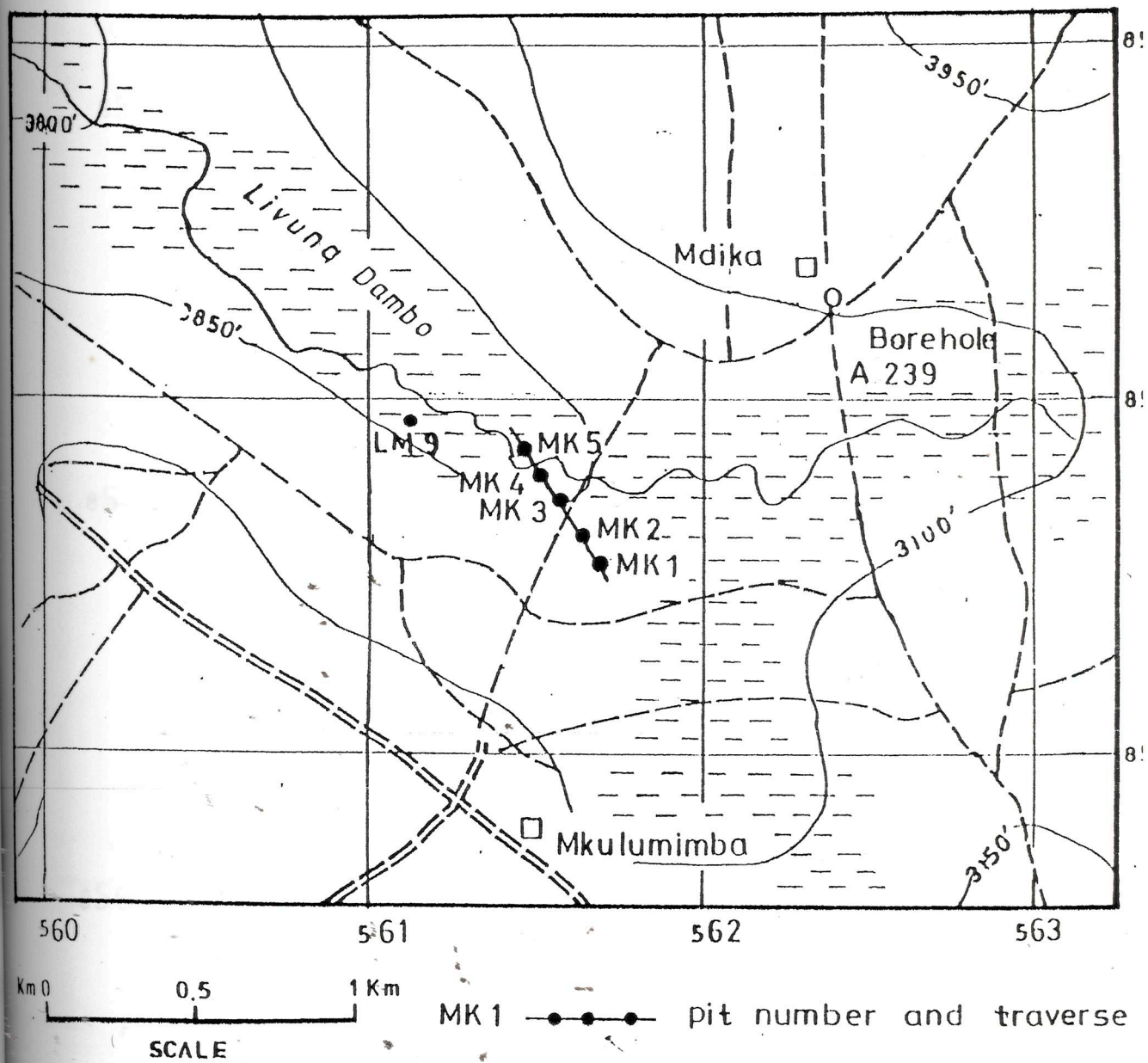


Fig. 3.2 Location of pit profiles across Livuna dambo

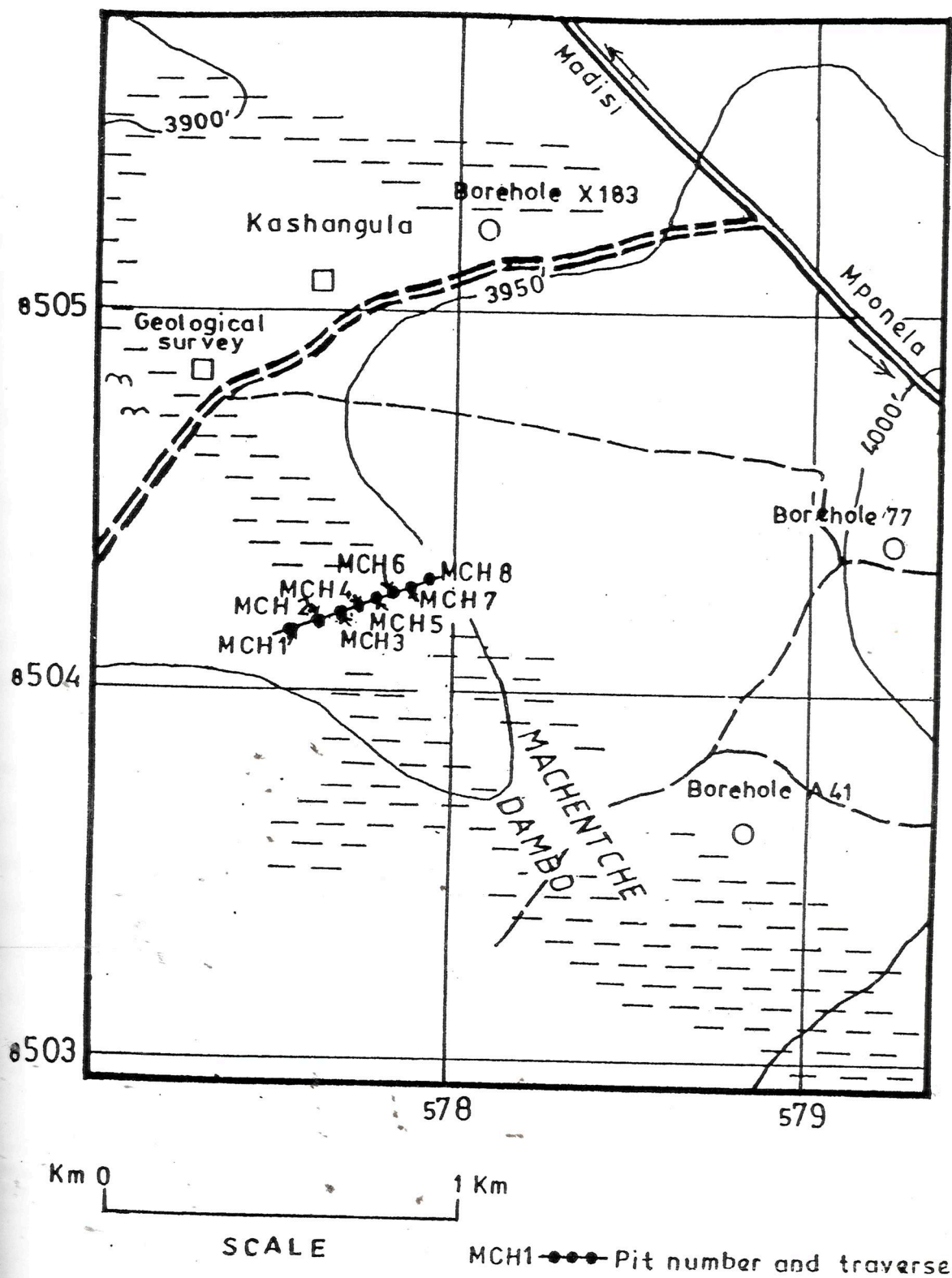


Figure 3.3 Location of pit profiles across Machentche dambo

therefore, acted as controls for the *dambo* environment in which gypsum could not have crystallised. Gypsum crystals collected from the sediment samples were analysed for major oxides to check for its quality. Selected samples were collected at rock outcrops for petrographic studies in order to account for mineralogical degradation leading to release of ions from the interfluvial areas. The rocks and sediment samples were analysed using transmitted and reflected microscopic methods as described by Craig and Vaughan (1981).

3.3 Groundwater sampling

Water boreholes and shallow wells located in Dowa West areas were chosen as sampling stations for the groundwater; and twenty-nine stations were established during the geochemical survey. This did not form a regular sampling pattern specially designed for the survey; however, the borehole locations as sited some time back still provided a sampling pattern adequate to collect the groundwater samples from dambos and interfluvial areas as high ground. Water samples from the two types of environment provided remarkable contrast for chemical analysis (Sjostrom, 1993). Sampling of water from boreholes was conducted in March 1999 during the rainy-season and November, 1999 in the dry-season. These two sampling times of the year were fixed in order to check for seasonal changes with regard to dilution and mobility of ionic species. The water from boreholes was put in bottles with its mouths tightly covered to prevent volatile chemical species such as carbonic acid from escaping. Two drops of 10% hydrochloric acid solution were added to the water samples to preserve metal ions in solution before analysis.

3.4 Chemical analysis of sediment and groundwater samples

3.4.1 Determination of silicon dioxide

Sediment samples were analysed for silicon dioxide (SiO_2) using the molybdenum-blue colorimetric method. Sediment material was decomposed by fusing with sodium hydroxide to provide chemical attack by flux as described by Matsudaira, 1992.

One-tenth of a gram (0.1g) powdered sample was weighed in duplicate ($n=2$) and two grams (2 g) sodium hydroxide pellets were added to each sample. The mixture of the two was homogenised to ensure thorough mixing in a nickel crucible and later gently heated using a gas burner for three (3) minutes until the material became fused. The fused material was then allowed to cool and then placed in a 500ml polypropylene beaker. The fused material in the crucible was washed down into the beaker with boiled distilled water; and the crucible was thoroughly rinsed. The solution collected in the beaker was then transferred into a 250ml volumetric flask and later diluted with water to the mark and was filtered into the 500ml polypropylene using the No. 421 whitman filter paper. A pale yellow to yellow filtrate was collected in a plastic bottle from which 1ml of solution was pipetted and subsequently run into a 100ml volumetric flask. A drop of p-Nitrophenol indicator was added followed by several drops of 20% hydrochloric acid (analytical grade reagent) until the yellow colour changed to colourless. The solution was diluted to 50ml with distilled water; and 1ml of 20% hydrochloric acid was added followed by an addition of 4ml 5% ammonium molybdate solution. A blue complex of silicon and molybic acid formed making the solutions turn to blue colour. The solution was shaken up to ensure thorough mixing and allowed to stand for 10 minutes. 5ml of 10% tartaric acid solution were added followed by an addition of 2ml ascorbic acid. The solution in the flask was diluted to 100ml mark with distilled water and was left to stand for 30 minutes.

Diluted silicon dioxide solutions were made from a silicon dioxide standard solution in concentrations of 0.02, 0.05, 0.10, 0.15 and 0.2mg/ml silicon respectively in the same way as the

samples with 50ml solution diluted to a volume of 100ml in the volumetric flask. The samples and standards were run in duplicate ($n=2$) on the UV-Visible spectrophotometer (UV-2201 Shimadzu model) set at 650nm wavelength. A reagent blank was also included in the runs to provide background absorbance in contrast to the samples and standards. Distilled water was run on the machine to calibrate it after 10 runs of the samples to ensure the accuracy of the absorbance readings. A graph of absorbance against concentration was drawn by the computer system linked to the spectrophotometer to give the concentrations of silicon dioxide in solution.

The actual concentrations of silicon dioxide were then calculated as the product of mass of silicon, the ratio of volume of dilution to the aliquot used and the conversion factor for silicon to silicon dioxide (Bennet and Hawley, 1965).

3.4.2 Determination of aluminium, iron, lead and cadmium by AAS

Iron, lead and cadmium were determined following digestion of the samples with aqua regia, a mixture of hydrochloric and nitric acids, in a water bath. The digestion method was similar to that described by Roberts *et al* (1992) except for a few modifications in mixing the acids as Vogel (1961). The three elements were analysed using the Atomic Absorption Spectrophotometer (AAS) following the method as described by Skoog and West (1976).

The powdered sediment sample weighed to 0.1g in duplicate ($n=2$) and was digested using a mixture of 12.5ml hydrofluoric acid, 5ml nitric acid and 11ml perchloric acid in order to dissolve silica, iron oxides and aluminosilicates. The solution was left to stand for 48 hours and was thereafter heated on a hot-plate to almost dryness in 250ml Teflon beaker. The emerging fused material was subsequently dissolved in distilled water and transferred into a 100ml volumetric flask and topped up to the mark.

The atomic absorption spectrometer (AAS) was then respectively set with appropriate lamps for the elements, namely aluminium (Al), lead (Pb), cadmium and iron (Fe). The sample solution was run in duplicate ($n=2$) on the AAS after the instrument was calibrated with blank solutions

(distilled water). The air-acetylene flame was used to atomise the samples for the AAS analysis. The absorption levels of elements were collated with concentrations in solution and read-off from the AAS instrument (Shimadzu model AA-680) synchronised with a computer in which analytical results were processed. Concentrations of elements were calculated by a dilution factor based on the dilution made.

3.4.3 Determination of sodium and potassium by the flame photometer method

The sediment samples were digested based on the procedure as described by Vogel (1961). The analysis of sodium and potassium by the flame photometer was conducted following the modified steps as given by Roberts *et al* (1992).

Half a gramme (0.5g) of sample was weighed in duplicate ($n=2$) and put in a Teflon beaker. 15 ml of hydrofluoric acid, and 5ml nitric acid were sequentially added to the sample in a Teflon beaker under a fume-hood. The solution was evaporated to almost dryness on a hotplate and cooled. 5ml of perchloric acid and then 5ml nitric acids were respectively added to the contents of the beaker. The resulting solution was once again evaporated to dryness. Perchloric acid (5 ml) and distilled water (20ml) were added; and the solution boiled for two (2) minutes on a hotplate. The solution was diluted to the 100ml mark and shaken to ensure mixing.

Standard solutions for sodium and potassium were prepared in series of 0, 10, 20, 40, 60 and 80 $\mu\text{g/l}$. The Eel flame-photometer was set with sodium and potassium filters and the standards were run on the instrument starting with the lowest to the highest concentration. Samples were run later. Propane gas was used to give a flame on the flame-photometer. Distilled water was aspirated into the instrument to attain a transmittance of zero. A graph portraying the relationship between energy transmittance and concentrations of sodium and potassium was plotted based on prepared concentrations of standard solutions. The concentrations of sodium and potassium for the samples were read-off from the graph and were expressed as %Na or %K by multiplying with a factor of 0.02.

3.4.4 Determination of sulphate in sediments by gravimetric analysis

Sulphate ions were determined using the gravimetric method as described by Jeffrey (1975) and Bennet and Hawley (1965) respectively. 0.5g of quartered sediment samples were weighed in duplicate ($n=2$) and were each fused with 7g of sodium hydroxide pellets. The sample and sodium hydroxide pellets were mixed in a nickel crucible and heated in a muffle furnace at 800°C for eight minutes. The fused material was then cooled with running water. The crucible with the mixture was placed in a 250ml beaker and covered with a watch glass. The content of the crucible was washed down in a beaker using hot water starting with the cover glass. Having washed the contents of the crucible into the beaker, the crucible was further rinsed with hot water while scrubbing the material stuck to the beaker with a rubber policeman (bobby). The content of the beaker was filtered with Whatman paper No. 541; and sodium carbonate (1%) solution was further used to wash all the material into the beaker. The filtrate was transferred into a 250ml beaker and 2ml of concentrated hydrochloric acid (1.18, density) was added. The solution was boiled on a hot plate for 2 minutes to expel carbon dioxide and 5ml barium chloride solution (10%) was added while the solution was being boiled for 2 minutes. The solution was allowed to stand on a steam bath for 1 hour and left to cool overnight. The solution together with the precipitate was then filtered with Whatman paper No. 42 to recover the precipitate and discard the filtrate. The precipitate was washed with hot water into the funnel with filter paper to remove excess chlorides. The precipitate together with the filter paper was transferred into a nickel crucible whose weight was pre-determined. The crucible with the precipitate was cautiously heated to make the residue dry and the filter paper charred. The carbon material was burned off over a gas-burner flame and left to cool. A few drops of sulphuric acid (1+1) were added to the sample followed by 5ml of hydrofluoric acid (40% w/v). The sample was gently heated to slowly evaporate to dryness. The dry residue in the nickel crucible was ignited to 1000°C in a muffle furnace and weighed as barium sulphate. The actual weight of the sulphate was calculated by multiplying with a factor of 0.4116; and the percent sulphate content was expressed relative to the weight of the sample.

3.4.5 Calcium and magnesium analysis in sediments by titrimetry

The analysis of calcium and magnesium were made following the method described by Skoog and West (1976). The method was modified to include the procedures on digestion as described by Vogel (1961).

One-half (0.5g) sample was weighed in duplicate ($n=2$) after passing through 80 mesh and digested with 25ml of 5% hydrochloric acid (v/v) by adding the acid to the ground sample in 250 ml beaker and covering it with a watch glass. The digested sample was heated to boil for about 10 minutes and allowed to cool. The watch glass and the contents were transferred into a 100ml conical flask by thoroughly washing with distilled water. The solution in the flask was diluted to the 100ml mark and was allowed to settle for about two (2) hours. The samples were prepared in duplicate.

8g of ethyl diamine tetra-acetic acid (EDTA) was first dissolved in magnesium chloride solution diluted to 2 litre volume. This EDTA solution was used to react with the samples by titration. A buffer solution of pH 10 was made from ammonia and ammonium chloride by adding 70g of ammonium chloride to 570ml of ammonia and making up the solution to a litre to maintain the required pH condition for the titration reaction. Potassium cyanide solution, triethanolamine in water, and Erichrome Black T indicator were also added to the sample solutions as reagents and indicator respectively. The standard solutions were made from one gramme (1g) calcium carbonate and magnesium carbonate (Analytical Reagent grade). These were respectively dissolved by 50ml 5% hydrochloric acid by boiling for 10 minutes. The contents of the beaker were transferred into a litre-graduated flask and distilled water; and distilled water was added to a three-quarter level on the flask. The solution was shaken before titration. Both standards and samples had 10ml of buffer (pH 10) solution added and swirled. 5ml 2% potassium cyanide and 4% triethanolamine were in turn added; and the solution swirled to mix respectively. Four grammes (4g) of Erichrome Black T indicator were added swirled to mix with the solution. The solution was then titrated with the colour change from red to lilac. The volume of EDTA solution

used in the complexometric reaction was recorded. 5ml of 2 molar potassium hydroxide solution was added to adjust the pH of the solution. Titration with EDTA was continued until the solution changed from lilac to blue. The volume of the EDTA run was then recorded. Precautionary measures were taken in handling potassium cyanide as a poisonous chemical when preparing solutions for titration.

Percent calcium oxide was calculated by multiplying fifty-six (56) with the ratio between sample and mean standard titres. Percent magnesium oxide was determined by finding the difference between the calculated total carbonate of calcium and magnesium and the calculated calcium carbonate following the first titration to lilac.

3.4.6 Analysis of groundwater

The groundwater samples were analysed for K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Fe^{3+} , SO_4^{2-} and HCO_3^- using the methods described by AWWA and APHA (1970; pp 84-86; pp 188-189 and pp 333). Concentrations of K^+ and Na^+ were determined by the flame photometer. Magnesium and calcium ions were analysed by the titrimetric method with ethylene diamine tetra-acetic acid (EDTA) as the complexing agent and eriochrome black T as the indicator. Sulphate ions (SO_4^{2-}) were mainly analysed by the gravimetric method. The carbonate related ions were analysed by the titrimetric method with HCl solution as a reagent and methyl orange as the indicator. The measurements for Eh and pH were made on the water samples using the digital Eh/pH meter. Fe^{3+} was determined using the AAS method by running the water samples on the instrument after adding 10% HCl.

3.5 Grain size distribution analysis

The grain size analysis was made following the method described by Bloodworth (1990). *Dambo* sediment samples were air dried at 110 °C and weighed to about 500g. The weighed samples were wet-sieved through a stack of sieves placed in the order 2mm, 1mm, 630µm, 500µm, 355 µm, 200µm, 112µm, and 63µm. The sieve stack was mounted on the sonic vibrator to ensure turbulent flow of the water with the sediments. The sediment lots retained on each sieve was dried and weighed. The percent sediment-lot passed through each sieve was expressed through the equation 8 (Bloodworth, 1990).

Cumulative percentages of retained sediments for each sieve were plotted on the logarithmic graph against the aperture diameter. Grain size distribution curves for each sample collected from the pits were drawn on the semi-logarithmic graphs using a Windows compatible software called WinSieb 5.0.

3.6 Gypsum mining and processing methods

3.6.1 Gypsum mining

Gypsum was mined by stripping the overburden (0.5 to 1m thick) first and then excavating the gypsiferous layer extending downwards for 1 to 2m. The open pits designed in the mining process took up 2-m-wide trenches covering the lateral extent of deposits (Allen, 1983).

The stripped top layer of alluvial soil was heaped on one side of the pit or trench whereas the mined gypsiferous material was heaped on the other side ready for wet-screening. The mining of gypsum is conducted by the labour-intensive method with persons using picks, hoes, shovels and wheelbarrows.

A mining trial by "stripping and back-fill" was also made on the Livuna deposit around pit MK 3 during the dry-season of the year 2001 with three (3) persons excavating strip of overburden and gypsite.

3.6.2 Gypsum winning by screening

Wet-screening method was used using aperture series of three sieves as 4.699mm (4 mesh), 2.36mm (8 mesh), and 1.168mm (14 mesh). These sieves were chosen based on the available sieves and a combination of the closest apertures by design (Richard and Locke, 1953). This combination of sieves provided a series with a ratio of 2 for one sieve aperture size to the other below. However, the actual sieves available at the time of use were 6.3mm (3 mesh), 2.81mm (7 mesh), and 1.4mm (12 mesh) with an aperture ratio of slightly greater than 2 (2.12).

The screening method was further modified by mounting three sieves on a deck to hold them for operation as a mini-plant. The 45-cm-diameter sieves were spaced at a distance of 25cm in the aperture series of 6.3mm, 4mm, 2.8mm and 1.4mm (Fig. 2.1). The spacing distance allowed ample room for scrubbing the gypsum ore material against the sieves. The screening mini-plant was operated in a stationary mode with the metal frames holding the sieves and a water jet dislodging particles stuck to the screening. The head grade assay for the ore samples was calculated according to the method used by Mitchell and Briggs (1991).



Fig. 3.5 Wet-sieving of gypsum ore on a screen deck with sieves inclined at 10° slope

3.6.3 Gypsum ore processing using shaking table

The shaking table method was used as described by Wills (1988) and McDivitt and Lock (1990). The material to be processed was modified by calcining to make it lighter than gangue minerals. The $>2.8\text{mm}$ and $-2.8\text{mm}/+1.4\text{mm}$ size fractions of the MK 5 were calcined at $160\text{ }^{\circ}\text{C}$; and the calcined gypsum crystals (POP) co-existed with the gangue minerals. This meant that the POP emerged as a new component after losing water of crystallisation; and calcined crystals became less dense than the gangue minerals. Dry separation using the shaking table helped to win part of the calcined gypsum (POP) from the gangue minerals. The calcined gypsum crystals were sifted from the gangue by the dry shaking table slanted at 7° slope. The heavy mineral grains moved fast and got discharged into the lower bin whereas the light minerals followed upper grooves of the shaking table and got dumped into the upper collecting bin.

3.6.4 Gypsum ore processing using semi-autogenous method

The semi-autogenous method provided by Gilchrist (1980) was used to process the gypsum ore. A ball-mill of 500g-capacity milled a feed of particles greater than 1.4mm in size. The milling was conducted with the rotational force of the ball-mill medium consisting of the feed material, the porcelain balls and a little water. The ball-mill was allowed to run for seven hours. The ball-milled material was later screened through sieves with apertures of 1.4mm and $500\text{ }\mu\text{m}$. The ball-milling and screening was used to improve the separation of finely ground gypsum from the coarse gangue by further reducing gypsum crystals. The hard gangue minerals such as quartz, calcrite nodules and porcelain balls crushed the soft gypsum crystals in an aqueous medium as a little water was added. This was semi-autogenous as the mineral grains within the ore material and the porcelain balls were simultaneously used to crush the gypsum crystals. The ball-milled material was screened with the sieves finer than the size of the ball-mill feed.

3.7 Calcination of gypsum

The calcination was made according to the method described by Kinamambo (1988). Gypsum was calcined to produce Plaster-of-Paris in an electric laboratory oven set at known temperature points. Gypsum placed in metal trays was calcined for 5 hours. The oven used had a controlled temperature system; and hot air calcined gypsum material. The heat was confined to the inside of the oven as the metal lining radiated it to the sample at set temperature. The heat loss from the oven was therefore kept minimal with the tightly closed door. The selected temperatures for calcination were 100 °C, 130 °C, 160 °C, 175 °C, 180 °C and 190 °C as various authorities in such studies gave different calcination temperatures within the range 90 °C and 210 °C (Groves, 1958; Noltholt, 1973; and Kinamambo, 1988). The electric laboratory oven was also used to heat gypsum to POP at a temperature of 160 °C for 3 hours to compare its efficiency with the prototype oven (Figure 3.6). The POP was left to cool for 20 minutes before it was bagged in sealed plastic bags to avoid hydration from humid air.

Whole crystals of gypsum were completely calcined; and the POP was ground in porcelain motor. A similar calcining process was undertaken in a prototype oven fabricated for the Chemistry Department, Chancellor College. This prototype oven was made up of two heating coils placed at the two sides of the oven walls. A metal tray was placed at the level directly opposite the two coils as shown in the sketch in Figure 3.6. The gypsum in the tray was left heating for 3 hours with the topside door of the oven closed. By using a thermometer, the heating temperature for the oven was monitored to be varying between 140° and 180° C with an average of 160° C. After three (3) hours of heating, the gypsum crystals looked calcined, but this was done on the outside only with the inside uncalcined. The calcined portion was recovered from the partly calcined gypsum material by gently grinding it in a porcelain motor and screening with 1mm sieve.

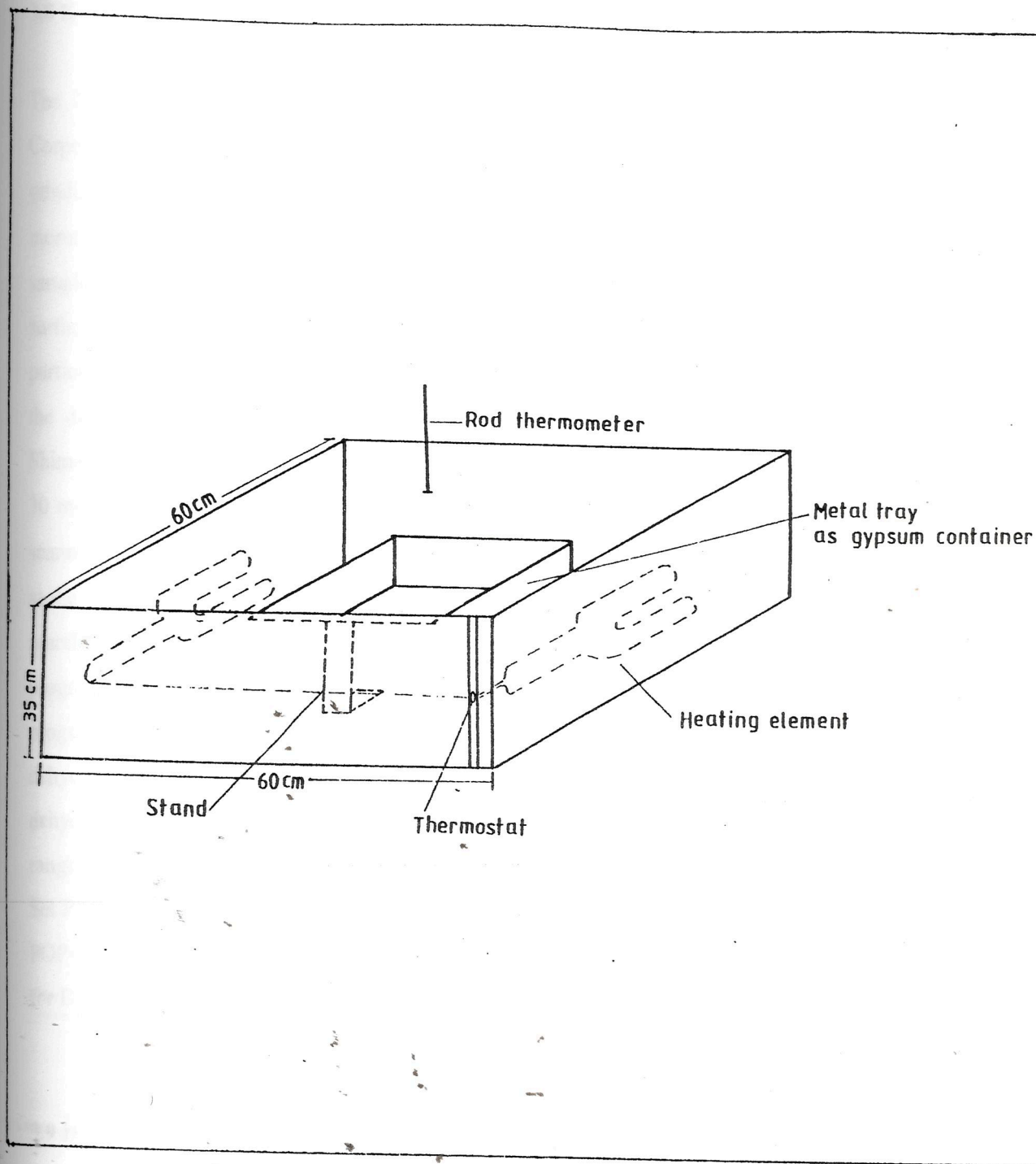


Figure 3.6 Proto-type oven used for calcining gypsum

3.8 X-ray diffraction analysis of gypsum and plaster-of-Paris powder

The X-ray diffraction analysis used was adopted as described by manuals of Shimadzu Corporation (1998). The gypsum crystals and plaster-of-Paris material were pulverised in a grinding machine for about three minutes and further ground manually using agate pestle and mortar. The ground sample was passed through the 100-mesh (150 μ m) sieve. The powdered sample was impressed into the hollow stainless steel holder with a glass plate until the powdered surface was ensured flat; and the particles of sample were homogeneously spread. The mineral particles were randomly oriented without preferred crystal faces placed in positions relative to the direction of X-rays. Samples were analysed by X-ray diffraction using the X-ray 6000 Shimadzu diffractometer. The copper X-ray tube was set at a voltage of 40 kV and a current of 30 mA. The divergence and scatter slits were used with the receiving slit set at 0.15mm. The scanning parameters were set as at 2θ for the drive axis; and 10° to 80° angle for the scan range at the rate of 2 degree/min. The emerging spectrograms were drawn using a computerised peak search method on the Personal Computer Powdered Diffraction File Windows (PCPDFWIN) programme. The X-ray diffraction patterns were compared with the standards on the computer programme. Selected temperature points of calcination covered a reasonable range for dehydration of gypsum to calcium sulphate hemihydrate. Partial and almost complete dehydration of gypsum was reflected by the X-ray diffraction spectrograms over the temperature range, which defined calcination levels of hemihydrate (POP) products at different temperatures. Set POP products were also analysed on the X-ray diffractometer as set POP-130 $^\circ$ C product and POP-175 $^\circ$ C product. Spectrograms for analysed samples were also drawn (International Centre for Diffraction Data, 1997).

3.9 Heat of reaction measurements

The heat-of-reaction measurements were made according to the simple calorimetric method given by Frantz and Malm (1961). The method was adapted to the experiment with POP by mixing it with water in the ratio 2:1 by weight. The mixing of reactants was done in a simple

calorimeter made from a polystyrene container. Temperature rise of the mixture due to the heat evolved by the POP/water reaction was measured for every 15 seconds for a period of 30 minutes. The polystyrene calorimeter was also standardised based on the water equivalent of the calorimeter with the use of two polystyrene calorimeters and accuracy of ± 0.1 °C at 1-minute interval for 3 minutes while temperature for 50ml of the cool tap water was also measured in the same manner. The cold tap water was quickly poured into the warm water in another calorimeter and the temperature readings were taken for another 3 minutes. A graph of the temperature change against time was plotted after average readings ($n=2$) of cold water, warm water (heated water), mixture of the cold (room temperature) and the warm water (Figure 3.7). The heat lost by the warm water to the calorimeter was calculated as the product of weight of water (1g/ml), increase in temperature (ΔT °C) and specific heat (1.0 cal/g) (Frantz and Malm, 1961). The heat lost to the calorimeter was determined by subtracting the heat gained by the cold water from the heat lost by the warm water. The water equivalent of the calorimeter was then calculated as the result of heat lost to the calorimeter divided by the temperature change between the cold water and warm water. By this method of standardisation, the water equivalent of the polystyrene calorimeter was determined as 38.1 J/°C. The temperature change due to heat of reaction for the POP/water mixture was measured and plotted into curves against time. According to Barrow (1961), the measurements of heat of reaction in the polystyrene calorimeter may be considered valid with the understanding that the POP-water reaction was fast and complete to produce the calcium sulphate dihydrate.

The calcium sulphate dihydrate products hardened with different levels of heat energy evolved from 100 °C-set, 130 °C-set and 175 °C-set products. The heat evolved from the reaction between POP and water in the mixture ratio of 2:1 by weight was calculated using the equation (13) below (Brown, 1961):

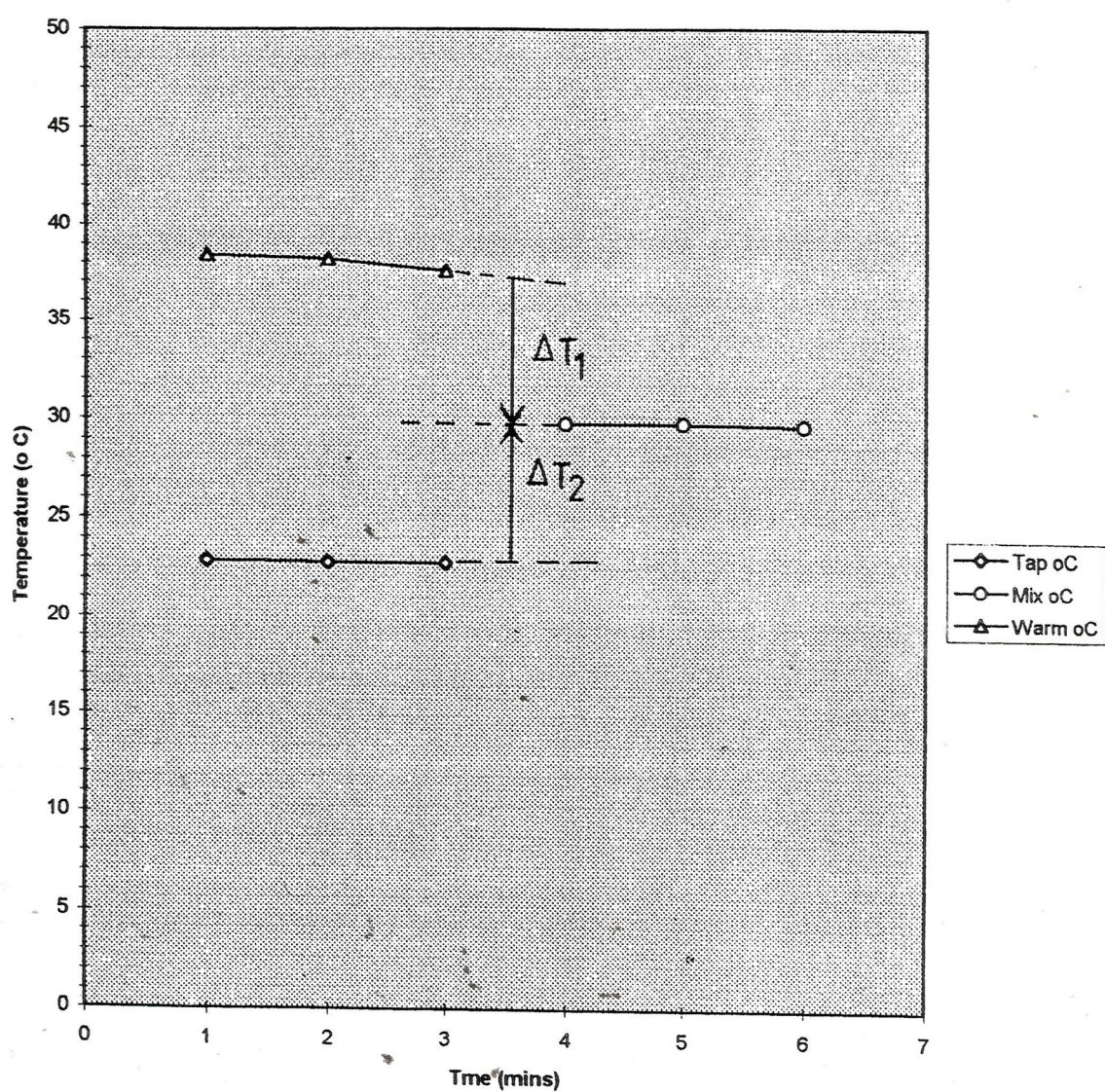


Figure 3.7 Time-temperature relationship for standardising polystyrene calorimeter with water

$$C_p = m \cdot s \cdot \Delta T \quad (13)$$

where C_p denotes the heat evolved, m denotes mass of the calcium sulphate dihydrate product, s denotes the specific heat capacity, and ΔT denotes the increase in temperature. The thermodynamic characteristics of the dihydrate products were identified with the calcined gypsum derived at definite temperature points.

3.10 Evaluation of plaster-of-Paris

The chalk-sticks were also analysed for CaO, SO₃, MgO, Fe₂O₃, Na₂O, K₂O, Cd and Pb using chemical methods already described to establish the chemical quality of the POP with regard to various applications (Börgarts, 1991). This marked the tests relative to the chemical composition of POP and also checked for deleterious elements that affect the quality of POP. Physical tests on chalk-sticks made were modulus of rupture (MOR), breaking-strength, and abrasion. MOR and breaking strength were determined according to Ryan and Radford (1987). The drying method to determine the moisture content was undertaken according to Malawi Bureau of Standards (1999). In this case, chalk-sticks of 10mm diameter and 5cm length were used. The diameter of each chalk-stick was measured twice to an accuracy of 0.01mm and averages were taken. The chalk-sticks were dried in an oven at 38°C for 24 hours and transverse breaking was conducted on each sample twice using the Modulus of Rupture Machine (M 20). The transverse breaking force was measured with the steel-rod supports set at 63mm apart. The breaking force was then applied with the electric motor pulley rolling the wire rope upwards until the chalk-stick ruptured into two separate pieces; and the kilogram force (kg-f) was read on an analog spring-balance synchronised to the rolling wire-rope. The modulus of rupture (MOR) was calculated using the formula expressed in equation 14 below (Ryan and Radford, 1987):

$$MOR = 8LD/\pi d^3 \quad (14)$$

where L denotes the breaking force, D denotes distance separating the supporting steel rods, d denotes diameter for the chalk-stick. The abrasion test was also conducted by streaking chalk-stick pieces of measured weight along 5 cm lines on silicon-carbide abrasive paper, and weighing the broken-off chalk grit on a digital balance (Ryan and Radford, 1987; MBS 187:

1999). Abrasive paper of grit No. 600 was used. The weight of the chalk-grit was expressed as a percentage of the weight piece under test.

3.11 Statistical analysis

The chemical and physical data were statistically analysed according to Till (1982). Means and standard deviations were calculated and compared at 95% confidence level ($p > 0.05$) of validation.

The grain size data from sieve tests were plotted into semi-logarithm curves as described by Leeder (1982) and Bloodworth (1990) respectively. Cumulative percentages passing through sieve sizes at 25%, 50% and 75% were denoted D_{25} , D_{50} and D_{75} respectively. The D_{25} , D_{50} and D_{75} were also used to represent the lower quartile (25%), median (50%), and upper quartile (75%) values of the grain size distribution curves. The grain size distribution in the sediment samples was quantified as sorting co-efficients calculated as the square root of the ratio D_{75}/D_{25} (Leeder, 1982). The *dambo* sediment samples were analysed for major oxides in duplicates. The chemical data generated from analyses of sediment samples were also averaged to characterise the major oxide content in the *dambo* sediments along pit profiles.

In the case of chemical data for groundwater, ranges of the data were tabulated to show extreme variations of values. Samples were also collected from different environmental conditions such as *dambo*, interfluvial slope and interfluvial crest. The significance of ionic concentrations was gauged by using the univariate analysis for the respective sample points and concentrations of calcium and sulphate ions and pH. Concentrations of Ca^{2+} and SO_4^{2-} ions and pH values were plotted as dot maps to portray the spatial variations with regard to types of environment for sampling. The Ca^{2+} and SO_4^{2-} ions were specifically chosen for the univariate analysis as the building units of the gypsum. The multivariate analysis as described in literature (Davis, 1986; Ratha and Sahu, 1993) was used to determine the inter-relationship between the ions, pH and Eh.

The multivariate inter-relationship was defined by correlation co-efficients calculated from chemical data for pairs of ions and chemical parameters.

The chemical species and parameters were characterised by ranges and means for individual chemical species with respect to seasons. The concentrations of chemical species in the borehole water varied from one location to the other and the magnitudes of variation were portrayed by the classified data sets for calcium, sulphate and pH. The classes of data were fixed by the customised data sets for calcium, sulphate and pH. The classes of the data were fixed by the customised method on the Mapinfo GIS software. The variation of the chemical data was spatially plotted as dot maps relative to geo-referenced sample stations on topographical survey maps. This provides a univariate analysis of spatial data for calcium, sulphate and pH for Dowa West.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Physico-chemical properties of rocks, *dambo* gypsum and sediments

4.1.1 Availability of calcium and sulphate ions in the Dowa West area

From the present studies, it is found that calcium ions originate from calcic-feldspar and calcic-amphibole due to weathering of the rocks. The rocks that release calcium ions are quartz-feldspar pegmatite and kyanite-hornblende schist (Piper *et al*, 1989). Minerals that provide calcium ions are plagioclase and calcium-rich hornblende in metamorphic rocks (Goldich, 1938). The sulphate ions emerge from the oxidation of pyrite appearing as a bright massive mineral in a dark background of silicate minerals as exhibited in Fig. 4.1. Pyrite formed in pelitic schistose rocks (Piper, 1994).

Mineral grains of plagioclase and hornblende were rarely encountered in the *dambo* sediments as they weathered to clay minerals and iron oxides as explained in equations 3 and 4 of Chapter 2. Calcium and sulphate ions were transported by surface and ground water to the *dambo* environment resulting in the increase in concentrations of ions in *dambo* sediments. The investigations into rocks and minerals revealed that sulphate ions form from the chemical weathering of pyrite in the rocks. Calcium was released from calcic-feldspars (plagioclase) and calcium-rich hornblende. The high concentration of the sulphate and calcium ions in solution led to precipitation of calcium sulphate dihydrate as gypsum.

4.1.2 *Dambo* stratigraphy and gypsum occurrence

The *dambo* stratigraphy was characterised by the 'Geosols' as shown in gypsum in Fig. 4.2, 4.3 and 4.4 (Botha, 1996). Gypsum profiles in Fig 4.2 indicated varied thickness to a depth of less than two metres. The top 'Geosol' consisted of muddy, dark mottled grey clay close to the Kasangadzi river course as shown in gypsum profile KSN1 in Fig 4.2. The middle 'Geosol'

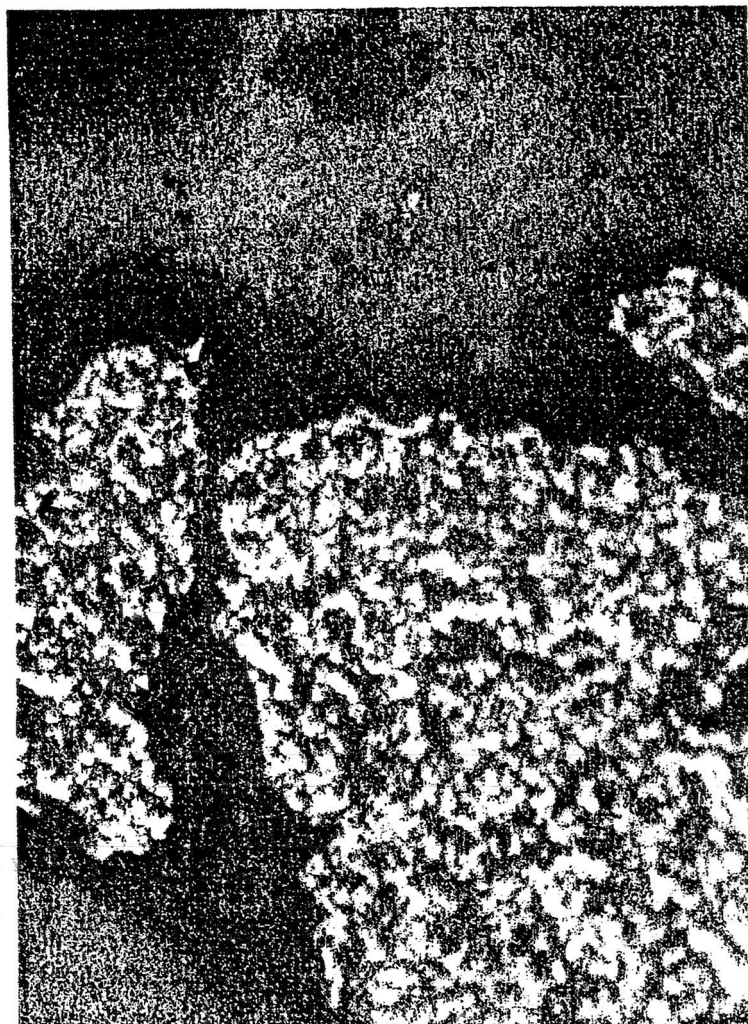


Figure 4.1 Microphotograph showing the pyrite (white) and altered rim (dark) of pyrite as goethite; the aluminosilicate minerals appear gray under reflected light in a polished section CH1 (Magnification X100)

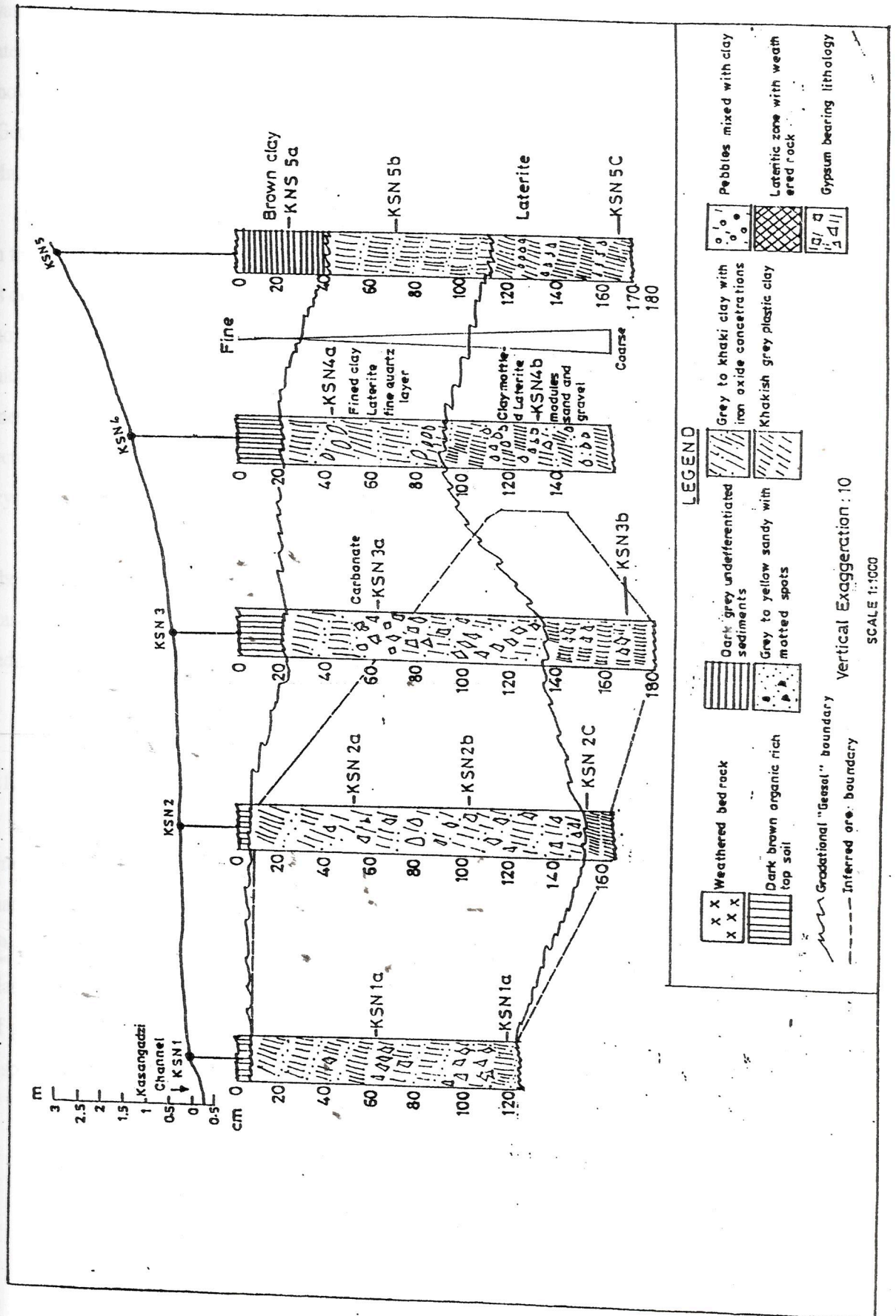


Figure 4.2 Gypsum profiles across Kasangadzi dambo

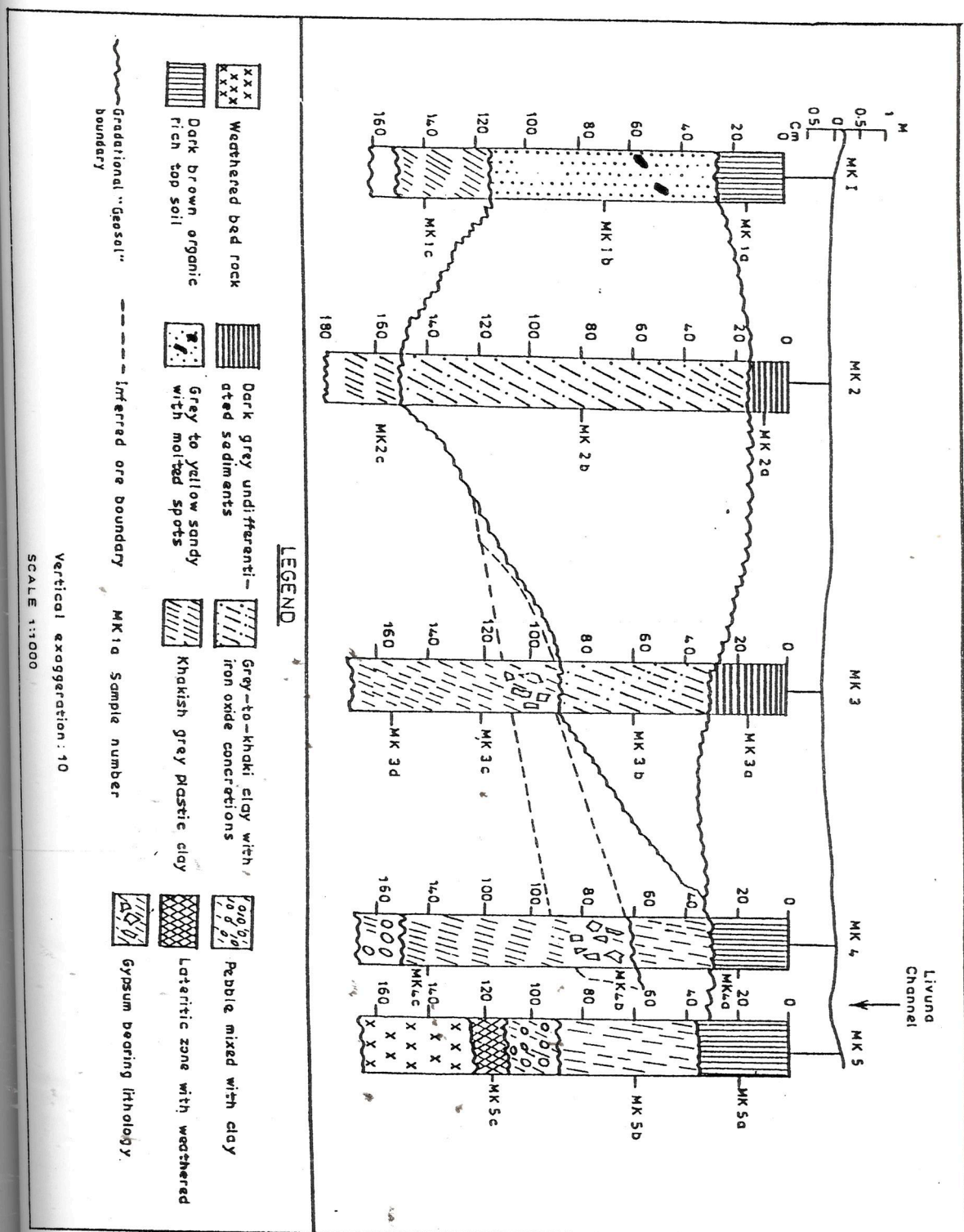
was enriched with gypsum crystals embedded in clay. The gypsum-rich 'Geosol' overlies the lateritic weathered zone farther down. This lateritic zone was modified to sandy, pebbly layer as shown in gypsum profiles MK 4 and 5 in Figure 4.3 for Livuna *dambo*. The gypsum-rich 'Geosol' was in some instances thin with a lot of sand and less clay as shown in Figure 4.4 for Machentche *dambo*.

In the three *dambos*, the gypsum-bearing zone was confined to the highly plastic clayey 'Geosol' as described by Freshney (1985). Gypsum crystals precipitated in the fine plastic clay that appear mottled with iron (II) oxidised to iron (III) (Walder and Chazev, 1995). This gypsum-profile thickened in plastic clay laden *dambos* such as Kasangadzi and Livuna compared to sand-rich ones as indicated by Machentche (Figure. 4.4). Large gypsum crystals (>2.8mm in diameter) were precipitated in the plastic clay covering Kasangadzi and Livuna *dambos*. Small gypsum crystals form in Machentche where grey sandy sediments are abundant.

The gypsum profiles indicated that gypsum-rich sediments are plastic-clay-rich 'Geosols' like in Kasangadzi *dambo*. Gypsum formed in association with the plastic clay layers. Quartz-rich sediments were extremely poor in gypsum as evidenced from Machentche profiles.

4.1.3 Grain size distribution of *dambo* sediments

Grain size distribution revealed that Kasangadzi gypsum profiles (Table 4.1, KSN series) were made up of alluvium with very fine grain size; hence, the sieve retained grains gave a median (D_{50}) in the upper quartile (D_{75}) range of 0.027 to 0.49mm. The gypsum-profile sediments were plastic clay laden with the average median diameter of $0.06\text{mm} \pm 0.03$ and provided the medium of gypsum crystallisation in Kasangadzi *dambo* (Fig. 4.2; Table 4.1). The grain size distribution also showed that Livuna (Table 4.1, MK series) and Machentche *dambo* gypsum profiles (Table



4.1, MCH series) are made up of moderately sorted sediments with less clay. The *dambos* were typified with average sorting co-efficients of 3.94 ± 1.09 for Livuna and Machentche (Table 4.2).

Large gypsum crystals occurred in fine grain size sediments in Kasangadzi *dambo* with a lot of clay. In such a situation, the grain size distribution was biased towards silt or mud (Figure 4.5). The sediments in Machentche contained a lot of quartz grains. They were better sorted in grain size distribution with a sorting coefficient of 3.94 ± 1.09 ; thus, the curves giving low clay content as shown in Figure 4.5.

Table 4.1: Grain size distribution and cumulative curve parameters

<i>Dambo</i> Site	Range (mm)	D ₂₅ (mm)	D ₅₀ (mm)	D ₇₅ (mm)	Sorting $\sqrt{D_{75}/D_{25}}$
Kasangadzi	0.027-0.49	NA	0.06 $\pm$ 0.03 (n=3)	0.36 $\pm$ 0.12 (n=3)	NA
Livuna	0.024-0.62	0.025 $\pm$ 0.001 (n=3)	0.089 $\pm$ 0.08 (n=7)	0.42 $\pm$ 0.19 (n=3)	3.94 $\pm$ 1.09 (n=3)
Machentche	0.021-0.50	0.034 $\pm$ 0.02 (n=9)	0.096 $\pm$ 0.08 (n=12)	0.33 $\pm$ 0.15 (n=12)	3.94 $\pm$ 1.09 (n=9)

Note: NA stands for Not Applicable

Large gypsum crystals (>1.4mm) in Kasangadzi gypsum ore occurred together with clay. The clay together with silt provided the grain size curves such as KSN 3a and 3b showing fine sand as retained material upon sieving. In contrast, large-mesh screens were used on the screen deck to trap large gypsum crystals while letting small gangue particles (clay) fall through. This grain size relationship assisted in having the coarse (>1.4mm) gypsum screened in large amounts. The sorted sediments from Livuna and Machentche provided small gypsum. Quartz was the most abundant gangue mineral. Very little clay made up the gypsum ores. This showed that the little clay reduced the likelihood of gypsum precipitating in the sediment layers of Livuna and Machentche *dambos*. No large gypsum particles (>1.4mm) formed in the two *dambos*.

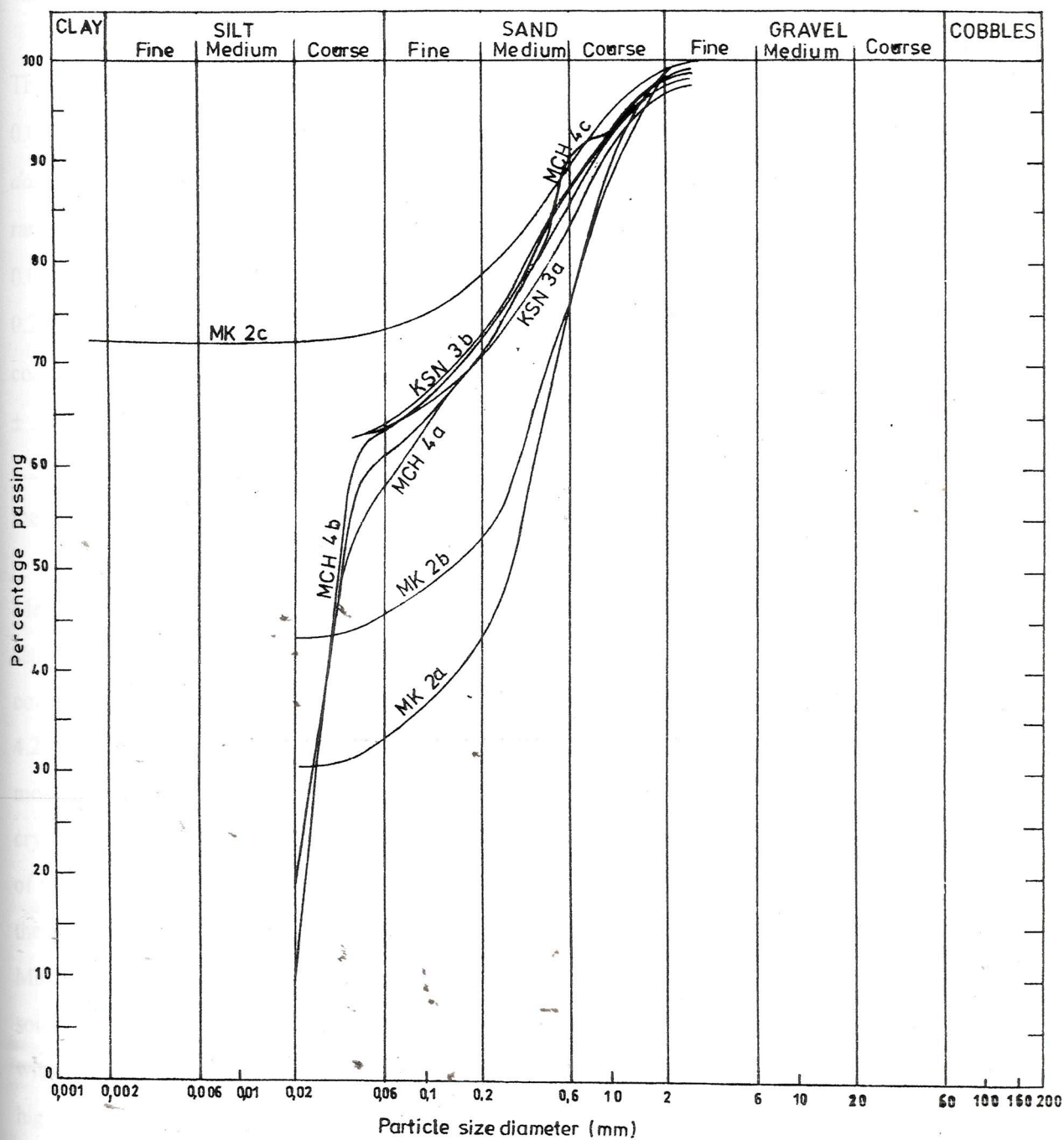


Figure 4.5 Cumulative grain size distribution curves for samples of Kasangadzi (KSN 3), Livuna (MK 2), and Machentche (MCH 4) dambos

4.2 Geochemistry of gypsum profiles of Dowa West *dambos*

4.2.1 Metal oxide contents of *dambo* gypsum profiles

The gypsum profiles in the three *dambos* indicated that the mean CaO content ranged from $0.08\% \pm 0.09$ to $3.75\% \pm 5.98$ in the gypsum profiles. However, CaO content was moderate over *dambos* with mean contents of $>1.80\%$ CaO (Fig. 4.2b; Table 4.2). The mean sulphate content ranged from $0.08\% \pm 0.13$ to $4.37\% \pm 0.58$ (Table 4.2). The mean MgO content gave a range of $0.04\% \pm 0.02$ to $1.39\% \pm 0.07$. The alkali oxides (Na_2O and K_2O) had mean ranges of $0.05\% \pm 0.2$ to $1.39\% \pm 0.07$ for Na_2O and $0.02\% \pm 0.01$ to $0.20\% \pm 0.01$ for K_2O . Silica and alumina contents indicated mean ranges of $23.16\% \pm 11.55$ to $65.67\% \pm 4.35$ and $7.23\% \pm 3.52$ to $15.97\% \pm 2.69$ respectively. The carbonate content was typified with a mean range of $1.65\% \pm 0.98$ to $5.25\% \pm 1.05$. Iron oxide content gave a mean range of $2.23\% \pm 0.03$ to $9.60\% \pm 3.96$. All these mean metal oxide contents were significant at 95% confidence level using two-tailed t-test.

Mean CaO contents were higher than the expected mean average abundance of 1.40% in sediments, except in some parts of Livuna and Machentche profiles (Goldshmidt, 1954). CaO content was a little high in profiles where gypsum mineralisation became predominant (Table 4.2). The mean sulphate contents were higher than the normal average abundance of 0.36% in most profiles, except one profile where most of the sulphate was taken up by the gypsum crystallisation process (Table 4.2). Mean iron oxides (Fe_2O_3) contents were a little high because of the lateritic nodules and dissolved iron oxides. Mean silica and alumina contents showed that the gypsum profiles were clay laden (Bloodworth, 1990). The high sulphate ion contents in Machentche and Livuna *dambo* indicated that the ions did not crystallise into gypsum owing to solubility conditions and interference from the sodium and potassium ions forming soluble salts within the local environment (Karacan and Yilmaz, 1997). The mean silica content was very high due to high quartz content in the gypsum profiles (Table 4.3). The mean silica and alumina contents were lower in Kasangadzi sediments due to clay minerals in contrast to quartz particles in the other two *dambos*. Mean carbonate concentrations was high in Livuna and Machentche profiles due to high dissolved carbon dioxide in groundwater leading to precipitation of calcium

carbonate nodules (Larsen and Chilingar, 1983). The mean alkali oxide contents depended on the extent to which sodium and potassium were released from the alkali bearing-minerals. Magnesium oxide content was based on its release from minerals such hornblende and biotite upon weathering (Walter, 1972).

4.2.2 Chemical composition of *dambo* gypsum

Gypsum from Livuna showed mean CaO content of $30.75\% \pm 0.98$. Mean sulphite content came to $54.58\% \pm 0.23$. Mean MgO content was extremely low with 0.0025%. Iron oxide came up to $0.19\% \pm 0.01$. Gypsum from Kasangadzi profiles indicated mean CaO content of $34.75\% \pm 1.05$. Sulphite content was 46.51 ± 0.36 whereas MgO content and iron oxide content were found to be 0.01% and 0.69% respectively. The mean CaO content range of $30.75\% \pm 0.98$ to $34.75\% \pm 1.05$ included the specification of 32.3% (Börgardtts, 1991). The mean sulphite content range of 46.51 ± 0.36 to $54.58\% \pm 0.23$ included an average of 46%. Other metal oxides contents were with acceptable limits. With consistent matching of results, Dowa West gypsum is of very good quality.

4.3 Groundwater chemistry and gypsum formation

Groundwater was sampled from borehole sites in the rainy and dry seasons respectively (Figure 3.4). The water samples collected in March, 1999 (rainy season) were typified by ion concentrations. The concentrations of K^+ and Fe^{3+} ranged from 0.95 to 35.15 ppm and 0 to 27.92 ppm respectively. Mg^{2+} and Na^+ ions gave concentrations with ranges of 0.63 to 168.94 ppm and 2.40 to 195.89 ppm respectively. Ca^{2+} and SO_4^{2-} ions indicated concentrations with ranges of 0.63 to 168.94 ppm and 2.40 to 195.89 ppm respectively. The mean concentrations of Ca^{2+} and SO_4^{2-} were calculated as 58.40 and 212.21 ppm respectively. The mean pH value was 6.80 whereas the mean Eh was 0.02 V.

In the dry season (November 1999), the concentrations of K^+ and Fe^{3+} remained low by showing ranges of 0.40 to 55.58 ppm and 0 to 5.55 ppm; and means of 7.05 ppm for potassium and 28

Table 4.2 Metal oxide contents (%) in the Kasangadzi, Livuna, and Machentche gypsum profiles

Site and Profile No.	CaO	MgO	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	CO ₃ ²⁻	Fe ₂ O ₃	SO ₄ ²⁻
Kasangadzi									
KSN1 (n=4)	1.84±1.19	1.39±0.07	0.65±0.07	0.32±0.38	27.26±0.01	15.97±2.69	3.88±0.85	8.20±4.43	0.37±0.23
KSN2 (n=4)	1.89±1.05	1.21±0.52	0.56±0.24	0.25±0.23	23.16±11.55	13.85±5.64	2.98±1.31	7.71±2.58	0.33±0.13
KSN3 (n=4)	1.95±1.20	1.14±0.44	0.57±0.23	0.21±0.18	23.87±10.68	13.17±5.06	2.81±1.12	7.34±2.58	0.61±0.96
KSN5 (n=6)	0.33±0.09	0.42±0.11	0.38±0.09	0.07±0.01	41.85±5.56	13.24±2.87	1.65±0.98	8.38±1.38	0.66±0.58
Livuna									
MK1 (n=6)	0.27±0.40	0.33±0.27	0.05±0.03	0.22±0.07	65.67±4.35	10.82±1.10	5.25±1.05	8.67±2.45	4.37±1.06
MK2 (n=6)	0.20±0.26	0.42±0.27	0.05±0.02	0.16±0.07	54.80±21.74	7.57±4.74	4.20±1.59	9.60±3.96	3.79±1.30
MK3 (n=8)	2.29±5.59	0.42±0.25	0.05±0.04	0.15±0.06	53.60±19.37	7.66±4.01	3.88±1.43	8.73±3.99	3.83±1.37
MK4 (n=6)	2.43±4.85	0.53±0.29	0.08±0.05	0.13±0.07	53.72±18.56	7.23±3.52	3.72±1.35	8.13±3.71	4.13±1.76
MK5 (n=6)	2.22±4.40	0.54±0.28	0.09±0.07	0.12±0.07	53.91±18.66	7.33±3.31	3.79±3.77	7.33±3.77	4.11±1.39
Machentche									
MCH3 (n=4)	0.08±0.09	0.05±0.01	0.44±0.22	0.02±0.01	43.90±11.62	12.39±0.47	4.35±0.84	2.23±0.03	1.14±0.93
MCH4 (n=6)	2.21±4.97	0.04±0.02	0.27±0.19	0.02±0.01	40.37±17.14	10.42±4.41	4.29±1.73	2.38±1.17	0.80±0.53
MCH5 (n=4)	3.75±5.98	0.05±0.02	0.37±0.31	0.021±0.01	43.27±19.36	10.37±4.22	4.52±1.94	2.59±1.24	0.99±0.87

ppm for iron. In the dry-season (November, 1999), the pH mean rose to 8.37 whereas the Eh mean dropped to - 0.06V.

The concentration of calcium was affected by dilution as groundwater increased due to infiltration of rainwater into the ground in the rainy season (Mc Farlane, 1992). Increased concentration of sulphate ions may be attributed to sulphate ions forming due to oxidation of sulphur to the sulphate around pyritic rocks (Thomas, 1974). The Change in seasons led to concentration of iron becoming much lower in the dry season than in the wet season.

Concentrations of Na^+ and Mg^{2+} ions dropped with mean concentrations being less than 20 ppm. The concentration of Ca^{2+} increased because of restricted groundwater whereas that SO_4^{2-} concentration decreased reflecting less release of the ions through oxidation of sulphur in pyrite.

4.3.1 Solubility products of calcium and sulphate ions

With the solubility product limit at a $\log_{10}$ of -5.52 for calcium sulphate, borehole sites showed relatively high values of calculated solubility products for the rainy-season (March, 1999) in Table 4.3. The boreholes with high solubility products were Kabata (MS002), James Madise (R34), Mpatsa (P47), Mlengwe (KB54), Mandala (DW62), Kachisa (RJ 79), Mphimbi (Z82) Kabwinja (KB 130), Sendeza (JG 145), Kashangula (X183), Kayembe Health Centre, and GSD Mponela.

In the dry season (November, 1999), borehole sites that yielded high calculated solubility products as shown in Table 4.3 were Mandala (DW62), Kachisa (RJ 79), Mphimbi (Z82) Kabwinja (KB 130), Sendeza (JG 145), Kashangula (X183), Kayembe Health Centre, Kabata (MS002), James Madise (R34), Mpatsa (P47), Chitete (Z83), Mbewa (R155), and GSD Mponela.

For the two seasons, high solubility products were yielded at boreholes named Kabata, Mpatsa, Kashangula, and GSD Mponela all situated in the dambo environment. High solubility products were also obtained on the interfluvial slopes at sites Kachisa (RJ 79), Mphimbi (Z82) and KB 130. On high ground, high solubility products ($\log$ values >-5.52 ; Table 4.3) were obtained at borehole sites named James Madise (R34) and Mandala (DW 62). These high solubility products obtained for the rainy season matched with the increase in concentrations of calcium and sulphate due to ions being released in solution by rainwater from their sources on the surface and underground. The recharge of the aquifer (groundwater rock reservoir) in the rainy season was associated with increase in borehole sites with high solubility products (Mc Farlane, 1992).

Table 4.3 Solubility Products of Calcium and Sulphate Ions in Borehole Water Sampled from the Dowa West Area

Field Location or Borehole No.	November, 1999				March, 1999				Geo-environment	
	Ca ²⁺ Mol/l	SO ₄ ²⁻ Mol/l	[Ca ²⁺][SO ₄ ²⁻] Mol/l	Log ₁₀	Ca ²⁺	SO ₄ ²⁻	[Ca ²⁺][SO ₄ ²⁻]	Log ₁₀		
Kabata MS002	6.38 x 10 ⁻³	4.21 x 10 ⁻³	2.69 x 10 ⁻⁵	-4.57094	2.27 x 10 ⁻³	5.57 x 10 ⁻³	1.26 x 10 ⁻⁵	-4.8981	Dambo	
Kachisa II MS022	5.52 x 10 ⁻⁴	4.81 x 10 ⁻³	2.65 x 10 ⁻⁶	-7.57608	3.75 x 10 ⁻⁴	3.10 x 10 ⁻⁴	1.16 x 10 ⁻⁷	-6.93461	Interfluve Slope	
Dzoole DEC RS030	2.65 x 10 ⁻⁴	1.60 x 10 ⁻³	4.26 x 10 ⁻⁷	-8.3711	2.95 x 10 ⁻⁴	2.08 x 10 ⁻⁴	6.14 x 10 ⁻⁸	-7.21211	Interfluve Slope	
Mkulumbimba KB060	8.50 x 10 ⁻⁵	1.08 x 10 ⁻³	9.16 x 10 ⁻⁸	-8.03833	1.01 x 10 ⁻⁴	4.16 x 10 ⁻⁴	4.2 x 10 ⁻⁸	-7.37659	Interfluve Slope	
Kabulungo DW10	1.39 x 10 ⁻³	8.43 x 10 ⁻³	1.17 x 10 ⁻⁵	-6.93146	1.99 x 10 ⁻³	3.12 x 10 ⁻³	6.21 x 10 ⁻⁶	-6.20699	Interfluve Slope	
James Madise R34	3.68 x 10 ⁻³	1.01 x 10 ⁻³	3.72 x 10 ⁻⁶	-5.42943	1.68 x 10 ⁻³	3.44 x 10 ⁻³	5.78 x 10 ⁻⁶	-5.23813	Interfluve Slope	
Chakhaza DW62	5.40 x 10 ⁻⁴	5.15 x 10 ⁻³	2.78 x 10 ⁻⁶	-7.55615	5.36 x 10 ⁻⁴	2.08 x 10 ⁻⁴	1.11 x 10 ⁻⁷	-6.95277	Interfluve Slope	
Nyongani DW47	5.52 x 10 ⁻⁴	1.55 x 10 ⁻⁴	8.54 x 10 ⁻⁸	-7.06871	1.28 x 10 ⁻⁴	2.08 x 10 ⁻⁴	2.66 x 10 ⁻⁸	-7.57473	Interfluve Slope	
Mpatsa P47	2.97 x 10 ⁻⁴	2.35 x 10 ⁻⁴	6.98 x 10 ⁻⁸	-7.15618	8.15 x 10 ⁻⁴	7.29 x 10 ⁻³	5.94 x 10 ⁻⁶	-5.22611	Dambo	
Mlengwe KB54	2.76 x 10 ⁻⁴	1.05 x 10 ⁻⁴	2.89 x 10 ⁻⁸	-7.53916	4.41 x 10 ⁻³	1.04 x 10 ⁻³	4.59 x 10 ⁻⁶	-5.33853	Interfluve Slope	
Mandala DW62	9.20 x 10 ⁻⁵	5.00 x 10 ⁻³	4.61 x 10 ⁻⁸	-4.33605	4.67 x 10 ⁻³	1.67 x 10 ⁻²	7.8 x 10 ⁻⁵	-4.10797	Interfluve Slope	
Kachisa I RJ79	1.08 x 10 ⁻³	2.40 x 10 ⁻⁴	2.6 x 10 ⁻⁷	-6.58518	3.25 x 10 ⁻³	5.21 x 10 ⁻⁴	1.69 x 10 ⁻⁶	-5.77128	Interfluve Slope	
Mphimbi Z82	2.04 x 10 ⁻³	8.95 x 10 ⁻⁴	1.82 x 10 ⁻⁶	-7.3934	1.29 x 10 ⁻³	4.17 x 10 ⁻³	5.38 x 10 ⁻⁶	-5.26927	Interfluve Slope	
Chitete Z83	9.96 x 10 ⁻³	3.74 x 10 ⁻³	3.72 x 10 ⁻⁵	-4.42894	1.55 x 10 ⁻⁴	4.17 x 10 ⁻⁴	6.46 x 10 ⁻⁸	-7.18953	Interfluve Slope	
Mdika DEC MM88	3.82 x 10 ⁻⁴	1.36 x 10 ⁻⁴	5.19 x 10 ⁻⁸	-7.28488	7.13 x 10 ⁻⁴	3.12 x 10 ⁻⁴	2.22 x 10 ⁻⁷	-6.65276	Interfluve Slope	
GM99	5.38 x 10 ⁻⁵	6.16 x 10 ⁻⁵	3.31 x 10 ⁻⁹	-8.48031	6.27 x 10 ⁻⁵	1.04 x 10 ⁻³	6.52 x 10 ⁻⁸	-7.1857	Interfluve Slope	
KB130	8.66 x 10 ⁻⁵	4.43 x 10 ⁻⁵	3.84 x 10 ⁻⁹	-4.41604	5.86 x 10 ⁻⁵	1.46 x 10 ⁻²	8.56 x 10 ⁻⁵	-4.06775	Interfluve Slope	
Sendeza JG145	8.49 x 10 ⁻⁴	5.65 x 10 ⁻⁴	4.8 x 10 ⁻⁷	-6.31906	1.35 x 10 ⁻³	1.04 x 10 ⁻²	1.4 x 10 ⁻⁵	-4.85263	Interfluve Slope	
Nihondowa JG145	1.91 x 10 ⁻⁴	7.56 x 10 ⁻⁴	1.44 x 10 ⁻⁷	-6.8406	3.00 x 10 ⁻³	1.04 x 10 ⁻³	3.12 x 10 ⁻³	-8.50585	Interfluve Slope	
Mbewa RI55	7.64 x 10 ⁻⁴	2.58 x 10 ⁻³	1.97 x 10 ⁻⁶	-5.7048	2.17 x 10 ⁻⁴	3.12 x 10 ⁻³	6.77 x 10 ⁻⁷	-6.16939	Interfluve Slope	
Kaufa EI58	9.12 x 10 ⁻⁴	4.22 x 10 ⁻³	3.85 x 10 ⁻⁶	-7.4147	9.90 x 10 ⁻⁴	1.04 x 10 ⁻³	1.03 x 10 ⁻⁸	-7.98733	Interfluve Slope	
Kashangula X183	1.80 x 10 ⁻⁴	5.67 x 10 ⁻⁵	1.02 x 10 ⁻⁸	-7.9908	5.83 x 10 ⁻³	1.04 x 10 ⁻²	6.06 x 10 ⁻⁵	-4.2173	Dambo	
Mdika Sch. A239	2.55 x 10 ⁻⁴	1.02 x 10 ⁻⁴	2.6 x 10 ⁻⁸	-7.58491	1.99 x 10 ⁻⁴	3.12 x 10 ⁻⁴	6.21 x 10 ⁻⁸	-7.20699	Interfluve Slope	
Kamphenga PI 437	5.30 x 10 ⁻⁴	1.46 x 10 ⁻⁵	7.73 x 10 ⁻⁹	-8.11166	4.58 x 10 ⁻⁴	1.04 x 10 ⁻⁴	4.76 x 10 ⁻⁸	-7.3221	Interfluve Slope	
Kabanga S/W	5.41 x 10 ⁻⁴	5.18 x 10 ⁻⁴	2.8 x 10 ⁻⁷	-6.5528	5.31 x 10 ⁻⁴	1.25 x 10 ⁻³	6.64 x 10 ⁻⁷	-6.178	Dambo	
Kachiwale GK	2.44 x 10 ⁻⁴	2.76 x 10 ⁻⁴	6.74 x 10 ⁻⁸	-7.17131	8.33 x 10 ⁻⁴	4.17 x 10 ⁻⁴	3.47 x 10 ⁻⁷	-6.45922	Dambo	
Kawere CBM	4.77 x 10 ⁻⁴	5.30 x 10 ⁻⁵	2.53 x 10 ⁻⁸	-7.59681	3.42 x 10 ⁻⁴	2.08 x 10 ⁻⁴	7.11 x 10 ⁻⁸	-7.14791	Interfluve Slope	
Kayembe H/C	8.81 x 10 ⁻⁴	3.43 x 10 ⁻⁴	3.02 x 10 ⁻⁷	-6.51995	1.56 x 10 ⁻³	1.56 x 10 ⁻³	2.43 x 10 ⁻⁶	-5.61375	Interfluve Slope	
GSD Mponela	7.32 x 10 ⁻⁴	1.73 x 10 ⁻⁴	1.27 x 10 ⁻⁷	-6.89713	2.58 x 10 ⁻³	3.85 x 10 ⁻³	9.93 x 10 ⁻⁶	-5.00292	Dambo	

The solubility products values for some sites remained greater than the solubility product constant (log value > -5.52) due to local concentrations of calcium and sulphate ions despite the change in seasons. The sites with such values were Kabata, Mpatsa and Kashangula. These sites are favourable lead sites for locating gypsum-bearing *dambos* in Dowa West. However, the other sites with seasonal high values can also be used to identify gypsum occurrences near borehole sites such as GSD Mponela, Kayembe Health Centre, Sendeza (JG 145), Kabwinja (KB 130), Mphimbi (Z82), Mandala (DW 62), Kachisa (RJ 79), and James Madise (R34).

4.3.2 Thermodynamics and environmental conditions of *dambo* gypsum

Dambo gypsum crystallised with $\Delta S^{\circ}_{\text{universe}} = +3363.3 \text{ J/K/mole}$ which is much greater than zero. The reaction between calcium sulphate and water was inherently characterised by a drop in energy level by losing -1018 kJ/mole to the surrounding. This proved that thermodynamic conditions in the *dambos* favoured the formation of gypsum in Dowa West area. Gypsum crystallised in groundwater with reducing conditions for most chemical species; thus, giving a redox potential ranging from -0.012 V to +0.113 V and a pH ranging from 5.12 to 8.84 (Figure 4.6). The pH plotted from low pH (5) to neutral pH (7) for the rainy season, and from above pH 7 to high pH (9) for dry season. The redox potentials changed from high to low in the rainy season and from almost zero to negative in the dry-season.

From Figure 4.6, it was established that precipitation of gypsum occurred under reducing acidic (pH < 6) conditions in the rainy season and reducing basic (pH > 8) conditions in the dry season (Krauskopf, 1967). It was also shown that gypsum precipitation in the *dambos* first depends on the availability of sufficient source of sulphate ions resulting from oxidation of pyrite or other sulphur-bearing minerals. Secondly, calcium ions were supplied from the degradation of calcic-

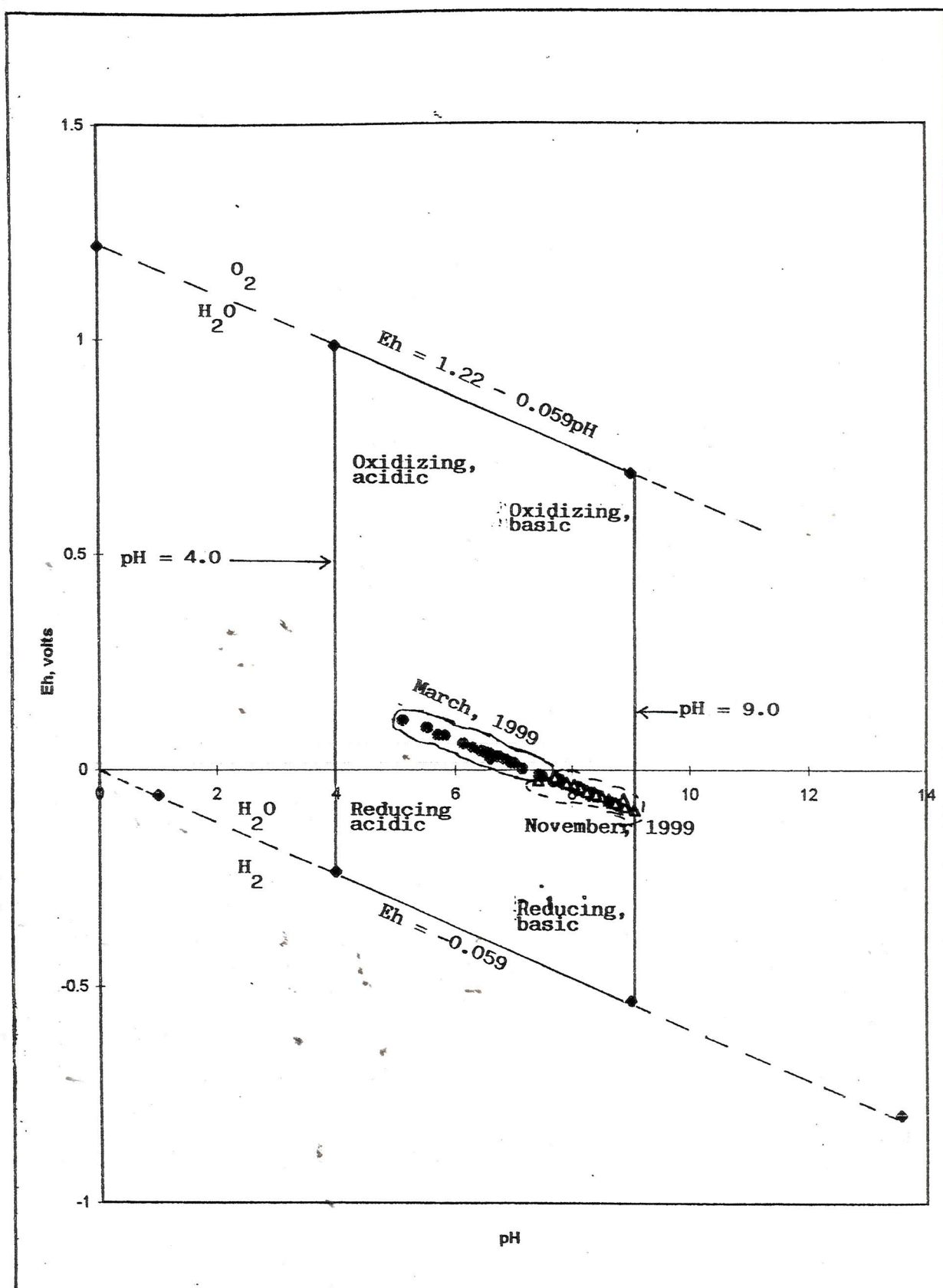


Figure 4.6 Plot of water samples relative to the Eh/pH conditions of the near surface environment in the parallelogram (Krauskopf, 1967)

feldspars and calcic-amphiboles contained in the Dowa West metamorphic rocks. Thirdly, the dambo clay-mineral layers acted as the medium of gypsum crystallisation (Figures 4.2, 4.3 and 4.4). Fourthly, semi-arid conditions prevailed to give high solar heat influx that accelerates crystallisation of gypsum through loss of water by evaporation.

4.3.3 Univariate analysis of calcium, sulphate and pH

The spatial variation map of calcium concentration in the dry season indicated very high concentration in the range 283 to 490 ppm for boreholes located at Chitete (Z83), R34, Dokotala (DW62), Nauchi, KB130 and MS002 (Figure 4.7). The southern dot cluster from Kawere down to Katanga through Khumbulasi, Kachisa (JG145) and Kayembe (Ky H/C) represented low concentrations of calcium (<61ppm). The rest of the dot points were within the medium concentration classes of 61 to 172ppm and 172 to 283ppm. In the rainy season as portrayed in Figure 4.7, relatively high concentrations of calcium (162 to 275ppm) are shown in borehole water at DW62, Kashangula (X183), KB54 and KB130.

The bulk of the water samples were characterised by low calcium concentrations falling in two classes in the range 0 to 100ppm. High concentration dots (331 to 530ppm) for sulphate shown in the dry season in Figure 4.7 were confined to boreholes at Mandala (DW62), Z82, KB130 and Kabata (MS002). Most of the low sulphate concentrations (<66ppm) covered the dot-cluster from Kawere down to Chatanga through Kachiwale and Kachisa (JG145). This pattern is similar to that of calcium. In the rainy season as shown in Figure 4.6, high concentration dots for sulphate (800 to 1600ppm) emerge at locations such as Mandala (DW62), KB130, and Kashangula (X183). Most ion concentration dots fall into the low classes (<140ppm), except for Z82, James Madise (R34) and Kabata (MS002) that occur among those with high pH values.

DW 5.6 • Chikn above
 • Chigondalipanga
 • Chikrow DW 5.2 • De Motola
 • DW 36
 • R156
 • K32A
 • KSJMN
 • KCBM/Kuweere
 • GM 39
 • X181
 • GSD/Mponela
 • Simbi • SM/Motola
 • Kumbulasi
 • DW 47
 • Kalwinda
 • KBN30
 • GML5/SW
 • PI 437
 • W5/Kachigole
 • MS002 • DW10
 • R155 • SW/Sindeya
 • PL7
 • MS28
 • Z82
 • Lipiti
 • E156
 • A239
 • R179
 • MS22
 • JG145/Kachiso
 • KB 060
 • KB 52
 • Chisepo DEC
 • Chidanga
 • KYH/C
 • R5 020
 • Z 83

Calcium (Water) in ppm

Dry Season

283 to 430

172 to 283

51 to 171

0 to 51

DW66 • Chiknobwe
 Chigondipenga • DW52
 Machi • Chikwowe
 DW36 •
 GK14.5/SW → R456
 KB130 • Kabwinja • KSJMN
 W47 •
 SW/Kabanga • GM 99
 SW/Matola • GS O/Mponela
 MS002 • MS23 • MS28 •
 PI 437 • SW/Sindeya • P4.7
 E156 • JG14.5 • JG14.5/Kachiso • Z32
 M33 •
 Chisepo DEC • KB060 • KB54
 KYH/C
 Chatanga •

Calcium/Water in ppm
 Wet Season
 152 to 275
 100 to 152
 37 to 100
 0 to 37

Chiganduenga
 W3M
 Chikwawe
 SM 212
 W116
 Machi
 R155
 G145/35
 K1330
 DW47
 Kachwija
 SW/Kachwija
 Simbi
 G50/Manzela
 CBM/Kwera
 G1439
 XT181
 Kimbuluti
 Z 81
 P 47
 MS 28
 SW Kachwate
 MS 28
 R155
 DW7
 SW/Sindaya
 Lipiti
 RS 030
 Z01
 JG175
 MS022
 R173
 K852
 G145/Kachwija
 MS022
 R173
 A238
 M18
 K0860
 Chiganga
 KYH/C
 Chisepo DEC
 Supphat/Wattapin
 Dry Season
 111 64 51.0
 13960 137
 86 60 139
 0 14 16

The map displays the study area with various sampling stations marked by dots and labeled with codes. The stations are distributed across the map, with some clustered together and others more isolated. The map also shows the coastline and the location of the study area relative to the surrounding land.

Sampling Stations:

- W311
- SM212
- OW62
- OW66
- OW68
- OW69
- OW70
- OW71
- OW72
- OW73
- OW74
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- OW467

Chisapo DEC
Chattanooga

KR 130
GK165/SW
Kabwemja
SW/Kabanga
GM 39
SW/Matola
GSD/Mponela

W 311
SM 212
OW 36
R 3
K 5/MN

MS 28
MS 002
P 47
Z 32
RS 030
Z 03

E 156
JG 145
M 88 A 229
K 3 050
K 8 56
KYN/C

JG 165/Kachisa

Water [Borehole] pH
Dry Season

3.73 to 3.06
3.43 to 3.73
3.12 to 3.43
2.82 to 3.12
2.72 to 2.82
2.70 to 2.72

Chisepo DEC ————— Chirango —————

• W 311
• W 31 • SM 212
• W 31 • DW 36
• R 34
• R 32
• R 31
• R 30
• R 29
• R 28
• R 27
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• R 8
• R 7
• R 6
• R 5
• R 4
• R 3
• R 2
• R 1

• K 145/SW
• K 143 Kobwinia
• K 141
• K 139
• K 137
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• K 133
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In the dry season as shown in Figure 4.7, pH was high (>7.38) as reflected by the dot cluster from location GSD Mponela to M88. Nucleated dots around Kabata (MS002) and its neighbouring boreholes also displayed high pH values. A few locations showed low pH (<6.36). The dots for calcium ion concentration coincided with alkaline conditions with a mean pH of 8.30. The groundwater certainly leached out the calcium from aluminosilicate minerals in the Dowa West area following mineral degradation series (Walter, 1972; Thomas, 1974). The sulphate ions emerged from near-surface pyritic rocks through leaching by the groundwater (Thomas, 1974); thus, giving a few large concentration dots for Kashangula (X183), KB130, and Mandala (DW62) for both seasons in Figure 4.7. The potential targets for exploration of gypsum may be inferred from the high concentration dots for calcium and sulphate on maps for both the rainy- season and the dry season in the near-*dambo* environment. The *dambo* areas around boreholes KB130, Mandala (DW62), Kabata (MS002) and Kashangula (X183) can be explored for gypsum as the high concentration dots of calcium and sulphate ions coincided at these localities (Figure 4.7). The spatial variation of the ion concentrations provide a way of locating gypsum occurrences in the *dambos*. However, this can be combined with the results with high solubility product values to characterise the spatial variations of gypsum-bearing *dambos*.

4.3.4 Multivariate analysis of major ions, pH and Eh

The multivariate analysis showed that K^+ , Na^+ , Mg^{2+} and Ca^{2+} indicated good positive correlation co-efficients ($> +0.67$) in the rainy- season (Table 4.4a). Sulphate ion correlated very highly with the four aforementioned cations yielding correlation co-efficients $> +0.82$. These were tending to be best correlated (Davis, 1986). The pH and Eh showed extremely high negative correlation (-0.99) as the best negatively correlated level; and this relationship did not change in the dry season (Table 4.4b). Iron was weakly correlated with all the ions and chemical parameters. The bicarbonate (HCO_3^-) ion was poorly positively ($+0.42$) correlated with pH and poorly negatively (-0.46) correlated with Eh. Eh and Fe^{2+}/Fe^{3+} showed no correlation with each other (-0.11).

In the dry season in November, 1999 (Table 4.4b), a very strong positive correlation (+0.92) emerged between Ca^{2+} and SO_4^{2-} . Good correlation (+0.70) marked the relationship between Mg^{2+} and Ca^{2+} as alkaline metallic ions. Potassium ion (K^+) indicated weak positive correlation with Ca^{2+} (+0.32), pH (+0.38) and a weak negative correlation with Eh (-0.39). Eh, pH and Fe^{2+}

4.4 Opportunities for processing of the Dowa West gypsum ore

4.4.1 Mineral grain quantification

Values of gypsum contents in the *dambo* sediments after sieving are indicated in Table 4.6. These values show that the gypsum crystals in the sediment profiles are predominantly in Kasangadzi *dambo* with >50% particles being < 2.8mm in diameter. However, gypsum crystals with >2.8mm diameter were recovered average amounts of 7.58% for Kasangadzi, 12.67% for Livuna, and 0.22% for Machentche. Quartz grains were abundant (>20%) in -2.8/ +1.4 mm size fractions. The gypsum particles included in these size fractions (Table 4.6) proved difficult to separate by screening due to gypsum being of equal size with quartz (Daniel, 1986). In Kasangadzi samples gypsum occurs together with lateritic nodules with the diameter ranging from 6.3 to 1.3 mm. Very little quartz was encountered in Kasangadzi samples. Carbonate nodules were abundant (>10%) in Livuna and Machentche samples (Table 4.6).

Mineral grain quantification has shown that gypsum occurs in association with lateritic nodules in Kasangadzi *dambo* and with quartz in Livuna and Machentche *dambos* respectively. Gypsum would easily be separated from the gangue, mineral waste, when it is abundant in one size fraction compared to the others with abundant gangue. The presence of clay particles in contrast to particulate minerals in gypsum ore allows the clay to be removed by washing through sieves.

Table 4.4: Correlation matrix for metal ions and parameters-
(a) rainy season-March, 1999

Variable	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Fe ²⁺ /Fe ³⁺	SO ₄ ²⁻	HCO ₃ ⁻	pH	Eh
K ⁺	1								
Na ⁺	0.719	1							
Mg ²⁺	0.785	0.876	1						
Ca ²⁺	0.755	0.737	0.673	1					
Fe ²⁺ /Fe ³⁺	-0.398	-0.255	-0.269	-0.178	1				
SO ₄ ²⁻	0.890	0.878	0.868	0.823	-0.461	1			
HCO ₃ ⁻	0.140	0.109	0.198	0.328	0.482	0.026	1		
pH	0.242	-0.058	-0.005	0.217	0.108	0.0530	0.415	1	
Eh	-0.189	0.078	-0.012	-0.167	-0.113	-0.019	-0.457	-0.992	1

(b) dry season-November, 1999

Variable	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Fe ²⁺ /Fe ³⁺	SO ₄ ²⁻	HCO ₃ ⁻	pH	Eh
K ⁺	1								
Na ⁺	0.060	1							
Mg ²⁺	0.239	-0.073	1						
Ca ²⁺	0.317	0.130	0.679	1					
Fe ²⁺ /Fe ³⁺	-0.058	0.249	-0.127	0.336	1				
SO ₄ ²⁻	0.206	0.089	0.704	0.920	0.207	1			
HCO ₃ ⁻	-0.068	0.154	0.204	0.338	0.263	0.265	1		
pH	0.382	0.138	0.150	0.207	0.067	0.064	0.410	1	
Eh	-0.385	-0.010	-0.145	-0.211	-0.044	-0.049	-0.435	-0.983	1

Fe²⁺/Fe³⁺ represents total iron content

Table 4.5 Results of mineral grain quantification

Site No.	No.	Size Fraction (mm)	Weight Retained (g)	Gypsum (%)	Laterite (%)	Quartz (%)	Carbonate nodules (%)
Livuna	MK	M +6.3	470.6	0	0.62	0.47	14.04
		K -6.3/+2.8	1183.5	1.25	11.16	1.67	18.82
		4 -2.8/+1.4	2513.9	2.18	8.07	56.18	13.60
	LM	M +6.3	122.2	1.11	0	1.76	7.48
		K -6.3/+2.8	425.2	3.63	3.76	16.46	7.93
		5 -2.8/+1.4	2412.0	13.34	13.87	23.32	7.34
	LM	L +6.3	1317.5	12.23	0.31	0.33	0
		M -6.3/+2.8	2163.3	20.09	4.11	20.41	1.98
		9 -2.8/+1.4	2124.4	11.14	3.86	29.98	3.15
Kasangadzi	KSN	2 +6.3	104.4	0.15	0.11	0	2.04
		a -6.3/+2.8	850.5	11.07	5.54	0.009	1.61
		-2.8/+1.4	3680.9	56.18	15.41	3.85	3.88
	b	2 +6.3	303.4	0	1.81	0	4.29
		-6.3/+2.8	1915.7	3.94	32.73	2.14	0
		-2.8/+1.4	2724.0	6.47	26.62	22.01	0
Machentche	6	+6.3	548.7	0	0.15	3.28	6.25
		-6.3/+2.8	1569.5	0	10.06	10.48	10.06
		+2.8/1.4	3536.5	4.17	12.55	37.75	5.35
	MCH	+6.3	574.6	0	0.005	6.11	3.93
		-6.3/2.8	1629.2	0.44	6.37	11.85	11.83
		-2.8/1.4	3481.4	3.77	13.85	37.07	6.33

Note: 0 stands for mineral not trapped by the sieve from the sample

4.4.2 Gypsum ore grades of the Dowa West deposits

The gypsum grain quantification revealed that average ore grades of Kasangadzi, Livuna, and Machentche deposits were 7.58 %, 12.67 %, and 0.22 % gypsum for sediment ore >2.8 mm diameter respectively (Table 4.5). However, head grade assays from the wet-screening deck provided the results in Table 4.6. The results indicate that Kasangadzi deposit gave the highest grade (84.21% -KSN 2a) followed by Livuna (43.38%-LM 9) and Machentche deposits (4.66%-MCH 6). The Kasangadzi sample (KSN 2a) with the highest ore grade correlates with assorted sediments (Table 4. 1). Kasangadzi sediments were characterised by particle sizes ranging from fine gravel to fine sand (Figure 4.5: KSN 3a and 3b). All gypsum particles (>1mm diameter)

Table 4.6 Size fractions and gypsum ore grades of Dowa West deposits

Sample No.	Size Fraction (mm)	Weight(%)	Gypsum (%)	Gypsum ore Grade (%)
MK5 (11.43 wt -% retained)	+ 6.30	4.13	0.12	0.05
	-6.3/+2.8	14.37	11.86	1.63
	-2.3/+1.4	81.50	7.18	5.81
Head Assay				(7.49)
LM 9 (13.39 wt % retained)	+6.30	23.50	52.2	12.23
	-6.3/+2.8	38.59	52.05	20.01
	-2.8/+1.4	37.40	29.39	11.14
Head Assay				(43.38)
KSN2a (10.70 wt - % retained)	+6.30	1.84	6.55	0.12
	-6.3/+2.8	32.84	60.51	19.87
	-2.8/+1.4	65.32	70.76	64.22
Head Assay				(84.21)
MCH6 (4.88 wt % retained)	+6.30	9.66	0.02	0.01
	-6.3/+2.8	28.10	1.74	0.49
	-2.8/+1.4	62.24	6.67	4.16
Head Assay				(4.66)

provided high grade ore in the *dambos*. Livuna deposit indicated high ore grade and moderate head assay (43.38%). The sediment samples of Livuna tend to be poorly sorted and contain a wide range of material as shown by curves MK 2a, 2b and 2c in Figure 4.5. Machentche deposit showed low ore grade and very low head assay (4.66%). The deposit was correlated with samples rich in quartz and very little silt (Figure 4.5: curves MCH 4b and 4c).

The Dowa West gypsum deposits are similar to the Zambian gypsum deposit (>10%) at Lochinvar Gypsum Mine in the Kafue flood plain (Chanda and Lob, 1995). The *dambos* such as Kasangadzi and Livuna with the head assay values greater than 10% for some samples in Table 4.6 stand as feasible prospects for gypsum mining. Gypsum recovery would be very high in the *dambos* with high gypsum ore grade and very fine gangue minerals as clay (Mitchell and Briggs, 1991).

4.4.3 Gypsum ore processing by shaking table and semi-autogenous ball-milling

Separation of gypsum crystals using a shaking table proved very difficult because the density of quartz is close to that of gypsum. Therefore, the shaking table was not very effective in separating the gypsum. However, an attempt to separate the calcined gypsum (POP) using the shaking table by the dry method indicated that 45 wt-% of the gangue minerals were separated from the -6.3mm/+2.8mm size fraction. Gangue minerals separated consist of Lateritic nodules, carbonate nodules, and quartz. In the -2.8mm/+1.4mm size fraction, 32% of the gangue minerals were separated as lateritic nodules and quartz. The partially processed lot as middlings consisted of angular calcined gypsum and quartz.

After ball milling, -2.8mm/ + 1.4mm size fraction with gypsum was sieved through +1.00mm and 500 μ m mesh. The semi-autogenous method combined with sieving through 500 μ m mesh reduced the gypsum ore size further. Semi-autogenous ball-milling yielded 84.22 wt-% as material of -2.8 mm/+1.4 mm size fraction and 15.77 wt-% as -1.4 mm/+500 μ particles. It was

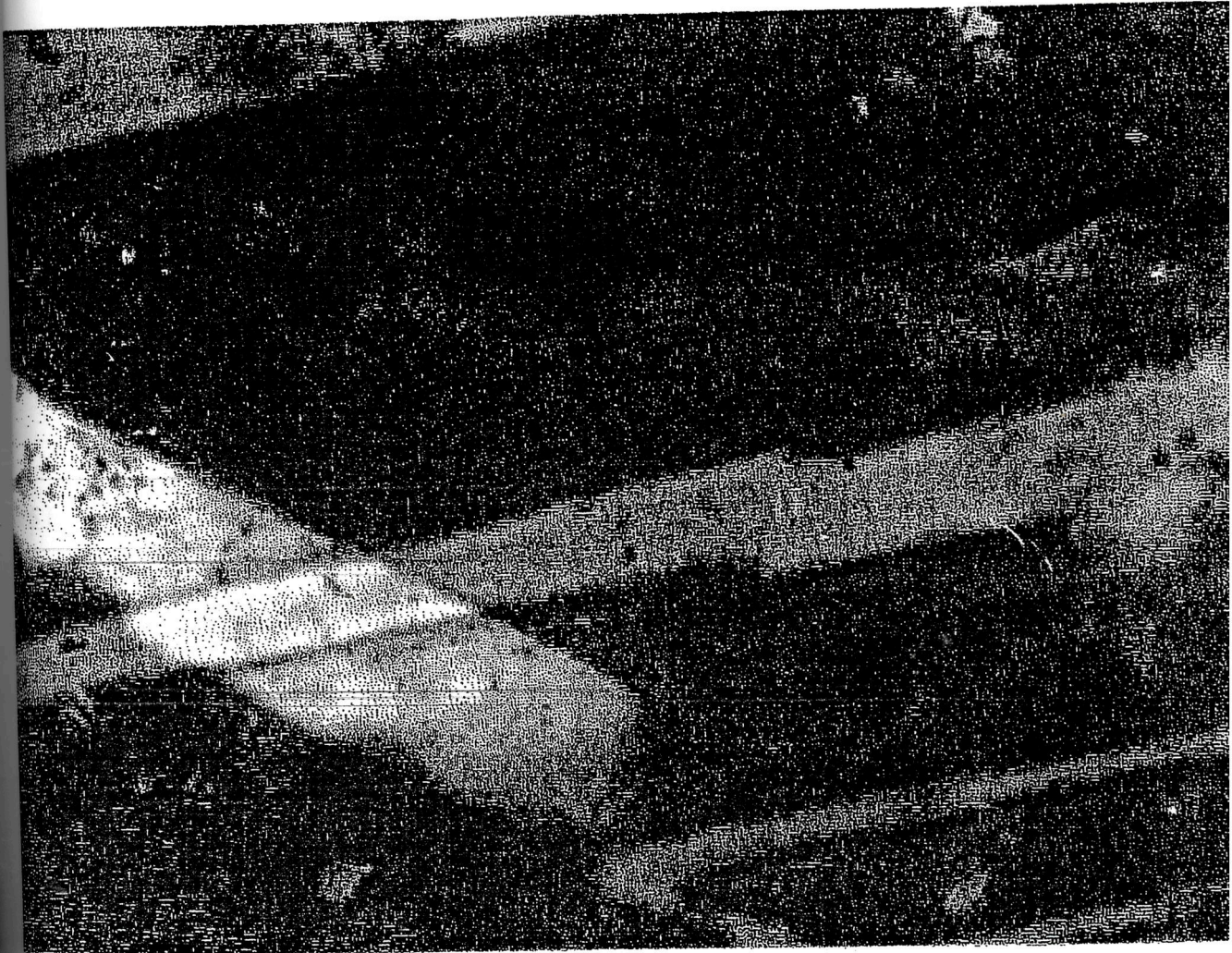


Figure 4.8 Gypsum crystals appearing white and low relief under the microscope (x 200 magnification) showing “swallow-tail” twin in the form of cross-cutting elongated mineral grains

realised that the semi-autogenous ball milling reduced 30 wt-% gypsum crystals to $-1.4\text{mm}/+500\text{ }\mu\text{m}$ size fraction. The lateritic nodules dominated the material in the $-1.4\text{mm}/+500\text{ }\mu\text{m}$ size fraction taking up 60 wt-%. However, semi-autogenous ball milling assisted in removing 40 wt-% quartz as a coarse hard mineral occurred in equal grain size with gypsum. Gypsum of the $-2.8/+1.4\text{mm}$ size fraction was reduced in size and quartz in the same lot underwent ball milling by the semi-autogenous method.

The small round grains of laterite and quartz got separated from the gangue by easily sliding down into the bin based on their density and shape. The undersized gypsum passed through 1mm sieve and got retained on 500 μm sieve. The dry shaking table proved partly successful as it yielded 30% gangue separated from the calcined gypsum. More investigations are required to test the method further. The semi-autogenous ball-milling can assist in removing gypsum from the quartz upon reducing its grain size and later recovering it by sieving.

4.5 Physico-chemical characteristics of gypsum, calcined gypsum and hydrated plaster-of-Paris

4.5.1 Crystallography of *dambo* gypsum

The grey gypsum crystals occurred as discrete grains with the tabular crystal habit in Dowa West sediments. These appeared colourless to pale grey and commonly exhibited anhedral aggregates with cross-cutting twinning of two distinct tabular crystals in thin-section (Figure 4.8). As shown in Figure 4.8, gypsum was characterised by low relief and was typified by white to pale yellow interference colours; and straight extinction under crossed polars occurred parallel to cleaved sections (010) (Kerr, 1954). However, the individual gypsum grains included tiny quartz grains (Figure 4.8). The quartz grains were, under crossed polars of the microscope, distinguished from the gypsum phase by their high relief and wavy extinction. The quartz grains exhibited that crystallisation of gypsum occurred around the tiny quartz grains as naturally seeded material. Crystal growth of the gypsum phase was initiated by the ions building a network from the minute

quartz grains as the nuclei (Jorgensen, 1978); hence, the gypsum microstructure inherently included quartz as impurity. The gypsum phase maintained the tabular crystal habit as evidenced in Figure 4.8.

4.5.2 Comparison of X-ray diffraction patterns of POP, gypsum, and set-POP

As indicated in Table 4.8, the parameters of X-ray diffraction patterns indicated that intensity peaks at 2θ angles 11.67° , 24.40° , and 29.11° for gypsum shifted to 29.65° , 14.65° and 25.59° for plaster-of-Paris (POP) upon calcining the gypsum at $>160^\circ\text{C}$. The hydration process of POP to set-POP does not change the X-ray diffraction pattern as shown by peaks for set-POP product for 175°C (Table 4.8; Figure 4.8b). Lack of shift in the peaks at 29.65° , 14.64° , and 25.58° for set-POP (calcium sulphate dihydrate) confirmed the stability of the calcined gypsum (POP) despite reacting with water during hydration. The remarkable difference in the X-ray diffraction patterns is that the Dow West gypsum shows the strongest peak at 2θ angle of 11.67° whereas its POP has the strongest peak at 29.65° .

4.5.3 Powder X-ray diffraction patterns of POP, gypsum, and set-POP

It is evident that the plaster-of-Paris products prepared at 100°C and 130°C showed a strong peak at a 2θ -angle of 11.64° (Figures 4.9a and 4.9b). These two POP products showed a strong peak at 11.64° like in the gypsum powder-diffraction patterns because the gypsum was partially calcined to calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) while the greater part of the material was preserved as the gypsum phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The co-existence of the hemihydrate and the gypsum phases were confirmed by the X-ray spectrograms showing three diffraction peaks for the gypsum phase with probably little hemihydrate phase ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) as shown in Figures 4.10a, 4.10b and Table 4.8. The X-ray diffraction analysis made on 130°C POP (Figure 4.10b) further revealed that the POP-product did only contain gypsum and calcium sulphate hemihydrate (synthetic bassanite), but also included synthetic quartz as a trace.

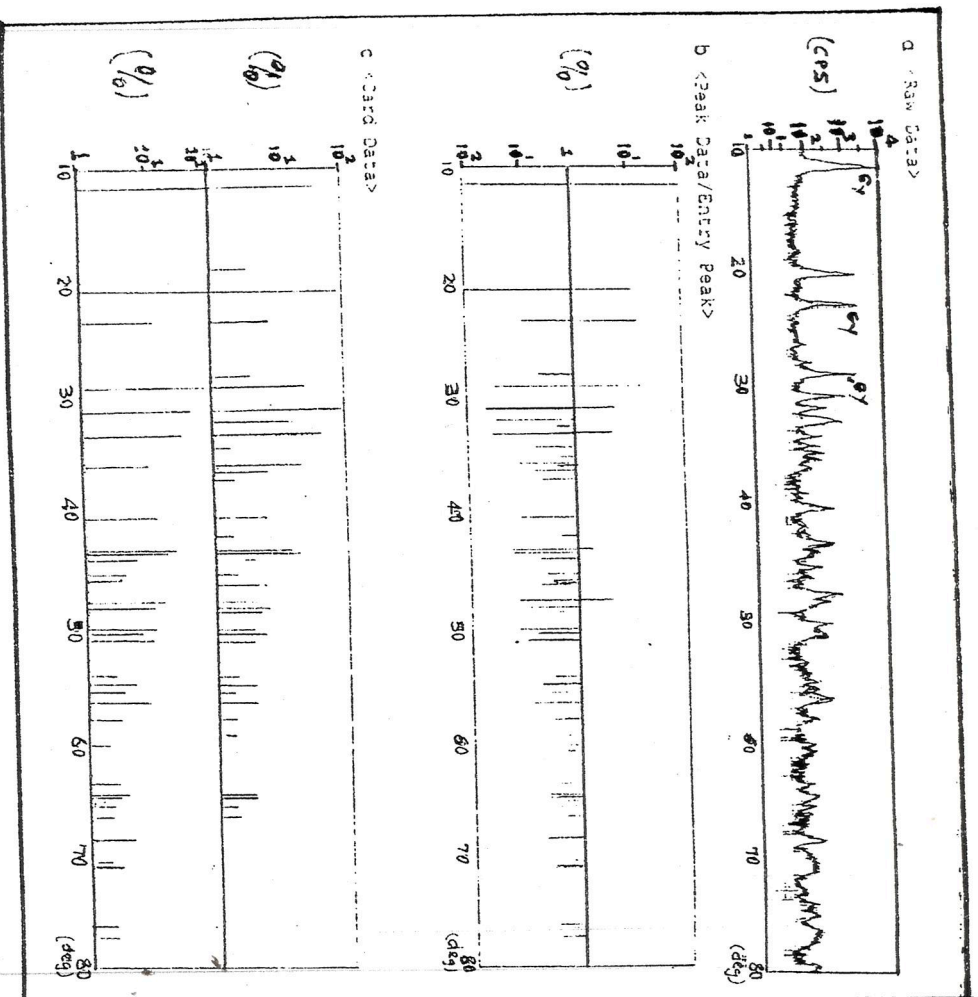
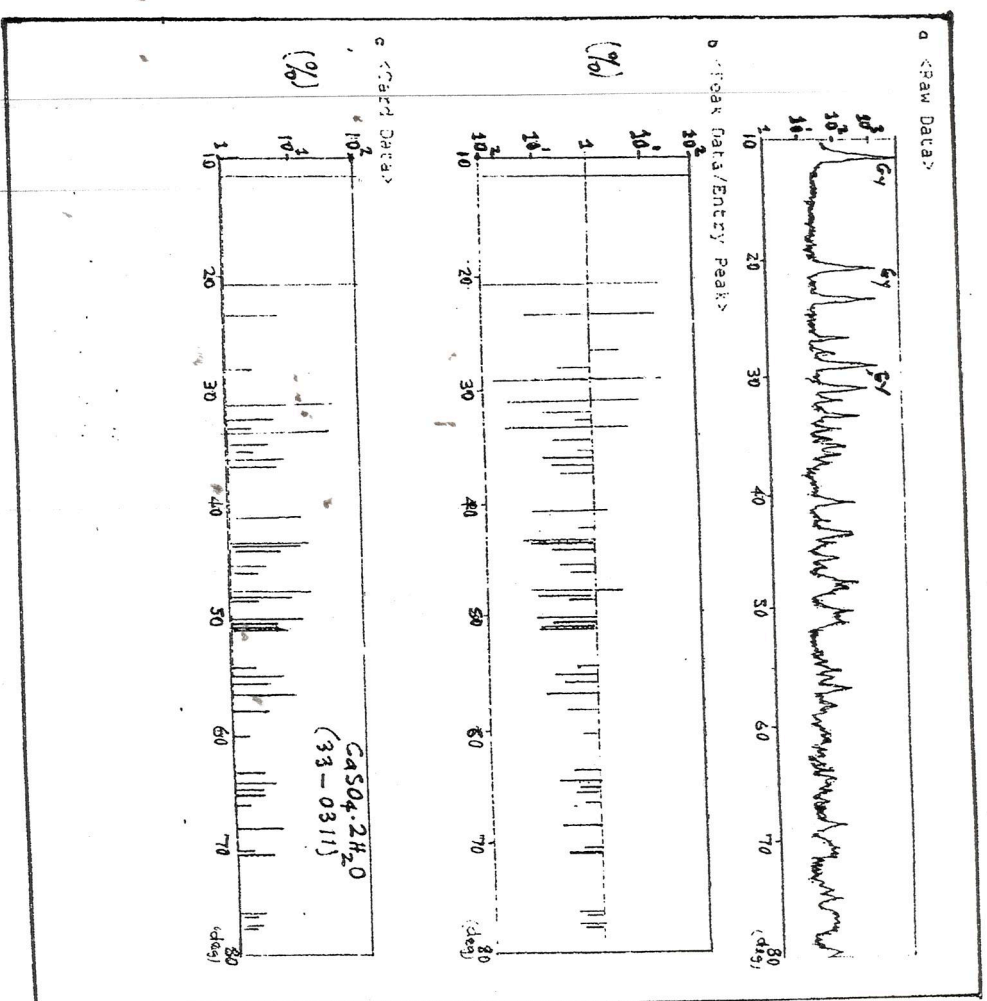


Figure 4.9 (a) X-ray diffraction spectrogram of the plaster-of-Paris product calcined at 100 °C (100 °C-POP) and comparison with PCPDF card data 41-0255



(b) X-ray diffraction spectrogram of the POP-175 °C set product and comparison with PCPDF card data 33-0311

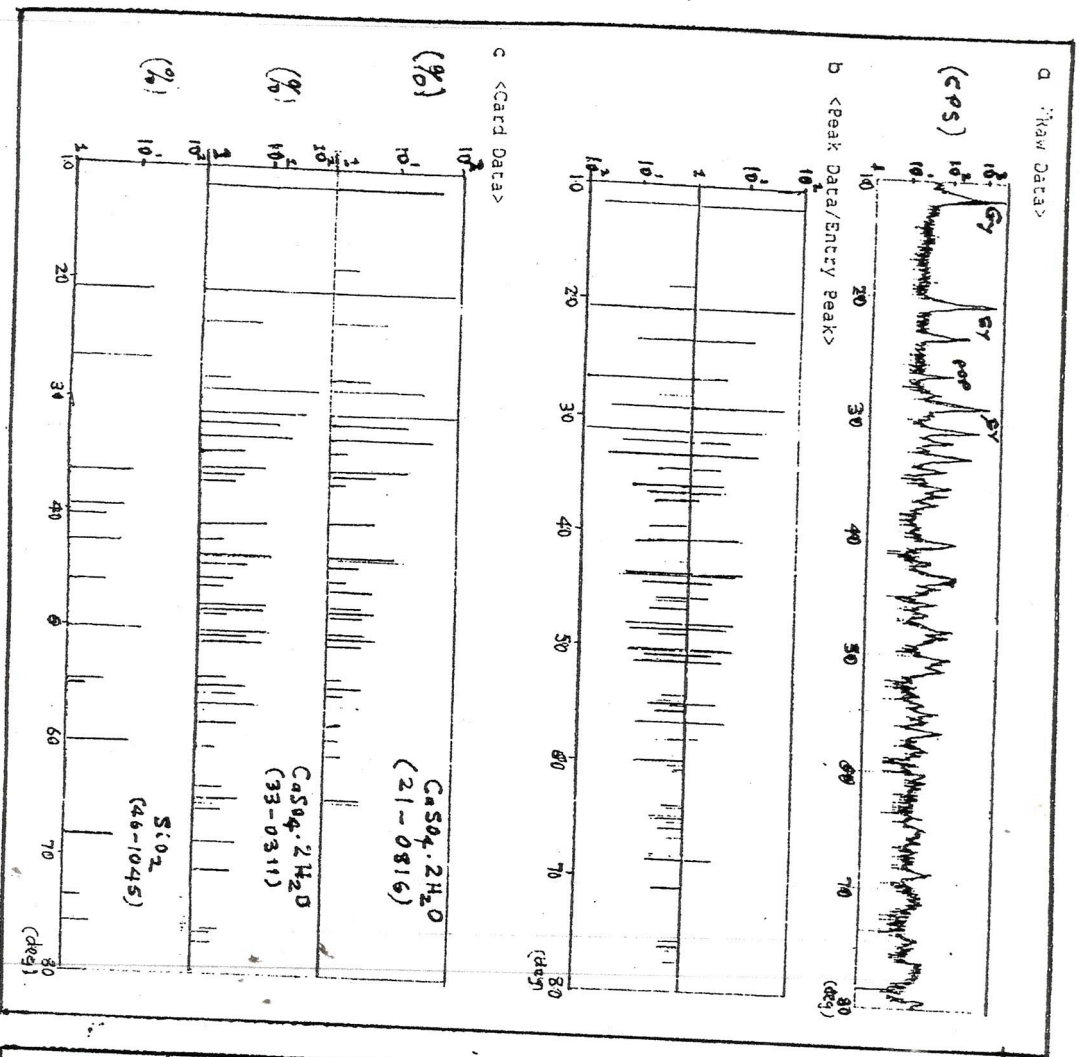
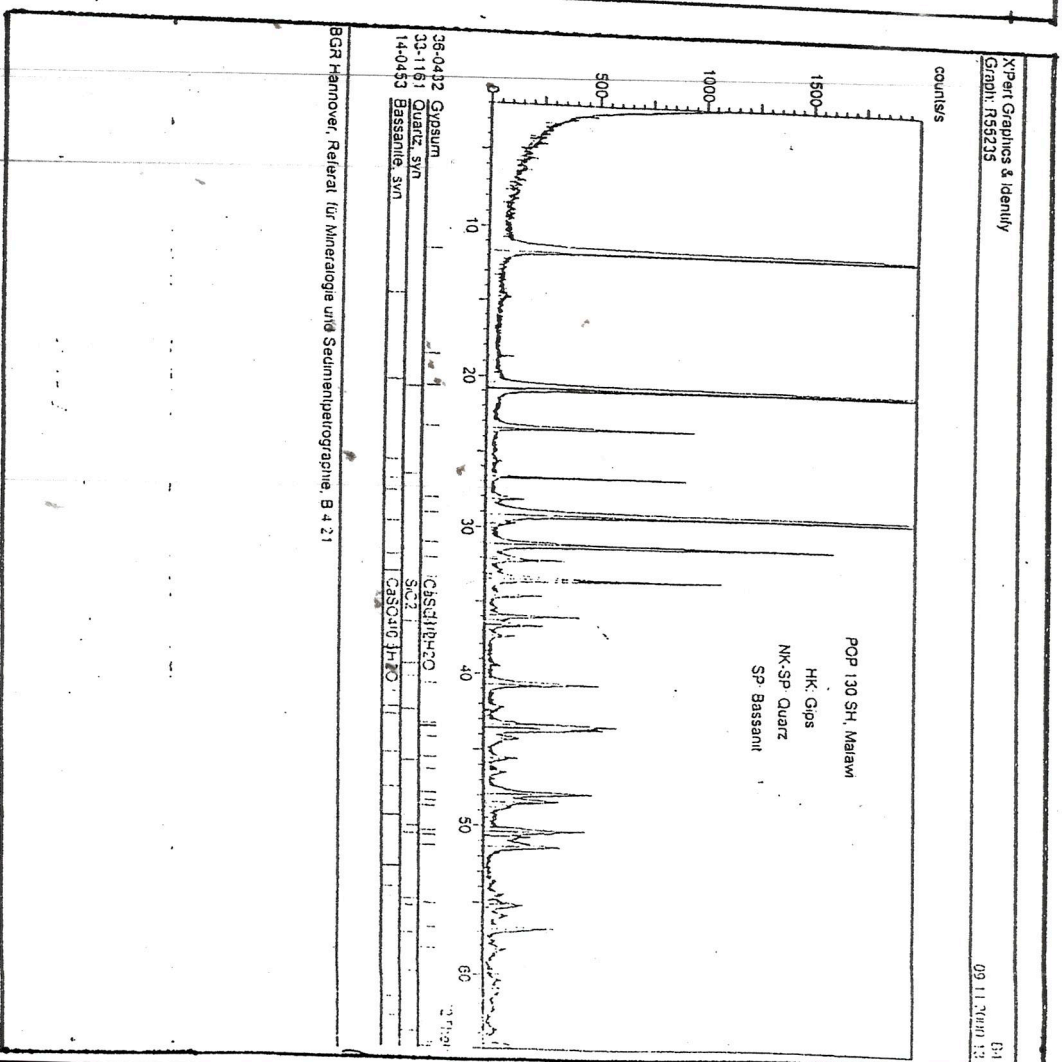


Figure 4.10 (a) X-ray diffraction spectrogram of the POP-130 °C set product and comparison with PCPDF card data 33-0311



(b) X-ray diffraction spectrogram of the POP-130 °C set product analysed in BGR Hannover-Germany

Table 4.7 X-ray diffraction data of Dowa West gypsum, POP, and Set-POP

Sample	Formula	X-ray spacing			Ref. Card Data No.	Colour
		2 θ (deg.)	d(nm)	I/I ₁ (%)		
Mpl-ks-gyp (Kasangadzi)	CaSO ₄ ·2H ₂ O	11.67	0.763	100	33-0311	Grey to Colourless
		24.40	0.381	19	close	
		29.11	0.307	6	ICCD ref.	
Plaster-of-Paris at 160 °C	CaSO ₄ ·0.5H ₂ O	29.65	0.301	100	41-02241	White
		14.64	0.604	79	close	
		25.59	0.348	58	ICCD ref.	
Set-POP-175 °C Set (dihydrate) POP/Water Wt-ratio 2:1	CaSO ₄ ·2H ₂ O	29.65	0.301	100	33-0311	White
		14.64	0.605	75	close	
		25.58	0.348	59	ICCD ref.	

The POP batches produced at 160 °C and 175 °C showed the three major diffraction peaks at 2 θ angles of 29.65°, 14.64°, and 25.58° respectively. These similar X-ray diffraction patterns are consistent with the Joint Committee Powder Diffraction Standard (JCPDS) file card data 41-02241 for CaSO₄·0.5H₂O (Figure 4.11b and 4.11b). POP was effectively produced at 160 °C and above; thus, the calcined gypsum showed powder diffraction peaks at 29.65°, 14.64°, and 25.58° as opposed to 11.70°, 20.79° and 29.17° for gypsum (Jasmund, 1979).

X-ray diffraction analysis of Kasangadzi (Mponela) is characterised by three major diffraction peaks at 2 θ -angles of 11.70°, 20.79° and 29.17° (Jasmund, 1979). Both Kasangadzi and Zimbabwe gypsum samples were consistent in showing a diffraction peak close to 11.70°.

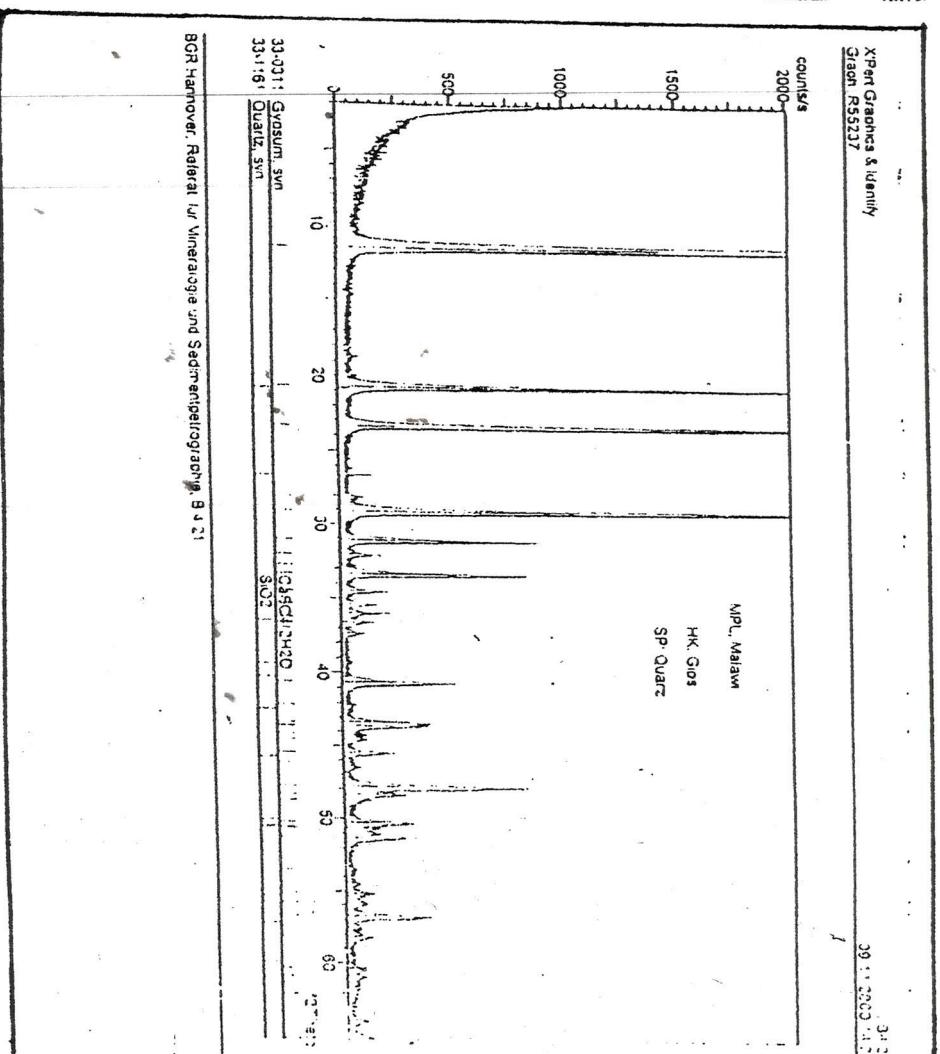
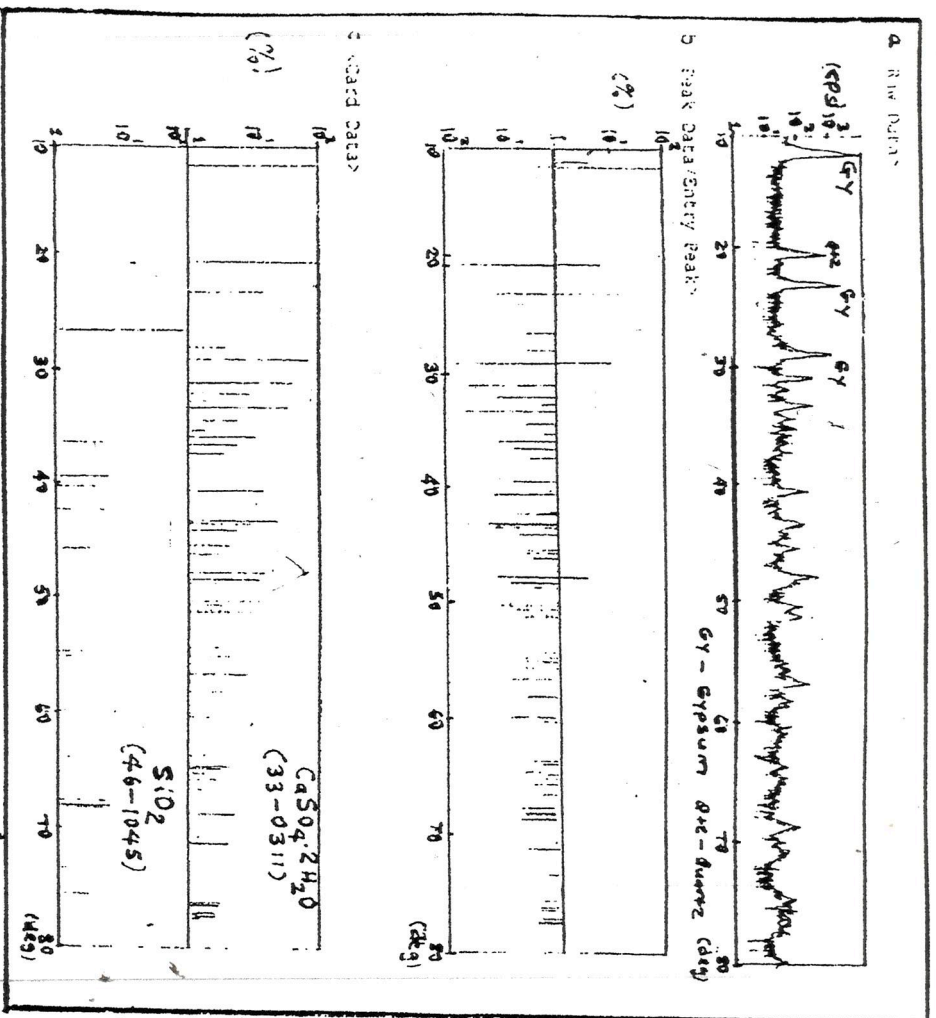
Table 4.8 X-ray diffraction data of plaster-of-Paris

Sample	Formulae	X-ray spacing			Ref. Card Data No.	Colour
		2 θ (deg.)	d(nm)	I/I ₁ (%)		
POP 100° C	CaSO ₄ . 2H ₂ O	11.64	0.765	100	41-02241 close ref.	White
		23.36	0.381	17		
		29.70	0.308	13		
POP 130° C	CaSO ₄ . 2H ₂ O	11.64	0.765	100	41-02241 close ref.	White
		23.37	0.381	16		
		29.09	0.307	15		
POP 160° C	CaSO ₄ . 0.5H ₂ O	29.65	0.301	100	41-02241 close ref.	White
		14.64	0.604	79		
		25.59	0.348	58		
POP 175° C	CaSO ₄ . 0.5H ₂ O	29.65	0.301	100	41-02241 close ref.	White
		14.64	0.605	75		
		25.58	0.348	59		
Calcium Sulphate Hydrate	CaSO ₄ . 0.48H ₂ O	29.76	ND	100	02-0653 reference standard	White
		32.06	ND	100		
		14.68	ND	90		

Note: ND stands for Not Determined

As shown in Table 4.10, slight shifts for the peak angles in samples were due to orientation of the powder with regard to the lattice structure and also the grain size of the sample. For Kasangadzi gypsum, the prominent peak appeared at 11.67° whereas the other two peaks

emerged at 23.40° and 29.11° (Figure 4.12a and b). The sample of gypsum from Zimbabwe was also typified by a prominent peak at a 2θ -angle of 11.64° (Figure 4.13b) with the other two peaks identified at 23.35° and 29.07° (Table 4.9; Figures 4.13a and 4.13b). Comparison of the gypsum samples with the standard X-ray card data for calcium sulphate hydrate (33-0311) indicated that the peaks for the Kasangadzi (mpl-ks-gyp) sample are identical to those of the gypsum standard Figures 4.12a and 4.12b. Its crystal structure and that of Zimbabwe gypsum did not provide as numerous peaks as the PCPDF standard card probably because of differences in the orientation and the grain size. It is also possible that the averaging effect of the crystal orientations may have resulted in certain peaks enhanced and others missing (Navrotsky, 1994). The few peaks that the Zimbabwe gypsum showed also reflect the amorphous state of the calcium sulphate dihydrate phase as produced from the industrial chemical process (Figures 4.13a and 4.13b). It is interesting that Kasangadzi gypsum showed some peaks at 2θ angles of 69° and 75° as markers for the presence of the quartz phase included in the gypsum material. The X-ray data shown in Figures 4.12a and 4.12b by the analysis made at BGR-Hannover in Germany also revealed that the Kasangadzi (Mponela) gypsum (mpl-ks-gyp) consist of gypsum as the major phase and quartz as a trace (Figure 4.12b). This corresponds with the analysis made at the Geological Survey of Malawi (Figure 4.12a) by the Kasangadzi gypsum showing similar X-ray diffraction peaks to those of synthetic gypsum (gypsum, syn) displayed in the PCPDF card 33-0311. The Kasangadzi gypsum was different from the normal gypsum mineral as evidenced from the short X-ray diffraction peaks indicated at 2θ angle of 11.59° in Figure 4.12a (part c: PCPDF card 33-0311). This is consistent with the findings on the petrographic examination of the gypsum crystals in Figure 4.8 in which quartz has been described to occur as tiny pods within the gypsum crystals. Diffraction patterns of set POP with a ratio 2:1 of POP to water by weight were compared with those of the naturally occurring gypsum and synthetic gypsum. The set POP as recrystallised calcium sulphate dihydrate indicated the strongest diffraction peaks at 2θ -angles close to 11.64° (Table 4.10). The other two strong peaks common to the calcium sulphate dihydrate (POP) products were displayed at 20.70° and 29.07° for 130°C -set and 175°C -set products as synthetic gypsum (Figures 4.9b and 4.10a). The major diffraction peak for set POP showed a slight shift from the JCPDS 33-0311 standard at 11.59° of 2θ -angle to 11.64° .



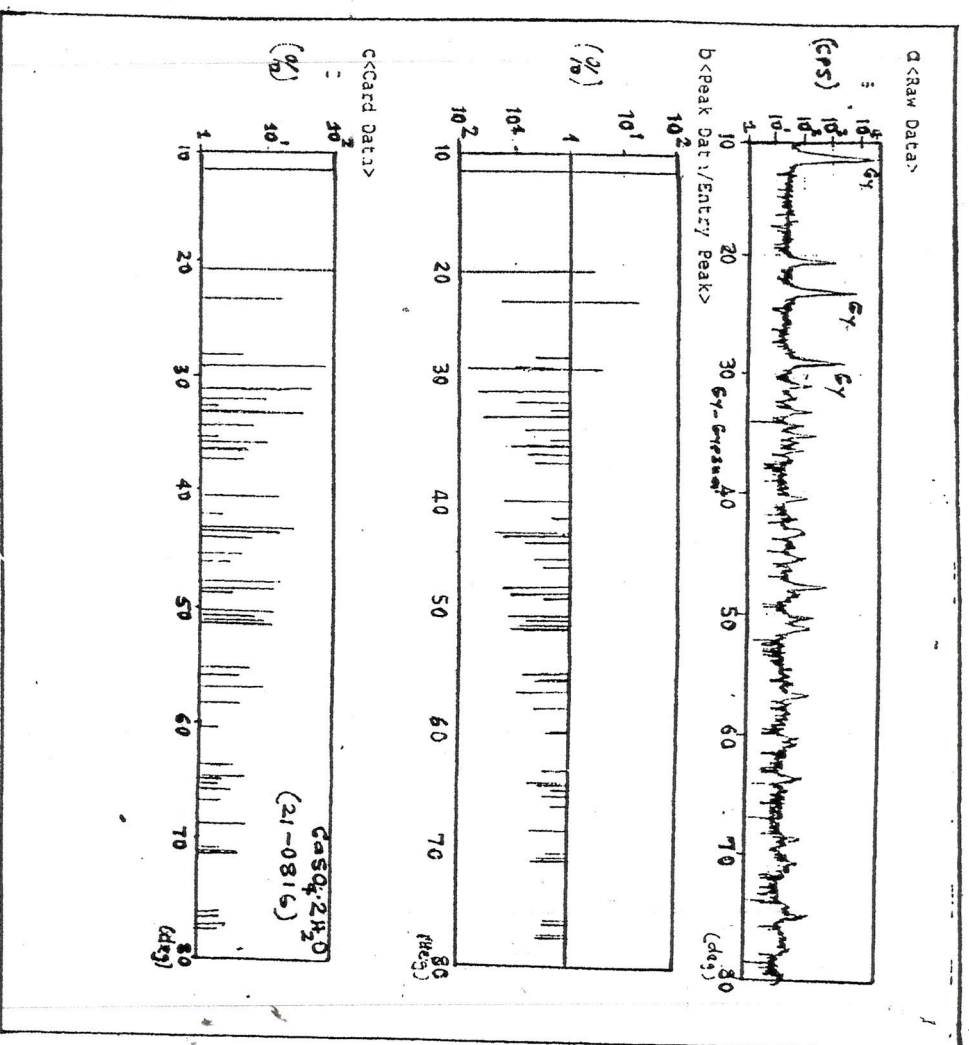
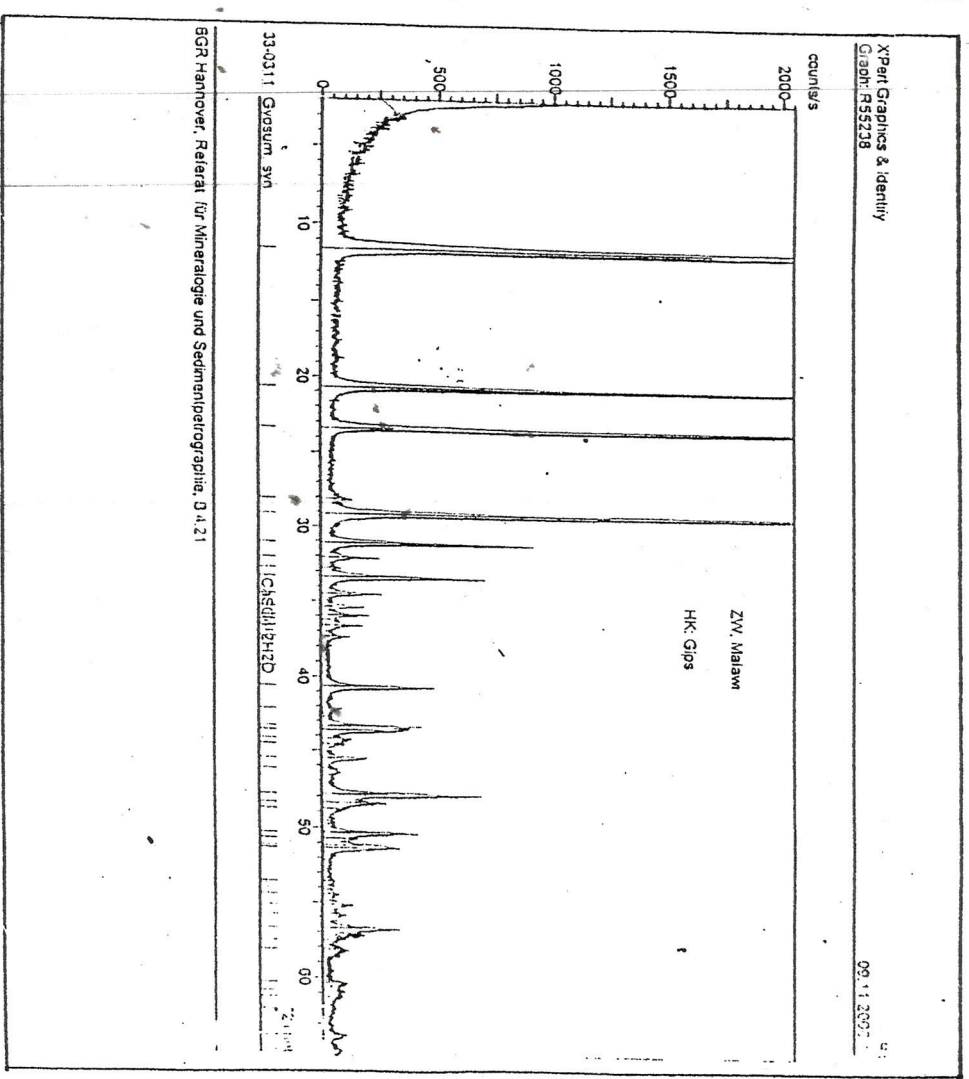


Figure 4.13 (a) X-ray diffraction spectrogram of the imported Zimbabwe gypsum (zw-gy) and comparison with PCPDF card data 21-0816



(b) X-ray diffraction spectrogram of the imported Zimbabwe gypsum, (zw-gy) analysed by BGR in Hannover-Germany

Table 4.9 X-ray diffraction data of gypsum samples

Sample	Crystal System	X-ray spacing			Colour	Crystal Morphology
		2 θ (deg.)	d(nm)	I/I (%)		
Mpl-ks-gyp (Mponela) CaSO ₄ .2H ₂ O	Monoclinic	11.67	0.763	100	Grey to White	Powder
		24.40	0.381	19		
		29.11	0.307	6		
Zw-gyp (Zimbabwe) CaSO ₄ .2H ₂ O	N.D.	11.64	0.765	100	White to cream	Powder
		23.35	0.381	19		
		29.07	0.307	6		
Gypsum (Jasmund, 1979) CaSO ₄ .2H ₂ O	Monoclinic	11.70	0.756	100	White	Powder
		20.79	0.427	50		
		29.17	0.306	55		

Note: N.D. stands for Not-Determined

(Table 4.11). This was so because of the crystal orientation relative to formation of the dihydrate phase (Navrotsky, 1994). The preferred crystal orientation in the set POP powder may have provided deceptive powder diffraction pattern which could lead to problems in deducing the type of material examined based on qualitative analysis. The 160 °C-set product yielded a powder diffraction pattern almost similar to the PCPDF card data 33-0311 as the intensity peaks correlated well (Figures 4.11a and 4.11b). The powder diffraction results from BGR, Germany confirmed that the 160 °C-set product consists of calcium sulphate hydrate (gypsum) phases, synthetic bassanite (calcium sulphate hemihydrate) and synthetic quartz. The 175 °C-set POP product also showed similar powder diffraction pattern in that its diffraction peaks coincided with the PCPDF card data 33-0311. The shift and low intensity of the peaks may be due to

Table 4.10 X-ray diffraction data of set POP products

Sample	Formula	X-ray spacing			Ref. Card Data No.	Colour
		2 θ (deg.)	d(nm)	I/I ₁ (%)		
POP-100 °C Set (dihydrate) POP/Water Wt-ratio 2:1	CaSO ₄ ·2H ₂ O	11.64	0.765	100	33-0311 close ref.	White
		23.37	0.381	17		
		20.70	0.430	15		
POP-130 °C Set (dihydrate) POP/Water Wt-ratio 2:1	CaSO ₄ ·2H ₂ O	29.65	0.301	100	33-0311 close ref.	White
		14.64	0.604	79		
		25.59	0.348	58		
POP-175 °C Set (dihydrate) POP/Water Wt-ratio 2:1	CaSO ₄ ·2H ₂ O	29.65	0.301	100	33-0311 close ref.	White
		14.64	0.605	75		
		25.58	0.348	59		
Calcium Sulphate Hydrate (Gypsum)	CaSO ₄ ·2H ₂ O	31.13	ND	100	21-0816 reference standard	Colourless
		20.74	ND	90		
		33.36	ND	50		
Calcium Sulphate Hydrate (Gypsum,syn)	CaSO ₄ ·2H ₂ O	11.59	ND	100	33-0311 reference standard	Colourless
		20.72	ND	100		
		29.11	ND	73		

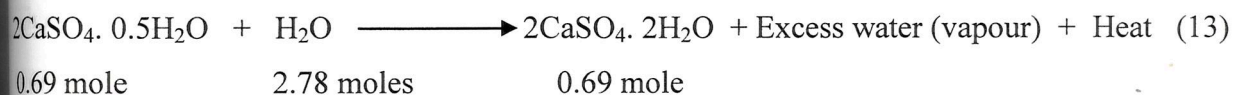
Note: ND stands for Not Determined

crystal orientation and grain size of the emerging crystals of calcium sulphate hydrate as gypsum.

4.5.4 Characteristics of POP hydration

The relative temperature increases in POP-water reactions for 100 °C-POP, 130 °C –POP and 175 °C-POP were 1.8 °C / minute, 1.04 °C/minute and 0.75 °C/minute respectively (Figure 4.14). The setting times for 130 °C-POP and 160 °C-POP are different as reflected by the shift of the peaks of the curves for the two products (Figure 4.14). The peak values are significantly different ($p < 0.05$).

With high concentration of water in the mixture with the POP, the reaction between POP and water was forced to proceed to the product side (equation 13).

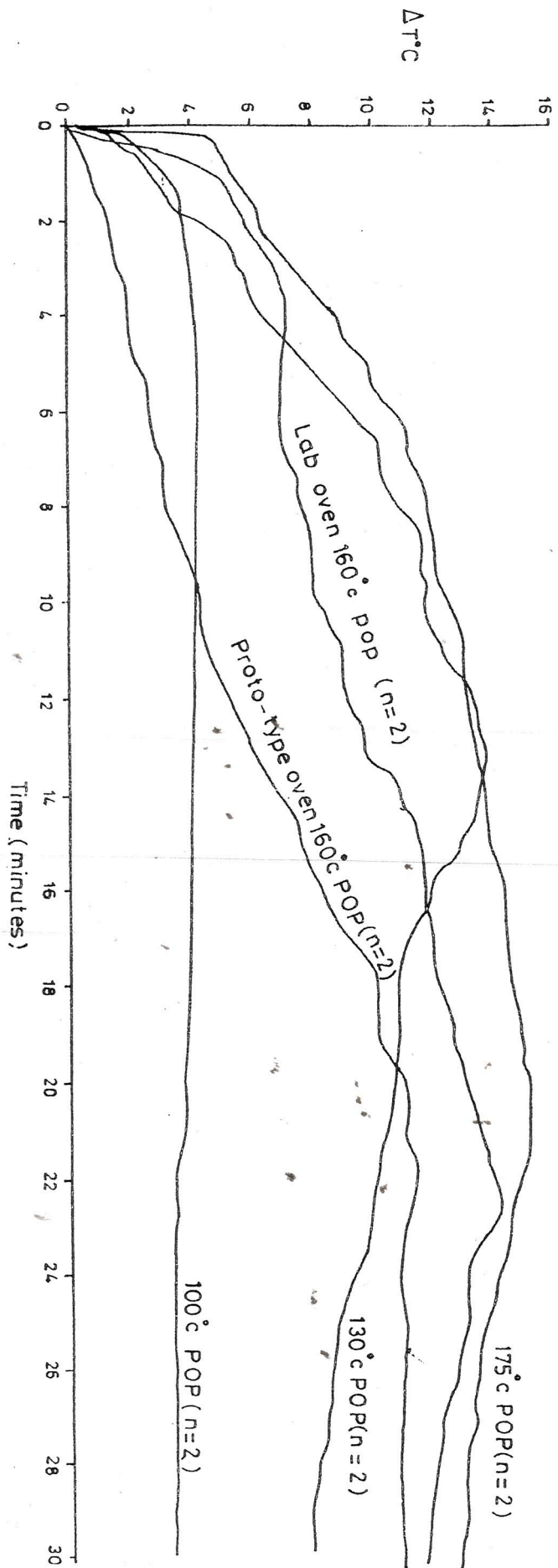


Le Chatelier's principle of off-setting the high concentration of one of the reactants towards a state of chemical equilibrium was followed (Brown, 1961). The actual heat evolved for POP products increased with temperature increases, setting times and temperatures of calcination. With the water-equivalent heat fixed at 38.1 J/ °C, 100 °C -POP produced -1182.39J/mole ($\Delta T = 4.5$ °C) and setting time of 3.5 minutes. The 130 °C –POP gave -3625.99J/mole ($\Delta T = 13.8$ °C) and setting time of 6.75 minutes. The 175 °C-POP yielded -3993.84J/mole ($\Delta T = 15.2$ °C) and setting time of 11.25 minutes. The setting time for the POP increased with the increasing heat evolved coupled with increasing temperature change. This was so because the gypsum calcined at high temperature consisted of fine hemihydrate crystals produced under high radiant heat that led to the calcined gypsum crystals disintegrating into smaller crystals. This condition certainly enabled the 175 °C-POP product to react more effectively than the 100 °C-POP and 130 °C-POP products.

According to Kelly *et al* (1941), the formation of calcium sulphate dihydrate occurred with a heat capacity (C_p) empirically defined by the equation $C_p = (21.84 + 0.076T)$ cal/mole.deg

within the temperature range of 25 °C to 177 °C (298K to 450K) at one atmosphere pressure. From this relationship, it was projected that the 100 °C-POP product yielded 24.46 cal/mole.deg (102.73 J/mole.K) at a maximum temperature of 34.5 °C. The 130 °C-POP product gave 25.78 cal/mole.deg (108.26 J/mol.K) at a maximum temperature of 51.8°C. The 175 °C-POP product provided 26.01cal/mole.deg (109.25 J/mole.K) at a maximum temperature of 54.9 °C. These values were almost two-and-half times smaller than the actual heat capacity of 62.56 cal/mole.deg (262.75J/mole.K) for formation of the Dowa West dihydrate POP products (Figure 4.14). The difference in heat capacities for the hydration of POP can be attributed to different experimental conditions set by Kelly *et al* (1941). Thus, gypsum-anhydrite equilibrium was maintained in the hydration reaction with the pressure strictly kept at one atmosphere.

The hydration process of POP calcined in the laboratory and proto-type ovens showed different trends (Figure 4.14). The hydration of the POP product (160 °C) evolved heat amounting to – 3915.01J/-mole with the average temperature increase of 14.9 °C. The average hydration rate was 0.63 °C/ minute. Hydration of the POP-product from the prototype oven was characterised by the



reaction curve with the average reaction rate of 0.52 °C/ minute and a temperature change of 11.6 °C. The heat of reaction in this case was quantified as -3047.93J/ mole. Hydration of POP produced using the proto-type oven evolved less heat by 867.08J/ mole compared to the laboratory-oven POP product. The cheap proto-type oven costing US\$ 250 can be improved in terms of its efficiency by insulating the metal walls with exfoliated vermiculite.

4.6 Characteristics of laboratory fabricated POP products

4.6.1 Chemical composition of POP chalk-sticks

In the calcined Dowa West (Mpl-180-(1:1)) and the calcined Zimbabwe gypsum (Zw-150-(1:1)) -Table 4.11, chemical results indicated that calcium oxide content (% CaO) of the Dowa West area and the Zimbabwe gypsum samples ranged from 30.66 to 30.89% whereas the sulphite content (%SO₃) ranged from 47.52 to 49.25%. In contrast, the Apex (dusty chalk) and Crayola (anti-dust) both sampled from the market were characterised by high CaO content (>40%) and low sulphite content (<35%). The latter was found least in Crayola (10.08%). Carbonate content of Crayola was determined as 42.75 % by loss-on-ignition method.

The POP material for the Dowa West area (Table 4.11; Mpl-180-(1.1)) indicated chemical characteristics compatible with the BS 1191 standard as SO₃ content was >35%, and MgO content showed a value <0.2%. The Dowa West POP proved almost similar in composition to the Zimbabwe POP (Table 4.12; ZW-150(1:1)) except that the Zimbabwe sample contained comparatively high lead (123 ppm). The Dowa West chalk-sticks contained less calcium oxide (<40%) and more sulphite (>35%) compared with the commercially available chalk-sticks as Crayola and Apex. This may be because POP for commercial chalk-sticks was manufactured by mixing POP with calcium carbonate as the loss-on-ignition test gave a value of 42.75% on Crayola. The Dowa West chalk-sticks also conformed to the chemical specifications of "Alabaster brilliant white" as a superfine water resisting calcium sulphate (Börgardts, 1991); thus calcium oxide (32.3%), sulphite (≈0.46%) are all in agreement with the chemical data of the

Dowa West sample (Table 4.11; Mpl-180-(1:1)) . In terms of chemical characteristics, the Dowa West POP qualifies to be an “ Alabaster brilliant white” product (Börgardts, 1991). It also conforms to the British Standard (BS:1191) for POP. However, the Dowa West POP requires mixing with other ingredients like calcium carbonate or lime to upgrade its quality as evidenced from the properties of Crayola and Apex samples. Concentration of Cd is far below the threshold for toxicity level of 200 to 250 ppm or 200 to 250 mg/kg in human kidney cortex (WHO, 1984). According to WHO (1984), the tolerable lead levels in human blood lie between 250 and 300 ppm. Therefore, the cadmium and lead concentrations in Cryola and ZW-150(1:1) samples (Table 4.11) are far below the toxicity limits and are safe chalk-sticks to use.

Table 4.11 Chemical data of plaster-of-Paris (POP) samples

Sample No.	%CaO	%SO ₃	%MgO	%Fe ₂ O ₃	%Na ₂ O	%K ₂ O	Cd ppm	Pb ppm
Mpl-180-(1:1)	30.66	47.52	0.01	0.24	0.08	0.01	6.55	38
Zw-150-(1:1)	30.89	48.25	0.05	0.46	0.19	0.02	8.29	123
Apex	40.28	34.68	0.035	0.031	0.10	0.36	2.45	52
Crayola	46.10	10.08	0.12	0.21	0.75	0.04	20.15	79

Note: Mpl-180-(1:1) includes Mpl for Mponela , 180 for 180 °C and (1:1) for Water to POP mixture ratio; Zw-150-(1:1) stands for Zw for Zimbabwe, 150 for 150 °C and (1:1) for water to POP

4.6.2 Physico-chemical properties of POP chalk-sticks

The values of breaking force for various chalk pieces are presented in Table 4.12. The stiffest of these sticks required a breaking force of 2.60 ± 0.10 for 160 °C-product. The 180 °C-product was less stiffer at 1.75 ± 0.21 kg –force; and the 150 °C-product yielded the least breaking force with a breaking force of 1.15 ± 0.07 kg. All the chalk-stick products produced at various temperatures were hydrated at the ratio of 1:1 for water to POP by weight. The variation in breaking-force the chalk-sticks was influenced by compactness and bonding of the dihydrate material based on crystallisation (Lach, 1985). The dihydrate form of calcium sulphate emerged following hydrogen bonding between water molecules and the ions in the calcium sulphate lattice. The 160

Table 4.12: Strength and modulus of rupture data for chalk-sticks and the imported samples (n=2)

Chalk-stick	Density (g/cm ³)	Length (cm)	Diameter (cm)	Force (kg)	MOR (kg/cm ²)
Mpl-150-(1:1)	1.46± 0.03	5	0.95±0.03	1.15±0.07	13.46±0.66
Mpl-160-(1:1)	1.85±0.08	5	0.90±0.01	2.60±0.10	35.72±1.10
Mpl-180-(1:1)	1.57±0.05	5	0.92±0.07	1.75±0.21	22.98±2.50
Apex	1.19±0.02	5	0.96±0.02	1.50±0.15	17.27±0.23
Crayola 12	2.43±0.03	5	0.97±0.01	5.00±0.32	55.79±0.65

°C-product gave good quality calcined hemihydrate that formed strong POP fabric upon hydration. This POP developed well-bonded microstructure compared to the 150 °C-product whose crystals were mainly less calcined to POP. 180 °C-product with crystals were partially over calcined (Lach, 1985); thus, the POP weakly reacts with water. The 160 °C-product has proved to be the best hemihydrate for making chalk-sticks on the basis of calcining temperature under the present study.

The MOR values for chalk sticks of the Mpl-180-(1:1) batch yielded an average of 22.98± 2.50 kg/cm² and fall between the MOR values for the two imported chalk sticks (4.12). With a high MOR value, the Mpl-160-(1:1) chalk sticks indicated that they are stronger than the Apex chalk sticks from South Africa (Table 4.12). The crayola-12 brand from the United Kingdom has proved to be a far much better chalk stick than the Mpl-160-(1:1) brand with a much higher MOR value of 55.79±0.65 kg/ cm². In this case, production of the local chalk sticks at 160 °C with POP/ water ratio of 1:1 has proved successful in producing comparatively strong chalk sticks that lie between Apex and Crayola-12. The breaking force values of the Dowa West (Mponela) chalk-sticks were higher than the recommended minimum strength of 0.90 kg/ cm² (Malawi Bureau of Standard, 1999; MBS 187).

4.6.3 Writing quality and gritness of chalk-sticks

The writing quality required chalk sticks to be free from gritness or sand particles. Uniform writing on a chalk-board was also examined (Malawi Bureau Standards, 1999; MBS 187). The chalk-sticks were assessed of their hardness and softness; dustiness; and readability based on usage by teachers (Zomba C.C.A.P, 1999: personal communication). The assessment reports from teachers of Zomba C.C.A.P were summarised as shown in Table 4.13 to reflect the quality of the chalk-sticks usability. Remarks on the quality of the chalk sticks from the teachers have shown that the chalk-sticks produced from 190 °C-POP gave the best quality chalk with less dust and highly readable irrespective of the range from the writing as denoted on the scale shown in

Table 4.13: Ranking of chalk sticks based on acceptability

Acceptability Scale	Calcination Temperature °C	Water:POP Mixture ratio by mass (g)	Drying Temperature °C	Ranking of properties: Softness-Dustiness-Readability
1 (a)	190	4:5	80	1-1-1
	(b) 150	4:5	60	1-1-2
	(c) 160	4:5	80	1-1-2
	(d) 150	1:1	80	1-2-1
	(e) 170	1:1	80	1-2-2
2 (a)	180	4:5	60	2-2-2
	(b) 190	7:10	80	2-3-1
3 (a)	160	4:5	60	1-2-4
	(b) 170	7:10	60	2-2-3
4	170	4:5	80	2-3-4
5	180	7:10	80	2-3-4

Codes : Hard (1)
Soft (2)

Less dusty (1)
Dusty (2)
Very dusty (3)

Highly readable (1)
Readable (2)
Readable at long range (3)
Readable at short range (4)

Table 4.13. The hardness or softness and dustiness were particularly influential on the level of acceptability of chalk-sticks at the scale of 1 and the average ranking score was close to 1 for the two respective properties within the acceptability scale of 1. The chalk sticks acceptable at scale

2 depended on the chalk being soft (2) and dusty (2) or very dusty (3) as shown in Table 4.13. All the chalk sticks with acceptability scales of 3, 4, and 5 gave poor writing on the blackboard at the short and long ranges respectively. The worst quality chalk sticks were characterised by very dusty and non-continuous writing on the blackboard. The quality of the chalk was affected by drying temperatures as free water was driven off the pores of the POP. Good quality chalk sticks favoured the mixture ratios of the range 4:5 to 1:1 (water: POP). The acceptability scale 1 showed these mixture ratios (Table 4.13; 1(a) to (e)). The grittiness of the chalk sticks decreased with temperature of calcination of POP from 150 °C to 180 °C (Table 4.14). The grittiness showed that the quality of local chalk sticks were more abrasive than commercial chalk sticks (Table 4.13; Mpl-180-(1:1) Apex). It was noted that the commercial chalk stick (Apex) yielded much less moisture content than the locally produced chalk stick. Therefore, the local chalk may be dried more to reduce the moisture content to recommended levels. The Cryola chalk-stick gave extremely low abrasion due to mixture of POP with calcium carbonate. However, it served as a very good contrast between other chalk-making material and POP (Table 4.14). The Dowa West gypsum was calcined to produce POP that was fabricated into good quality chalk sticks acceptable by teachers (Zomba C.C.A.P, 1999; personal communication). The good quality chalk needs to be improved on readability probably by keeping the moisture content low (Table 4.14; Apex).

Table 4.14 Abrasion of local and imported chalk sticks

Chalk stick No.	Weight of stick (g)	Weight of dust (g)	Abrasion (%)	Moisture (%)
Mpl-150-(1:1)	4.845	0.052	0.011	17.21
Mpl-160-(1:1)	6.069	0.054	0.008	12.52
Mpl-180-(1:1)	5.161	0.021	0.004	9.62
Apex	4.487	0.001	0.00022	2.17
Cryola	9.163	0.0008	0.000087	2.01

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Characteristics of gypsum, *dambo* sediments and groundwater

The present study revealed that sulphate ions formed by the chemical weathering of pyrite in rocks underlying the Dowa West area while calcium was released from calcic-feldspars (plagioclase) and calcium-rich hornblende. Subsequent reaction between sulphate and calcium ions in solution led to precipitation of calcium sulphate dihydrate as gypsum.

Gypsum profiles indicated that gypsum crystals occur in plastic-clay-rich layers of the *dambos* like in Kasangadzi *dambo*. Gypsum occurrence is therefore associated with the plastic clay layers. Clay minerals host the calcium ions through ion-exchange activity while releasing the cations to water as the water table rises and falls due to the change of seasons. Quartz-rich sediments are extremely poor in gypsum as evidenced from Machentche *dambo*. This is so because silica (quartz) does not provide the ion exchange capacity to hold the calcium or sulphate ions. With such difference in the gangue minerals, large gypsum crystals ($>1.4\text{mm}$) in Kasangadzi gypsum ore occurred together with clay. The clay together with silt gave grain size curves showing fine sand. To recover the gypsum, large-mesh screens were used on a deck to trap the large gypsum crystals while letting most small gangue particles fall through. This grain size relationship assisted in having the coarse ($>1.4\text{mm}$) gypsum screened in large amounts. The sorted sediments from Livuna and Machentche provided small gypsum crystals. This showed that the little clay reduced the likelihood of gypsum precipitating in the sediment layers of Livuna and Machentche *dambos*. No large gypsum particles ($\geq 1.4\text{mm}$) were formed in the two *dambos*.

The chemical composition of sediments in Kasangadzi, Livuna, and Machentche *dambos* showed that calcium oxide content ranged from $0.08\% \pm 0.09$ to $3.75\% \pm 5.98$, and sulphate content ranged from $0.33\% \pm 0.13$ to $4.37\% \pm 1.06$. The other oxides were determined with the ranges $0.04\% \pm 0.02$ to $0.54\% \pm 0.28$ for magnesium oxide; $0.05\% \pm 0.02$ to $0.65\% \pm 0.07$ for sodium oxide; $0.02\% \pm 0.01$ to $0.32\% \pm 0.38$ for potassium oxide; $23.16\% \pm 11.55$ to 65.67 ± 4.35 for

silicon dioxide; $7.23\% \pm 3.52$ to $15.97\% \pm 2.69$ for aluminium dioxide; $1.65\% \pm 0.98$ to 5.25 ± 1.05 for carbonate; and $2.23\% \pm 0.03$ to $9.60\% \pm 3.96$ for iron oxides. These results indicated that mean calcium oxide contents were higher than the expected average abundance of 1.4% in sediments, except in some parts of Livuna and Machentche profiles. Calcium oxide content was higher than the average abundance in profiles with gypsum mineralisation. Mean sulphate content was higher than the normal average of 0.36% in most profiles, except where most of the sulphate is taken up by the gypsum crystallisation process. The mean silica and alumina contents were lower in Kasangadzi sediments due to clay in contrast to the other two *dambos* with high quartz content. The chemical composition of gypsum gave the mean calcium oxide content range of $30.75\% \pm 0.98$ to $34.75\% \pm 1.05$. This range is normal as it included the specification of 32.3% for POP industry. Mean sulphite content ranged from $46.51\% \pm 0.36$ to $54.58\% \pm 0.23$. This range includes 46% as the specified average content for POP. Other metal oxide contents are within acceptable limits ($<1\%$). This shows that the Dowa West gypsum is of very good quality.

The chemistry of groundwater showed that concentration of calcium is affected by dilution by rainwater infiltrating the earth layers in the rainy season. High concentration of sulphate ions is attributed to sulphate ions emerging from oxidation of sulphur to sulphate around pyritic rocks. The change in seasons leads to concentrations of sodium and magnesium ions dropping with mean concentrations of less than 20 ppm. Concentration of calcium ions increased because of restricted groundwater whereas sulphate concentration decreased reflecting less oxidation of sulphur in pyrite.

The solubility product values in some sites of in Dowa West area were greater than the solubility product constant ($\log_{10}$ values >5.52) due to local concentrations of calcium and sulphate ions despite the change in seasons. Sites that showed consistently high values were Kabata, Mpatasa and Kashangula. However, the solubility product values indicate that sites favourable for gypsum formation were GSD Mponela, Kayembe Health Centre, Sendeza (JG145), Kabwinja (KB130), Chimbibi (Z82), Mandala (DW62), Kachisa (RJ79), and James Madise (R34). These results agree with the spatial univariate analysis which showed that gypsum precipitation occurred under

reducing acidic conditions ($\text{pH} < 6$) in the rainy season and reducing basic conditions ($\text{pH} > 8$) in the dry season. Calcium ion concentration at borehole sites coincided with alkaline conditions with a mean pH of 8.30. Sulphate ion concentration were high at Kashangula (X183), KB130, and Mandala (DW62) for both seasons.

The multivariate analysis revealed that high correlation between calcium and sulphate ions in groundwater was maintained despite the change in seasons. This is an assurance of gypsum precipitation occurring independent of the seasons. However, semi-arid conditions in the dry season accelerated the formation of gypsum due to high evaporation over the *dambo* areas.

5.1.2 Winning of gypsum from ore sediments

Mineral grain quantification showed that gypsum occurs in association with lateritic clay in Kasangadzi *dambo* and with quartz in Livuna and Machentche *dambos* respectively. Gypsum would easily be separated from the gangue, mineral waste, when it is abundant in one size fraction compared to the others with abundant gangue. Gypsum in clay is easily removed by washing through sieves. Kasangadzi and Livuna *dambos* showed head assay values greater than 10% as feasible prospects for gypsum mining. Gypsum recovery is very high in these *dambos* with high gypsum crystal content and very fine clay.

Upon using the dry shaking table and ball-milling, small round grains of laterite and quartz got separated from the gangue by easily sliding down into the bin. The undersized gypsum passed through 1mm sieve and got retained on 500um sieve. The dry shaking table proved partly successful with 30% gangue separated from the calcined gypsum.

5.1.3 Physicochemical properties of gypsum and POP

Microscopic examinations exhibited that gypsum crystallised around the tiny quartz grains as naturally seeded material. Therefore, crystal growth of the gypsum phase was initiated by the ions building a network from minute quartz grains as the nuclei. The X-ray diffraction analysis made on 130 °C POP further reveals that the POP-product did only contain gypsum and calcium sulphate hemihydrate (synthetic bassanite), but also included synthetic quartz as a trace.

The Dowa West gypsum shows a prominent peak at 11.67° and the other two peaks at 23.40° and 29.11°. These peaks are also indicated in Zimbabwe gypsum with the peaks at almost the same 2θ-angles values. X-ray diffraction patterns for POP (calcined at >160 °C) indicate peaks at 2θ angles 29.65°, 14.65° and 25.59°. This gave a shift from 2θ angles of 11.67°, 24.40°, and 29.11° for gypsum. The hydration process of POP to set-POP does not change the X-ray diffraction pattern as shown by peaks for set-POP product for 175 °C. Lack of shift in the peaks at 29.65°, 14.64°, and 25.58° for set-POP (calcium sulphate dihydrate) confirmed the stability of the calcined gypsum (POP) lattice despite reacting with water during hydration. The remarkable difference in the X-ray diffraction patterns is that the Dowa West gypsum showed the strongest peak at 2θ angle of 11.67° whereas its POP had the strongest peak at 29.65°.

It is evident that the POP products prepared at 100 °C and 130 °C showed a strong peak at a 2θ angle of 11.64°. These two POP products showed a strong peak at 11.64° like gypsum powder-diffraction patterns due to the gypsum phase being partially calcined to calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) while the gypsum phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was maintained. The co-existence of the hemihydrate and the gypsum phases was confirmed by the X-ray spectrograms showing three diffraction peaks for gypsum phase with probably little hemihydrate phase ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$).

Setting time for POP products increased with increased temperature of calcination from 3.5 minutes for 100 °C -POP to 11.25 minutes for 175 °C-POP. The heat of formation evolved from

POP hydration increased in magnitude from 1182.39 J/mole for 100 °C-POP product to 3993.84 J/mole for 175 °C-POP product. The setting time increased with the rise in calcining temperature. Fine hemihydrate crystals were produced under high radiant heat energy as calcined gypsum crystals disintegrated into small particles with greater surface area for reaction with water. This condition certainly enabled the 175 °C-POP product to react more effectively than the 100 °C-POP and 130 °C-POP products.

Hydration process of POP calcined in the laboratory and proto-type ovens showed different trends. Hydration of the POP (160 °C) from the laboratory oven gave 3915.01 J/mole of heat with an average temperature increase of 14.9 °C. Temperature rose with an average rate of 0.63 °C/ minute. Hydration of POP from the prototype oven yielded the reaction curve with the average temperature rise rate of 0.52 °C/minute and a temperature change of 11.6 °C. The reaction gave out heat at the rate of 3047.93J/ mole. The two POP products from the two ovens indicate that the proto-type oven requires improvement by oven-wall insulation to give effective calcination conditions.

The POP material for the Dowa West area indicated chemical characteristics compatible with the BS 1191 standard with SO₃ content >35%, and MgO content <0.2%. The Dowa West chalk-sticks also conforms to the chemical specifications of "Alabaster brilliant white" as a superfine water resisting calcium sulphate; thus calcium oxide (32.3%) and sulphite (≈0.46%) are both in agreement with the chemical data of the Dowa West sample.

The 160 °C-product gave good quality calcined hemihydrate that formed strong POP fabric upon hydration. This POP developed well-bonded microstructure compared to the 150 °C-product whose crystals were mainly less calcined to POP. 180-°C-product with crystals were partially over calcined; thus, the POP weakly reacted with water. The 160 °C-product has proved to be the best hemihydrate for making chalk-sticks on the basis of calcining temperature in this study.

Chalk-sticks of Dowa West batch showed high strength with an average Modulus of Rupture (MOR) of 22.98 ± 2.50 kg/cm² almost similar to the imported dusty chalk sticks. In this case,

production of the local chalk sticks at 160 °C with POP/ water ratio of 1:1 has proved successful in producing comparatively strong chalk sticks.

The quality of chalk was affected by water-POP mixture as good chalk sticks were made by mixing water to POP in the ratios 4:5 and 1:1 respectively. The gritness of the chalk sticks decreased with temperature of calcination of POP from 150 °C to 180 °C. The gritness showed that local chalk sticks are eighteen times more abrasive than commercial chalk sticks. Commercial chalk stick (Apex) yielded much less moisture content than the locally produced chalk stick. High water content increases gritness in the local chalk sticks as it is less friable, and water makes the POP more bound by hydrogen bonding.

5.2 Recommendations

Therefore, potential targets for gypsum exploration are borehole sites with high concentration of calcium and sulphate in the *near-dambo* environment. The *dambo* areas around boreholes KB 130, Mandala (DW 62), Kabata (MS002) and Kashangula (X183) emerged favourable.

More investigations are required to test the gypsum winning methods further. The semi-autogenous ball-milling can assist in removing gypsum from the quartz upon reducing its grain size and later recovering it by sieving.

The Dowa West gypsum was calcined to produce POP that was fabricated into good quality chalk-sticks acceptable by teachers, but the chalk needs to be improved on readability probably by keeping the moisture content low. The local chalk may be dried more to reduce the moisture content to recommended levels. Investigations can be made to find optimum moisture content that would make the local chalk friable and less gritty.

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Through their comments on chalk-sticks produced from the study.

Appendix I Physico-chemical data of water samples in the rainy-season

Field Location or borehole No.	K + (ppm)	Na+ (ppm)	Mg ++ (ppm)	Ca ++ (ppm)	Fe-Total (ppm)	SO4-- (ppm)	HCO3-- (ppm)	pH	Eh/ Volts
MS002 Kabata	8.06	48.17	94.88	90.97	14.19	550.00	135.38		0.025
MS022 Kachisa	4.39	8.13	13.1	15.01	14.84	30.00	31.98	6.14	0.059
RS030 Dzole DEC	0.95	5.17	4.87	11.81	11.59	20.00	79.95	6.44	0.042
KB060 Mkulumimba	2.46	14.24	7.21	4.05	4.82	40.00	18.12	5.12	0.113
DW10 Kabulungo	5.37	35.88	20.03	79.76	27.17	30.00	230.26	7.48	-0.015
DW11 Nkwana	3.23	18.10	43.06	20.83	18.92	40.00	183.35	8.35	-0.059
MS28 Toweza	1.05	12.79	8.15	6.80	7.24	20.00	51.17	7.68	-0.026
R34 James Madise	3.34	51.38	33.41	67.18	27.55	330.00	86.35	6.30	0.05
DW36 Chakhaza	4.22	10.60	11.22	21.45	20.78	20.00	132.18	6.46	0.042
DW47 Nyongani	3.28	15.2	3.44	5.11	6.67	20.00	15.99	7.43	-0.012
P47 Mpata	7.83	21.82	12.87	32.6	25.83	70.00	144.98	7.89	-0.034
KB54 Mlangwe	4.69	19.46	19.41	176.36	27.71	100.00	159	6.98	0.015
DW62 Mandala	35.15	131.37	168.94	186.73	0	1600.00	61	6.59	0.036
DW66 M'ndembo	6.49	16.33	5.59	7.90	9.33	50.00	93.81	7.15	0.002
RJ79 Kachisa I	6.32	9.80	18.13	130.14	26.63	50.00	158.83	6.74	0.03
Z82 Mphimbi	1.53	71.90	38.05	51.73	27.89	400.00	33.05	5.53	0.095
Z83 Chite	3.22	9.01	4.34	6.21	7.67	40.00	46.9	7.00	0.015
MM88 Mdika DEC	3.33	6.90	15.34	28.51	23.62	30.00	147.11	8.13	-0.048
GM99	0.97	8.94	0.63	2.51	3.39	1.00	24.52	5.52	0.096
KB130	22.86	195.89	140.2	274.39	0	1400.00	139.65	6.52	-0.04
JG145 Sendeza	3.47	46.95	29.13	53.85	27.92	100.00	195.08	6.94	0.017
JG145 Nthondowa	0.99	2.99	7.51	11.99	13.46	1.00	25.58	5.83	0.078
R155 Mbewa	5.58	59.45	63.17	86.85	21.36	300.00	230.26	6.86	0.023
E156 Kaufa	3.68	13.62	22.97	39.58	25.26	1.00	275.56	6.71	0.03
X183 Kashangula	17.22	41.15	13.4	233.3	0	1000.00	116.19	7.85	-0.033
A239 Mdika Sch.	1.86	8.30	6.28	7.98	9.18	30.00	46.9	5.71	0.079
PI 437 Kamphenga	5.22	12.00	8.68	18.33	17.37	10.00	135.38	6.46	0.041
SW Kabanga	2.69	34.79	11.2	21.24	19.77	120.00	44.77	5.77	0.079
GK Kachiwale	5.72	19.30	6.2	33.31	23.25	40.00	53.5	8.40	-0.039
CBM Kawere	1.01	5.99	6.92	13.69	13.87	20.00	66.09	6.44	0.04
Kayembe H/C	8.92	35.63	13.58	62.44	25.46	150.00	110.86	6.46	0.041
SW Matola CCAP	9.43	2.40	2.69	21.35	21.04	20.00	108.73	6.43	0.042
GSD Mponela	15.27	23.53	48.27	103.34	11.73	320.00	188.58	8.63	0.045

Appendix II: Physico-chemical data of water samples in the dry-season

Field Location or borehole No.	K + (ppm)	Na+ (ppm)	Mg ++ (ppm)	Ca ++ (ppm)	Fe-Total (ppm)	SO4-- (ppm)	HCO3 -- (ppm)	pH	Eh Volts
MS002 Kabata	4.10	30	11.1	255.1	1.55	404.28	104.72	8.46	-0.06
MS022 Kachisa II	22.06	9.2	4.58	22.06	1.28	4.62	62.26	8.44	-0.058
RS030 Dzoolo DEC	10.61	5	3.11	10.61	3.3	1.54	60.28	8.32	-0.052
KB060 Mkulumbimba	3.40	15	5.86	3.4	0.7	10.34	16.3	8.36	-0.054
DW10 Kabulungo	55.58	33	5.04	55.58	0.19	8.09	10.02	9.06	-0.093
R34 James Madise	3.50	40	24.8	147.2	5.16	97.05	94.87	8.62	-0.07
DW36 Chakhaza	3.50	11.00	11.63	21.6	0.36	4.94	126.49	8.84	-0.081
DW47 Nyongani	2.90	24.5	5.04	22.06	0	14.86	29.65	8.10	-0.039
P47 Mpatsa	0.60	11.9	3.25	11.88	0.7	22.56	90.91	8.50	-0.061
KB54 Mlengwe	2.90	19.5	4.88	11.03	0.36	10.060	56.330	8.93	-0.086
DW62 Mandala	24.00	5.5	71.7	368	0.36	481.320	61.270	8.25	-0.048
RJ79 Kachisa I	7.80	24.50	13.05	43.28	0.81	23.06	218.39	8.80	-0.08
Z82 Mphimbil	1.20	60.00	20.37	81.46	0.85	85.91	39.53	8.35	-0.054
Z83 Chilete	12.70	30	4	398.3	5.55	359.07	163.05	8.63	-0.07
MM88 Mdika DEC	1.20	15.00	8.88	15.27	0.41	13.05	79.06	8.37	-0.053
GM99	0.40	6.5	5.45	2.15	1.15	5.91	20.75	8.68	-0.074
KB130	16.10	8.9	98.4	346.3	0.2	425.44	109.65	8.74	-0.08
JG145 Sendeza	0.6	24.5	17.96	33.94	1.55	54.27	20.75	8.19	-0.045
JG145 Nthondowa	1.50	3	3.31	7.64	1.45	72.55	42.49	7.83	-0.024
R155 Mbewa	0.90	27	16.85	30.55	1.7	248.04	88.94	8.14	-0.04
E156 Kaufa	2.30	10.5	12.17	36.49	1.05	4.05	246.06	8.9	-0.09
X183 Kashangula	2.1	10	5.82	7.21	1.9	5.44	62.26	7.9	-0.03
A239 Mdika Sch.	2.10	9.20	6.97	10.18	1.15	9.81	56.33	7.78	-0.022
PI 437 Kamphenga	4.40	13.90	6.23	21.21	0.9	1.4	89.93	8.87	-0.082
SAW Kabanga	2.90	33.1	8.67	21.64	0.84	49.69	23.72	7.7	-0.016
GK Kachiwale	1.80	21.00	2.26	9.76	0.6	26.52	44.47	8.03	-0.034
CBM Kawere	0.60	5.5	3.21	19.09	0.1	5.09	61.27	7.42	-0.02
Kayembe H/C	9.50	28.5	10.9	35.22	2	32.93	67.2	8.4	-0.056
GSD Mponela	3.30	20.00	7.25	29.28	0.85	16.62	84.99	8.25	-0.05
Chikwawe SW	1.20	18.50	30.07	22.06	0.15	21.79	34.59	7.9	-0.02
Chigonalipenga	6.90	4.50	3.27	14.85	0.9	23.12	60.28	8.2	-0.05
Kawinjia SW	9.50	4.50	4.88	14.42	0.31	6.63	62.26	7.4	-0.019
Nambamba SW	1.30	14.50	9.3	108.2	0.63	72.55	59.29	7.8	-0.024
Nauchi Sch. BH	15.00	178.00	136.2	489.2	1.94	529.5	130.44	8.2	-0.042