Calcretes, silcretes and intergrade duricrusts

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Abstract

Calcretes and silcretes are the most widely encountered 'rocks' in the Kalahari sandveld that covers much of Botswana. This chapter presents the first holistic overview of current knowledge about these duricrusts at a national scale. It does so by considering the distribution, classification, macromorphology, geochemistry and mineralogy of each duricrust type in turn, alongside various models used to explain their formation. The chapter then reviews our understanding of a variant of duricrust encountered more in the Botswana Kalahari than anywhere else in the world – the silcrete-calcrete intergrade duricrust. The chapter concludes with a summary of knowledge about the age of duricrusts in Botswana before pointing to potential directions for future research.

Keywords: Calcrete, silcrete, geochemical sediments, Kalahari Group, Botswana

X.1. Introduction

Travellers visiting Botswana for the first time could be forgiven for thinking that much of the surface geology of the country consisted of sand. While it is true that the Kalahari Sands – the stratigraphically youngest component of the Kalahari Group sediments (Thomas, 1981; Malherbe, 1984; Haddon and McCarthy, 2005) – blanket much of the landscape away from the eastern hardveld, other rock types are also present. For example, Precambrian formations protrude through the sand cover in west and northwest Botswana, while inliers of the Mesozoic Karoo Supergroup occur in south-central regions. However, the most widely encountered 'rocks' in areas of present-day sandveld are various forms of geochemical sediment or *duricrust*. Of these, the most widespread (Figure X.1a) are calcium carbonate-cemented *calcretes* (section X.2) and silica-cemented *silcretes* (section X.3).

Research has been conducted on calcrete and silcrete in Botswana for over 100 years, commencing with Passarge's (1904) detailed descriptions of the regional geology in his monograph *Die Kalahari*. Examples from Botswana feature in Goudie's (1973) seminal book on *Duricrusts in Tropical and Subtropical Landscapes*, while Watts' (1980) work on pedogenic calcrete in the Kalahari remains one of the most cited on the subject. Other syntheses are included in the volume *The Kalahari Environment* by Thomas and Shaw (1991) and in the wide-ranging review of duricrusts in southern Africa by Nash (2012).

The aim of this chapter is to provide a state-of-the-art overview of research on duricrusts in Botswana. It does so by blending global research into the origins of calcrete and silcrete with regional studies from the Botswana Kalahari. It then considers a third, hybrid, variety of duricrust termed 'silcrete-calcrete intergrade duricrust' by Nash and Shaw (1998), which has been described extensively in Botswana. Iron oxide-cemented laterites and ferricretes have been documented in the eastern hardveld of Botswana (e.g. Goudie, 1973; Nash et al., 1994a; Dorland, 1999; Yang and Holland, 2003; Yamaguchi et al., 2007). However, despite their use in the construction of low-volume roads (Association of Southern African National

Roads Agencies, 2014; Paige-Green et al., 2015), these duricrusts have not been studied in sufficient breadth to be considered further here.

X.2. Calcrete

Botswana's generally flat topography, combined with the limited extent of landscape incision, restricts the exposure of thick sub-surface duricrusts. However, the available literature suggests that calcrete occurs beneath the Kalahari Sand cover across much of the country (Figure X.1a). The Botswana Kalahari contains some of the thickest calcrete sequences in the world (Watts, 1980; Linol, 2013). Calcrete is found both within sedimentary successions and at the surface (Goudie, 1973; Nash et al., 1994a; Linol et al., 2015). Calcretes reach their greatest thickness, and frequently outcrop, in the vicinity of fossil valleys and pans – see Chapter X. Some of the most extensive outcrops are seen around the Makgadikgadi and Mababe depressions, Lake Ngami and various smaller pans in central Botswana (Grove, 1969; Mallick et al., 1981; Lawrence and Toole, 1984; Nash et al., 1994a; Ringrose et al., 2005, 2009; White and Eckardt, 2006) – see Figure X.1b for locations. Considerable thicknesses are also exposed along the Okwa-Mmone drainage systems. These sequences may merge with similar deposits exposed along the Molopo-Auob-Nossop valleys in northern South Africa and southeastern Namibia (e.g. Boocock and van Straten, 1962; Goudie, 1973; Watts, 1980; Mallick et al., 1981; Nash et al., 1994a; Ringrose et al., 2002; Nash and McLaren, 2003; Haddon and McCarthy, 2005) to form part of a wider calcrete-capped surface referred to as the 'Kalahari Limestone' by Range (1912) or the Mokalanen Formation by Thomas et al. (1988). Borehole data indicate that calcretisation (and silicification; sections X.3 and X.4) is widespread deep within the Kalahari Group sediments, with thick calcretes identified many tens of metres beneath the Kalahari Sand cover (e.g. Meixner and Peart, 1984; Thomas and Shaw, 1990; 1991; du Plessis, 1993; Nash et al., 1994a; Haddon and McCarthy, 2005; Linol et al., 2015).

For readers seeking more general information about calcretes, reviews of the characteristics, formation and significance of calcareous duricrusts within desert landscapes are provided by Alonso-Zarza (2003), Wright (2007), Dixon and McLaren (2009) and Nash (2011). Detailed overviews of southern African calcretes are provided by Netterberg (1969a), Watts (1980), Nash and McLaren (2003) and Nash (2012). The unpublished PhD thesis by Shaw (2009) also contains detailed descriptions of calcrete exposures from across the Kalahari.

X.2.1 Definitions

Before focussing on studies of calcrete in Botswana, it is useful to consider some definitions. The word 'calcrete' was first used by Lamplugh (1902) to describe calcium carbonate-cemented gravels in the vicinity of Dublin, Republic of Ireland. The term was applied subsequently to geochemical sediments exposed in the vicinity of the Zambezi Valley where it forms the border between Zambia and Zimbabwe (Lamplugh, 1907). Numerous definitions now exist. Working mostly in South Africa, Netterberg (1969a, p.88) used the term calcrete rather broadly to describe almost any terrestrial material that has been cemented and/or replaced by calcium carbonate. Goudie (1983, pp.94-95) tightened up this definition, noting that calcretes may contain cementing agents in addition to calcium carbonate and that carbonate accumulation occurs primarily in the vadose zone (i.e. in the region above the water table). Machette (1985) urged that the term calcrete should be reserved for indurated duricrusts and that 'calcic soil' be used to describe weakly carbonate-cemented soils – which begs the obvious question, 'when is a material sufficiently indurated to be termed a calcrete'? The most widely used definition today is that introduced by Wright, who, building on Goudie (1983), identifies calcrete as "…a near surface accumulation of predominantly calcium carbonate, which occurs in a variety of forms from powdery to nodular, laminar and massive. It results from the cementation and displacive and replacive introduction of calcium carbonate into soil profiles, sediments and bedrock, in areas where vadose and shallow phreatic groundwaters are saturated with respect to calcium carbonate" (Wright, 2007, p.10).

Calcrete is a non-genetic term – in other words, its application to a carbonate-cemented material does not imply that the material formed in a particular way. Rather, various sub-types of calcrete have been identified that suggest specific genetic origins. The most fundamental distinction made in the literature is between varieties that develop as a horizon (or multiple horizons) within the vadose zone of soil profiles (these are termed *pedogenic calcretes*) and those that form at or around the water table or in the capillary fringe (often grouped for simplicity as *non-pedogenic calcretes*). Beneath this top-level classification are a range of different types of calcrete, defined according to their geomorphic context and whether the duricrust is considered primary or secondary. One way in which the different sub-types can be grouped is shown in Table X.1 (after Carlisle, 1983). The bipartite division between pedogenic and non-pedogenic calcrete is not without its problems, since some calcretes may result from a combination of pedogenic and non-pedogenic processes. For example, a non-pedogenic valley calcrete that developed in association with a fluctuating water table may be exhumed and modified by pedogenesis (Machette, 1985). However, the terms are widely used, so they are adopted here.

X.2.2 General characteristics of calcretes in the Botswana Kalahari

The majority of surface calcretes in Botswana are white, cream or grey in colour (Figure X.2), though pinkish mottling and banding is common where the calcrete is highly indurated and/or relatively mature. Calcretes exhibit a variety of forms, including weakly calcified, chalky, powdery, rhizocretionary, nodular, honeycomb, platy, laminar, stringer, pisolitic, brecciated, conglomeratic, massive and hardpan (cf. Wright, 2007). Of these, massive and hardpan forms are most commonly encountered in Botswana, though this may be more a product of where calcretes are exposed than their true geographic extent; as discussed in section X.2.3, massive hardpan calcretes are more likely to be developed in association with valleys and pans and this is also where they are most visible. Most calcretes have developed within sandy components of the Kalahari Group sediments, although there are exposures at the periphery of the Kalahari Group where calcretised gravels are present (e.g. Thomas, 1981; Shaw and de Vries, 1988; Nash et al., 1994a; Shaw, 2009).

Over much of Botswana, surface calcrete outcrops rarely exceed 2-3 m thickness. However, extremely thick stacked calcretes have been identified beneath the Molopo valley in southern Botswana and northern South Africa, where borehole records, confirmed by exposures, reveal sequences reaching up to 80 m in total (Goudie, 1973; Thomas et al., 1988). In Ngamiland, a recent drilling programme has identified widespread calcrete layers at the base of the Kalahari Group sediments; these range between 10 and 60 m thick, and have been termed the Nxau-Nxau Calcrete Formation by Linol (2013). Stratigraphic correlation of the Nxau-Nxau Calcrete Formation with the sequence in another Ngamiland core (described by McFarlane et al., 2010) is problematic owing to evidence for extensive deep weathering in the latter.

The macromorphology of calcrete profiles varies between pedogenic and non-pedogenic types. Well-developed pedogenic calcretes are distinct in having a highly organised profile dominated by a hardpan horizon (Figure X.3). This hardpan is typically capped by a laminar calcrete and – if recently exposed and not subject to subaerial erosion – brecciated calcrete clasts and a layer of weakly calcified sediment. Below the hardpan, the profile becomes less well-cemented with depth, grading into a nodular horizon, then a chalky or powdery horizon before passing into non-calcified sediment. In contrast, non-pedogenic calcretes (e.g. Figure X.2b,c) commonly comprise a hardpan layer only, sometimes capped by a laminar calcrete, but with a sharp basal boundary with underlying uncemented sediment or bedrock.

Regardless of whether a calcrete formed as a result of pedogenesis or other processes, its chemistry will be dominated by calcium carbonate. A sample of 300 bulk chemical analyses of calcretes published by Goudie (1972), including many from southern Africa, comprised on average 79.28% calcium carbonate (42.62% CaO), 12.30% silica, 3.05% MgO, 2.03% Fe_2O_3 and 2.12% Al_2O_3. Further data for the subcontinent are included within Netterberg (1969a).

Few analyses have been published specifically for calcretes from Botswana. However, Gwosdz and Modisi (1983) report calcretes from around Ghanzi, Letlhakeng, Machaneng, Mamuno, Maun, Mookane and Nata, and from the Bonwapitse River and Serorome valley, with $CaCO_3$ contents of up to 96.3%.

In terms of mineralogy, the most detailed investigations of calcretes in Botswana are from exposures in 'borrow pits' and valley flanks by Watts (1980). His analyses of pedogenic calcretes around the Makgadikgadi Basin and in southeast Botswana show that the carbonate component is dominated by low-Mg calcite, which occurs as micrite, microspar and sparite. Minor quantities of high-Mg calcite, aragonite and, in well-developed calcrete profiles, dolomite may also be present. Profiles incorporate additional authigenic silica (section X.3) and various authigenic silicates including palygorskite, sepiolite, montmorillonite, illite, mixed-layer clays, glauconite and, more rarely, chlorite, kaolinite and the Na-Ca zeolite clinoptilolite. Palygorskite and sepiolite are more abundant in mature calcrete profiles, while montmorillonite with minor palygorskite and traces of other clays characterise less developed profiles. Clinoptilolite was only identified by Watts (1980) in calcretes associated with pans.

X.2.3 Processes of calcrete formation

The degree of development, or *maturity*, of an individual calcrete profile is related to a series of interdependent factors: time, climate, host sediment characteristics, carbonate source(s) and supply, geomorphological context, organic influences, sedimentation (or erosion rates) and a variety of localised conditions. As Watts (1980) notes, "the interplay of such a number of parameters operating over an area as large as the Kalahari… results in a highly diverse suite of calcrete types" (p.89).

Carbonate sources, transfer mechanisms and drivers of precipitation

The formation of pedogenic and non-pedogenic calcrete requires three things: (i) a source of calcium carbonate, (ii) a mechanism for transferring this carbonate to the site of calcrete accumulation, and (iii) a means of triggering carbonate precipitation (Goudie, 1983). The carbonate sources and precipitation mechanisms described in this section are common to most calcrete types. However, the mechanisms by which carbonate is transferred to the site of accumulation differ between pedogenic and non-pedogenic sub-types.

Potential carbonate sources for any calcrete include solid and dissolved carbonate introduced into the soil or sediment from above (in Botswana this includes introduction via atmospheric dust, rainfall, surface runoff, plant materials and shells) or below (via groundwater) (Netterberg, 1969a; Goudie, 1983; Cailleau et al., 2004). The contribution of specific carbonate sources to calcrete formation will vary spatially and with calcrete type. By comparison with other desert and semi-desert regions, atmospheric dust and rainfall inputs are likely to be the most important for the formation of pedogenic calcretes in Botswana (e.g. Goudie, 1973; Watts, 1980; Capo and Chadwick, 1999; Chiquet et al., 1999) and subsurface sources for non-pedogenic calcretes (e.g. Arakel and McConchie, 1982; Arakel, 1986, 1991; Nash and McLaren, 2003; Nash and Smith, 2003).

Carbonates are concentrated into specific horizons of a soil or sediment by different dominant mechanisms in pedogenic and non-pedogenic calcretes. Pedogenic calcrete formation is characterised by vertical transfers of dissolved carbonate, largely as a result of illuvial-eluvial pedogenetic processes. Carbonate redistribution is driven by the leaching of dissolved carbonate in downward percolating soil solutions, with the zone of maximum accumulation controlled by the depth of penetration of the wetting front following rainfall events (Goudie, 1983; Klappa, 1983). If the water table is relatively close to the surface, dissolved carbonate may also move upwards to the site of accumulation due to capillary action. In contrast, much of the carbonate for non-pedogenic calcrete formation is provided by lateral transfers of carbonate-rich surface or groundwater (e.g. within lacustrine or channel-margin settings), with vertical movements of dissolved carbonate only really coming into play once close to the site of precipitation (Goudie, 1973, 1983; Bachman and Machette, 1977; Arakel, 1986).

Once at the horizon of carbonate accumulation, calcium carbonate dissolved in water may be precipitated by a variety of processes. These are well-described in general accounts of calcrete development (e.g. Wright, 2007), and include evaporation, evapotranspiration, pH shifts to above pH 9, organic life processes (Goudie, 1983), a decrease in the partial pressure of soil CO_2 (Schlesinger, 1985), CO_2 loss by degassing (e.g. as temperature increases; Barnes, 1965), and the common ion effect (Wigley, 1973).

Pedogenic calcretes

A mature pedogenic calcrete profile, such as the one shown schematically in Figure X.3, is the end product of a long period of pedogenesis that may span hundreds of thousands of years. Calcic soil and pedogenic calcrete development follows a well-established morphological sequence, with many of the carbonate morphologies described in section X.2.2 falling into an evolutionary continuum that relates to the relative maturity, or *stage*, of the calcrete profile (see Gile et al., 1966; Reeves, 1970; Bachman and Machette, 1977; Netterberg, 1980; Goudie, 1983; Netterberg and Caiger, 1983; Machette, 1985).

There are six widely recognised stages of pedogenic calcrete development (Bachman and Machette, 1977; Machette, 1985); these are summarised in Table X.2 and illustrated in Figure X.4. The upper routeway through Figure X.4 – relating to host sediments with a low gravel content – is most relevant to the sandy sediments of the Kalahari. Under this idealised continuum, Stage I calcified soils and chalky or powder calcretes may develop into Stage II nodular calcretes over time as calcium carbonate concretions increase in size. The concretions may coalesce to form Stage III honeycomb calcrete, with a Stage IV-V hardpan calcrete developing as surface horizons become plugged with carbonate. Degradation of a hardpan as a result of solutional processes may lead to the development of a Stage VI brecciated (or boulder) calcrete. Laminar calcretes consisting of finely banded carbonate often cap hardpan and brecciated calcretes, and the whole sequence may be buried by upper soil horizons containing carbonate pisoliths (Wright, 2007). The stage of development may be used in local regions for correlation and the determination of relative ages of soils and geomorphic surfaces (Bachman and Machette, 1977). However, attempting to describe non-pedogenic calcretes using the scheme shown in Table X.2 is problematic since non-pedogenic calcretes may not go through the same phases of development.

The seminal work by Watts (1980) includes logged pedogenic calcrete profiles from various sites along the Molopo valley and its tributaries (Figure X.5). The simplest depicted profiles comprise a single hardpan layer with underlying nodular calcrete and calcic soil; these represent a single cycle of calcrete development. In contrast, the thickest profile may – based on the presence of at least two hardpan calcrete horizons – represent two or more cycles of pedogenesis separated by periods of sediment accumulation. These sections are part of the 'Kalahari Limestone' first described by Passarge (1904) and Range (1912), which has undergone karstification beneath the Kalahari Sand cover in adjacent areas of Namibia (e.g. in the Weissrand area; Goudie and Viles, 2015).

Watts (1980) includes a flow diagram illustrating the main processes operating during the formation of pedogenic calcretes in the Kalahari (Figure X.6). Calcite precipitation from percolating solutions is thought to involve either rapid or slow evaporation and/or CO_2 loss. Slow evaporation results predominantly in the precipitation of low-Mg calcite with a consequent gradual increase of Mg concentrations in the resulting solutions. Rapid evaporation may precipitate high-Mg calcites that are in thermodynamic disequilibrium with the low Mg/Ca ratio vadose percolating waters. Both passive (void-filling) and replacive (of silicate grains) calcite may be formed, with silica being released as a result of replacement and migrating down-profile to accumulate in lower calcrete horizons. Under more saline conditions, optically length-slow chalcedony (when viewed in thin-section under cross-polarised light) and potentially clinoptilolite will precipitate, whereas optically length-fast chalcedony and/or mega-quartz cements are precipitated in non-saline micro-environments. Rapid evaporation may produce solutions that are highly supersaturated with respect to calcite, resulting in the displacive growth of calcite crystals. Neomorphism of high-Mg to low-Mg calcite takes place rapidly and leads to the release of Mg. This, combined with the increased Mg/Ca ratio due to low-Mg calcite precipitation, increases the Mg concentration of pore fluids to the degree that authigenic Mg-rich silicates may precipitate. Clay authigenesis also occurs during calcrete development. Clay minerals such as palygorskite may form through the reaction of magnesium with montmorillonite or may be precipitated directly from solution in association with neoformed sepiolite and dolomite.

The flow diagram in Figure X.6 assumes a dominantly closed system. However, episodes of high rainfall may obscure this and flush the system. Local precipitation of high-Mg calcite is also thought to occur as a result of capillary rise from groundwater in and around saline depressions such as the Makgadikgadi basin and larger pans (Watts, 1980).

Non-pedogenic calcretes

Few studies have considered the development of non-pedogenic calcretes in Botswana. One exception is work by Nash and McLaren (2003), which discusses the formation of late Pleistocene to Holocene valley calcretes in the Kalahari. Valley calcretes occur exclusively within the base of dry valleys (see Chapter X) and are commonly exposed either as a lag of calcrete gravel (where valley floors have not been incised) or within low terraces on valley sides. Calcrete-supported terraces are particularly prominent in the Hanehai and Okwa valleys where a single low terrace up to 4 metres high can be traced along much of the valley courses west of the Trans-Kalahari Highway.

The majority of valley calcretes are massive in appearance with little evidence of profile organisation or vertical structures. Many thicker outcrops in the Hanehai and Okwa valleys are well-cemented in their uppermost sections and underlain by slightly more friable cemented sands. Almost all exposures exhibit a thin (< 5 mm) laminar calcrete on their upper surfaces. Outcrops occasionally show abundant vertical to sub-horizontal tubular structures of up to 1.5 cm diameter, lined with laminar calcrete and partially infilled by sand, which are interpreted as either root or reed casts (Nash and McLaren, 2003). It is not possible to tell from field observations whether valley calcretes cement the full width of alluvial valley fills or 'pinch out' towards valley flanks. However, analyses of borehole transects across dry valleys in the Central Kalahari (e.g. Figure X.7) would tend to favour the latter (Nash et al., 1994a).

The micromorphology of Kalahari valley calcretes provides important insights into their development (Figure X.8). The majority are highly indurated, with total cement contents ranging from 70-90% of the calcrete bulk volume. Massive, structureless, pore-filling micrite is the most important component of the cement (Figure X.8a,b), suggesting that carbonate precipitation was relatively rapid. Relatively few of the samples analysed by Nash and McLaren (2003) contained more coarsely crystalline forms of $CaCO_3$ cement, reinforcing the relative rapidity of precipitation. Void spaces provide further clues into formational processes. In addition to uncemented inter-granular spaces, many elongate, crack-like voids are present. These tend to occur towards the top of profiles and may be a product of the final stages of desiccation of the rivers or ponds that formerly occupied the valleys. Evidence of biotic activity is also abundant (Figure X.8c,d), including the presence of rhizoliths, root hairs, fungal hyphae and needle fibre cements, most commonly within cracks and other void spaces. Authigenic silica cements may occur as void linings and rare void fills.

Kalahari valley calcretes appear to display at least two major phases of development (Nash and McLaren, 2003). It is likely that the main cementation of alluvial sediments by micrite occurred either immediately following the cessation of surface flows or, more probably, whilst flow was in decline and valleys were shifting towards their present-day hydrological 'fossil' status during the late Pleistocene (see Chapter X). Cracks developed within the calcrete and became the focus of biogenic activity. The final phase of precipitation in the vadose zone came in the form of silica cements in pore spaces and voids.

Thin-section analyses of the Nxau-Nxau Calcrete Formation at the base of the Kalahari Group sediments in Ngamiland reveal facies characteristic of both lacustrine and pedogenic environments (see Alonso-Zarza, 2003), suggesting that calcrete development took place in or near a shallow lake or wetland environment (Linol, 2013; Linol et al., 2015). Examples include extensive biogenic features (e.g. alveolar structures, rhyzoliths and burrows) that indicate intense biological activity during calcrete formation, as well as fenestral fabrics and circum-granular cracks within more muddy facies suggesting episodes of immersion and desiccation (Linol et al., 2015).

X.3. Silcrete

In comparison with other parts of the world, relatively little has been written on silcrete in Botswana. The situation is changing, however, mainly as a by-product of interdisciplinary research between geomorphologists and archaeologists seeking to identify the locations of silcrete ‘quarries’ used to supply materials for stone tool manufacture during the Middle Stone Age (e.g. Nash et al., 2013, 2016). For example, the large geochemical datasets arising from this work have been used by Webb and Nash (2020) to constrain the environmental controls upon silcrete formation in the Botswana Kalahari (see section X.3.3).

The distribution of silcrete in Botswana has not been mapped. However, like calcrete, published studies are restricted geographically to areas covered by Kalahari Group sediments (Figure X.9). The main areas of outcrop include the flanks (and occasionally beds) of drainage lines and the margins of ephemeral lakes and pans (e.g. Boocock and van Straten, 1962; Smale, 1973; Mallick et al., 1981; Summerfield, 1982; Shaw and de Vries, 1988; Nash et al., 1994a,b, 2004; Shaw and Nash, 1998; Ringrose et al., 2005, 2009; Kampunzu et al., 2007). Silcretes also occur as rare escarpment caprocks at the easternmost margin of the Kalahari Group sediments (Summerfield, 1982; Nash and Hopkinson, 2004), in some places forming a distinct unit overlying weathered basalt (Smale, 1973; Summerfield, 1982; see Figure X.9e). Recent drilling work in the vicinity of Tsodilo Hills has identified a 4 m thick silcrete at the interface between the basal Kalahari Group and underlying pre-Karoo bedrock (Linol et al., 2015), so it is possible that extensive silcretes occur at depth elsewhere.

For readers seeking general information about silcrete, useful reviews are provided by Milnes and Thiry (1992), Nash and Ullyott (2007), Nash (2011, 2012) and, from an archaeological perspective, Thiry and Milnes (2017). Overviews that focus on silcretes in Botswana are limited to early studies such as Goudie (1973) and Summerfield (1982; 1983b; 1983a) and the more recent syntheses by Nash (2012) and Webb and Nash (2020).

X.3.1 Definitions

The term silcrete was introduced by Lamplugh (1902) to describe the products of near-surface processes by which “silica accumulates in and/or replaces a soil, sediment, rock or weathered material to form an indurated mass” (Nash and Ullyott, 2007 p.95). Silcretes *sensu stricto* are defined as containing >85 wt% SiO_2 (as determined by bulk chemical analysis), with many comprising >95 wt% SiO_2 (Summerfield, 1983b). Most silcretes require stable geomorphological conditions to develop, although the formation of some may be related to actively evolving landscapes (see, for example, Thiry, 1999).

Like calcrete, silcrete is a non-genetic term, with various sub-types identified that suggest specific genetic origins. The most relevant scheme to classify these sub-types as they occur in Botswana is shown in Figure X.10 (after Nash and Ullyott, 2007). This scheme builds upon the classification proposed by Milnes and Thiry (1992), but includes additional sub-types only documented in the Kalahari. Echoing Carlisle’s (1983) classification for calcrete, silcretes are first subdivided into pedogenic and non-pedogenic varieties. Pedogenic silcretes are then divided into more opaline 'duripans' in which clay and iron are retained and those with abundant microquartz and titania that lack clay minerals and iron oxides (Thiry, 1999). Non-pedogenic silcretes are grouped into *groundwater*, *drainage-line* and *pan/lacustrine* types according to their geomorphological context. To the knowledge of the author, pedogenic silcrete has yet to be identified in Botswana; as such the remainder of this chapter discusses non-pedogenic silcretes only.

X.3.2 Characteristics of silcretes in the Botswana Kalahari

Surface silcrete occurrences in Botswana are usually localised and vary from small outcrops or gravel lags around the margins of pans (e.g. Summerfield, 1982; Nash and Shaw, 1998; see Figure X.9b) to layers up to several metres thick in the floors of rivers (Shaw and Nash, 1998), the flanks of dry valleys (e.g. Summerfield, 1982; Shaw and de Vries, 1988; Nash et al., 1994b; Kampunzu et al., 2007; Figure X.9d) and within cemented palaeolake shorelines (Ringrose et al., 2005, 2009). The colours of individual outcrops vary considerably, from pale to dark green in the case of silcretes at the northern and southern margins of the Makgadikgadi Basin (Boocock and van Straten, 1962; Summerfield, 1982) and in the Okwa valley (Nash et al., 2004), to white, grey, cream, buff, brown, reddish-brown and black elsewhere (see Nash et al., 2013). These colours are rarely uniform, with many silcretes including darker or lighter flecks, veins and inclusions or – in the case of silcretes along the Boteti River – 'whorl'-like patterns consisting of undulating, enclosed, parallel bands produced by variations in the degree of iron oxide staining within the cement (Summerfield, 1982).

Silcrete outcrops in Botswana exhibit a wide variety of morphologies. In part this depends upon whether the silcrete formed as a primary precipitate within aeolian, fluvial or lacustrine sediments or whether it developed via the replacement of a pre-existing calcrete (see section X.4). Primary silcretes in pan/lacustrine and drainage-line settings, such as those exposed along the Boteti (Shaw and Nash, 1998) and Nata rivers (Summerfield, 1982) and within the Makgadikgadi depression (Ringrose et al., 2009), are typically nodular, sheet-like or massive in appearance (Figure X.9). Those that formed by replacement of calcrete have more irregular morphologies and, where exposed in palaeolake strandlines, may be lenticular in appearance. The range of silcrete morphologies encountered across Ntwetwe Pan alone – including unusual tube-like silcretes likely formed via the silicification of root structures – is illustrative of the wider variability (Figure X.11).

Most silcretes in Botswana consist of a framework of quartz grains, inherited from the parent Kalahari Sands, cemented by chalcedonic silica and/or microquartz (Summerfield, 1982). Most exhibit grain-supported fabrics (using the terminology of Summerfield, 1983b) but floating fabrics are common where silicification of a precursor calcrete has taken place. Silica void fills are widespread and comprise silica polymorphs including α-quartz, opal-CT or opal-T and moganite (e.g. Summerfield, 1982; Nash et al., 1994a; Nash and Hopkinson, 2004).

Several studies of Botswana silcretes incorporate geochemical data (Summerfield, 1982; Nash et al., 1994b, 2004, 2013; Nash and Shaw, 1998). Meta-analysis of major and trace element data for silcretes within the Okavango-Makgadikgadi system (Webb and Nash, 2020) shows that the median composition comprises 94 wt% SiO_2 with small amounts (<1.1 wt%) of Al_2O_3, K_2O, Fe_2O_3, MgO, CaO and TiO_2 (in decreasing order of abundance). Barium is the most abundant trace element (~1000 ppm), with high levels of chromium (~200 ppm), strontium and zirconium (50 and 65 ppm respectively), low levels (3-20 ppm) of rubidium, cerium, lanthanum, neodymium and yttrium (in decreasing order of abundance), and very low levels (mostly <1 ppm) of other elements. The mineralogy of Botswana silcretes is dominated by quartz, with small amounts of calcite, Fe oxide/hydroxides and various heavy minerals also present. Glauconite has been identified in many silcretes (Summerfield, 1982; du Plessis, 1993; Webb and Nash, 2020), and imparts the green colour apparent in some outcrops. The occurrence of glauconite may explain the small amounts of Al_2O_3, K_2O, Fe_2O_3

and MgO present in most silcretes (Webb and Nash, 2020). Concentrations of rare earth elements vary spatially (Nash et al., 2013), and are very strongly correlated with each other (r^2 = 0.77-0.91) but not with any major elements or other trace elements; this suggests they are likely present as rare earth minerals such as bastnaesite and/or xenotime (Webb and Nash, 2020).

X.3.3 Processes of silcrete formation

Silica sources, transfer mechanisms and drivers of precipitation

Research by Webb and Nash (2020) has shown that the formation of non-pedogenic silcretes in the Botswana Kalahari was approximately isovolumetric (i.e. there was little or no volume change during silicification). More importantly, it required a substantial addition of SiO_2. Some of this silica may have been derived locally from within the Kalahari Group sediments, but much was transported from more distant sites (Nash and Ullyott, 2007). Few chemical elements were lost during silicification; Si and K were gained as microquartz precipitated in the sediment porosity and glauconite formed in suboxic groundwater conditions. This contrasts with other areas of southern Africa, such as the Cape coastal zone, where most silica for silcrete formation was derived from intense *in situ* weathering of bedrock (Webb and Nash, 2020).

Weathering of silicate minerals provides the ultimate source for most silica within surface and subsurface waters, the atmosphere, and plants and animals (Summerfield, 1983b). Enhanced silica availability may occur for a range of reasons. One of the most important controls in the context of Botswana is environmental pH. Silica solubility is relatively stable under weakly acidic to neutral pH but increases rapidly above pH 9 (Dove and Rimstidt, 1994). Such high pH levels are not uncommon in arid and semi-arid environments, where alkaline conditions may occur as a result of evaporation (Chadwick et al., 1989). Monitoring of hydrochemical conditions in Sua Pan over two wet seasons (1999-2000 and 2000-2001), for example, showed that the pH of lake waters ranged between pH 8.6 and 10, with maximum values recorded during the initial phases of seasonal flooding when pre-existing salts in riverbeds or pan margins were dissolved (Eckardt et al., 2008; McCulloch et al., 2008). This is consistent with other saline lakes in southern Africa rich in HCO_3^- + CO_3^{2-} ions.

In addition, there are a number of biological silica sources, with many plants, including grasses, reeds and palms concentrating amorphous silica within their tissues (Goudie, 1973); this may be released upon decay or temporarily stored as phytoliths. Diatoms, common in many fluvial and lacustrine environments in the Kalahari (Schmidt et al., 2017), extract silica from surface waters for their tests and may subsequently become a silica source upon death (McCarthy and Ellery, 1995; Ringrose et al., 2014; Struyf et al., 2015).

Most of the silica required for silcrete formation within the Okavango-Makgadikgadi system was likely provided by the Okavango River. The Okavango has an average annual discharge of ~1 x 10^{10} m^3 where it enters Botswana, with an annual flood pulse generated by seasonal rains over its headwater areas in the Angolan highlands. In most years, floodwaters dissipate within the Okavango Delta. However, in years of exceptional flood, waters may extend along the Boteti River and into the Makgadikgadi depression. Substantially higher flows during the late Quaternary formed extensive palaeolakes linking the now discrete Ngami, Mababe and Makgadikgadi basins to the Okavango Delta (cf. Burrough et al., 2009). The Okavango River presently delivers an estimated 360,000 tonnes of solutes to the Okavango Delta per year, ~50% of which can be dissolved silica, with concentrations up to 20 mg/L (McCarthy and Ellery, 1998; McCarthy, 2006); there is negligible solute input from rainfall (Milzow et al., 2009). Silica transport occurs mainly in solution as undissociated monosilicic acid, either as the monomer H_4SiO_4 or the dimer $H_6Si_2O_7$ (Dove and Rimstidt, 1994), although organic or inorganic complexes may also be formed. As the Okavango-Makgadikgadi system is endorheic, most of the silica supplied during low flows and large floods (other than that lost via deflation) is retained in the basin and is therefore available for silcrete formation.

Silica precipitation is controlled by the concentration of silica in solution, itself related to silica availability and a range of other factors (Nash and Ullyott, 2007). The most soluble silica species will be precipitated first from a supersaturated solution; this is usually amorphous silica (Millot, 1960). Silica monomers polymerise and aggregate to form colloids and these colloids may precipitate to form opal-A (Williams et al., 1985). If solutions are supersaturated with respect to quartz then precipitation can occur in the absence of other changes, providing solutions are slow moving (Summerfield, 1982).

Silica precipitation is influenced by pH, Eh, evaporation, the presence of other dissolved constituents and life processes. A fall in the pH of surface and/or groundwater to below pH 9 evaporation may initiate silica precipitation due to its effect upon silica solubility. Eh has a complex effect. As discussed by Nash and Ullyott (2007), quartz placed in solutions containing ferrous iron has been shown to become more soluble following exposure to oxidising conditions. Silica solubility is reduced if adsorption onto iron or aluminium oxides occurs. In contrast, the presence of NaCl may enhance solubility due to the ionic strength effect (Dove and Rimstidt, 1994). A range of solutes, including Fe^{3+}, UO^{2+}, Mg^{2+}, Ca^{2+}, Na^{2+} and F^{-}, react with dissolved silica to form complexes, thereby increasing silica solubility (Dove and Rimstidt, 1994). Biological influences upon silica precipitation have been proposed and may be of local significance. Shaw et al. (1990), for example, have documented the role of cyanobacteria in silcrete development in Sua Pan, whilst McCarthy and Ellery (1995) identified transpiration from aquatic grasses as a factor in the precipitation of amorphous silica from groundwater beneath islands in the Okavango Delta.

Groundwater, drainage-line and pan/lacustrine silcretes

As noted in section X.3.1, non-pedogenic silcretes occur as three main sub-types: groundwater, drainage-line and pan/lacustrine. The only location where a groundwater silcrete has been described in the Botswana Kalahari is within a core drilled near Tsodilo Hills (Linol et al., 2015). This core intersects a 42 m thick Kalahari Group sequence comprising: (i) a 2 m calcrete that caps the present-day land surface, underlain by; (ii) 8 m of sandy carbonate; and (iii) a further 32 m of sandy fluvial sediments. The succession overlies pre-Kalahari sandstones and green mudstones that are increasingly silicified upward to form a 4 m thick silcrete at the interface with the Kalahari Group. Linol et al. (2015, p.197) propose that the silcrete “likely formed by deep weathering and groundwater activity at the discontinuity that defines the base of the Kalahari Group [and] possibly correlates with the Nxau-Nxau (and Etosha) Calcrete Formation”. No further details are provided of the silcrete chemistry or mineralogy. However, as identified for groundwater silcretes developed in arenaceous sediments elsewhere, silica precipitation is likely due to meteoric and groundwater mixing (e.g. Milnes et al., 1991; Milnes and Thiry, 1992; Ullyott et al., 1998; Thiry, 1999; Basile-Doelsch et al., 2005; Lee and Gilkes, 2005; Ullyott and Nash, 2006).

Drainage-line silcretes are closely related to groundwater sub-types but develop *within* alluvial fills in current or former fluvial systems, as opposed to within bedrock *marginal* to valley systems (as is the case with many groundwater silcretes in France and Australia). Few models for the formation of drainage-line silcrete exist, in part due to a lack of such silcretes cropping out in the geomorphological context in which they formed (Nash and Ullyott, 2007). Perhaps the best-documented example occurs in the Boteti River (Figure X.9a). Here, analyses of surface exposures and samples from two ~20 m long cores drilled into the riverbed and adjacent floodplain at Samedupi Drift reveal a complex sequence of duricrusts (Figure X.12). Massive silcrete layers reaching 1-2 m thick, exposed in the riverbed, are suggested by Shaw and Nash (1998) to have developed via the accumulation of clastic silica transported by annual floodwaters alongside precipitation of amorphous silica from shallow groundwater. Silica precipitation is likely to have been induced by near-surface evaporation and transpiration from aquatic grasses within seasonal pools in the channel (cf. McCarthy and Ellery, 1998). In contrast, massive and pisolitic silcrete layers deep within the channel alluvium likely formed in response to salinity and pH shifts associated with vertical and lateral movements of the wetting front during flood events. Shaw and Nash (1998) propose that conditions beneath the channel floor shifted from unsaturated to saturated during groundwater recharge by floodwater, with associated drops in salinity due to dilution effects; silica precipitation subsequently occurred as the water table fell.

As noted in section X.1, silcretes are commonly found in ephemeral pan and lake settings in Botswana. In most modern evaporitic lacustrine environments, silica precipitation is driven by changes in salinity and pH (Thiry, 1999), both of which can vary spatially and temporally. An ingress of rain- or flood-water into an ephemeral lake, as noted above, can lead to fluctuations in salinity and pH and generate phases of silica mobility interspersed with periods of precipitation (Summerfield, 1982). The zone of maximum mixing of 'fresh' and more saline lake waters is likely to occur around the borders of the evaporitic depression and immediately above the water table (Thiry, 1999). This may explain why silicification often occurs marginal to ephemeral lakes and pans and may be linked to regression or to near-surface groundwater trapped by impermeable substrates (e.g. Summerfield, 1982; Bustillo and Bustillo, 1993; Armenteros et al., 1995; Alley, 1998; Bustillo and Bustillo, 2000; Ringrose et al., 2005). This is well-illustrated in the Kalahari (Figure X.13), where silcrete lenses within lake-marginal duricrust sequences often formed in association with former water tables (Summerfield, 1982). Biological fixing of silica may also occur in lake environments. Sua Pan, for example, contains sheet-like silcretes developed as a result of the desiccation of formerly floating colonies of the silica-fixing cyanobacteria *Chloriflexus* (Shaw et al., 1990).

X.4. Silcrete-calcrete intergrade duricrusts

So far in this chapter, the main categories of duricrust in Botswana have been discussed as discrete forms. However, silcrete and calcrete are only the chemical end members of a complex spectrum of silica- and carbonate-cemented duricrust types. For example, calcretes often contain evidence for localised or more pervasive silicification while, less commonly, silcretes may be partly calcified. Further, some duricrusts may contain silica and carbonate cements in close to equal proportions and cannot be easily classified as either silcrete or calcrete *per se* under existing definitions. Nash and Shaw (1998) proposed the term *silcrete-calcrete intergrade duricrust* to describe such hybrid materials.

Silcrete-calcrete intergrade duricrusts have been identified across the world, including North and South America, North Africa and Australia (see Nash et al., 2004, for a review). However, one of the most important areas of occurrence is southern Africa, where intergrade duricrust varieties form a conspicuous component of the Kalahari Group sediments (e.g. Passarge, 1904; MacGregor, 1931; Wright, 1978; Watts, 1980; Summerfield, 1982; Shaw and de Vries, 1988; Nash et al., 1994a,b, 2004; Nash and Shaw, 1998; Ringrose et al., 2002, 2014; Kampunzu et al., 2007).

X.4.1 Definitions

Much of the primary research into silcrete-calcrete intergrade duricrusts has taken place in Botswana. Here, three main types of intergrade material have been defined on the basis of silica-carbonate associations within the duricrust cement (Nash and Shaw, 1998). These are: (a) *sil-calcrete*, a term normally used where extensive secondary silicification has occurred within a pre-existing calcrete (but see below); (b) *cal-silcrete*, where secondary carbonate has been precipitated within a pre-existing silcrete; and (c) materials where layers of silica and carbonate cement appear to have been precipitated either contemporaneously or in close succession – these are defined according to the dominant chemical cement present. Further sub-types can be identified dependent upon whether secondary materials have either replaced pre-existing cements or have precipitated in pore spaces and voids, normally during the latter stages of development of a pre-existing duricrust.

Nash and Shaw (1998) offer chemical criteria for distinguishing the varieties of intergrade duricrust. As noted in section X.3, where the SiO_2 content of a duricrust is ≥ 85 wt% it is termed a silcrete. Providing a chemical definition for calcrete is more problematic since – as considered in section X.2 – the $CaCO_3$ content may vary from a few percent when weakly developed up to ~100% for an indurated hardpan. Following Goudie (1973), Nash and Shaw (1998) propose a $CaCO_3$ content of 50 wt% as the lower boundary for a well-indurated calcrete. If bulk chemical analysis shows that a duricrust sample falls into an intermediate range it is classified according to the dominant cementing agent; cal-silcrete where silica dominates the cement but ≥15 wt% $CaCO_3$ is also present, or sil-calcrete in a calcrete where ≥ 50 wt% silica is present. For samples falling close to these boundaries, point-count analysis of the percentage of silica or carbonate cement present is recommended to overcome the effect of host material influences upon bulk chemical composition.

It should be noted that the terms cal-silcrete and sil-calcrete do not necessarily indicate that a cement is primary or secondary in a stratigraphic sense. For example, cal-silcrete may refer to a silcrete with secondary $CaCO_3$ cement but may also be applied to an extensively silicified calcrete where secondary silica has replaced carbonate to become the dominant cement type (Nash et al., 2004).

X.4.2 Processes of silcrete-calcrete intergrade duricrust development

Limited research has been undertaken into the geomorphological factors controlling the distribution of silcrete-calcrete intergrade duricrusts. Experience from Botswana, however, suggests that cal-silcrete and sil-calcrete are more prevalent in association with drainage features (Mallick et al., 1981; Summerfield, 1982; Shaw and de Vries, 1988; Nash et al., 1994a, 2004; Ringrose et al., 2002, 2014; Nash and McLaren, 2003; Kampunzu et al., 2007). This is likely because such landscape settings offer the greatest potential for pre-existing calcrete and silcrete to be subjected to chemical alteration as episodic solute-bearing surface waters infiltrate into the sub-surface and/or groundwater tables fluctuate under wetter/drier conditions.

Much of the work on silcrete-calcrete intergrade crusts in Botswana has involved the analysis of small outcrops or grab samples. Where extensive outcrops of silcrete or calcrete are present, notably in fossil valley systems and around lakes and pans, the exposures have been invariably subject to long periods of weathering, making the interpretation of cement interrelationships problematic. There are, however, locations where relatively ‘fresh’ exposures of intergrade duricrusts have been described and their origins interpreted.

Intergrade duricrusts in pan-lacustrine settings

One of the most detailed process-related analyses of silcrete-calcrete intergrade duricrusts has been undertaken at Kang Pan (Nash et al., 2004). Here, a ~50 by 30 m roadstone quarry cut into the pan floor exposes a maximum of 5.5 m of duricrust. The exposure exhibits a massive jointed blocky appearance near the base and thinner layers towards the surface. Thin-section evidence indicates that the duricrust was originally a groundwater calcrete but has been extensively altered by silicification. The exposure is now dominated by silica-rich duricrusts in lower sections that grade upwards into materials with more $CaCO_3$-rich cements (Figure X.14). This gradation is not, however, progressive. Silicification occurs in distinct zones in lower parts of the quarry, both at the edges and towards the centres of inter-joint blocks, with chalcedony and cryptocrystalline silica cements replacing the original sparry calcite matrix, and chalcedony and opaline silica precipitating in void spaces. These zones have sharp boundaries with adjacent areas of unaltered calcrete and are rimmed by thin (<10mm) zones of powdery calcite, which appears to have been mobilised during silicification and then precipitated. Late-stage silicification has focused along cracks and fractures, mainly in upper parts of the profile, leading to the development of pale green silica-carbonate precipitates within and adjacent to some joints. Nash et al. (2004) suggest that the degree of silicification at the macroscale was determined by the position of the water table, with more extensive calcite replacement near the base of the profile associated with periods when groundwater levels were higher relative to the present day. At a local scale, the specific locations of silica replacement appear to be controlled by the degree of penetration of the wetting front into the pre-existing calcrete, both along joints and through the calcrete matrix.

Other studies of intergrade crusts in pan settings have combined sediment geochemistry with petrography to draw inferences about the environment of duricrust formation. For example, silcretes, calcretes and sil-calcretes formed within palaeoshoreline sediments have been examined at eleven sites in northern Sua Pan. These shorelines mark lake highstands within the Makgadikgadi sub-basin of the Makgadikgadi-Okavango-Zambezi rift depression and range in elevation from 945 m asl (~50 m above the present pan floor) to 904 m asl (close to the present pan margin) (Ringrose et al., 2005; Ringrose et al., 2009). Silcretes and sil-calcretes appear to have formed through the silicification of pre-existing calcretes, with the degree of silicification varying from "silicified litho-clasts", lenses and nodules within calcrete profiles to the complete silicification of already part-silicified calcrete (Ringrose et al., 2005, p.283). Chemical data show that the precursor calcrete formation took place under closed basin type evaporative conditions. As at Kang Pan, silicification occurred during periods of elevated water tables when the normally saline groundwater was diluted by relatively minor rainfall or inflow events (Ringrose et al., 2005). Repeated wet-dry cycles, with associated higher-lower water tables, are argued to have led to the progressive replacement of calcite cements within the precursor calcretes (Ringrose et al., 2009). The geochemistry of the groundwater during these events more closely resembled present-day Na-CO_3-SO_4-Cl-type brines (Ringrose et al., 2005).

Intergrade duricrusts in river and valley contexts

The other locations where intergrade duricrusts have been investigated are associated with dry valleys (see Chapter X) and palaeo-estuaries. The aggregate quarry at Tswaane (Figure X.15), in the Okwa valley east of the Trans-Kalahari Highway, exposes a 3.5 to 4 m thick sequence of calcrete, silcrete and silcrete-calcrete intergrade duricrusts overlying >8 m of bedrock (see Nash et al., 2004). The duricrust exposure comprises (from the surface down) 0.5-1 m of calcrete overlying 3-3.5 m of pale green silcrete and cal-silcrete. Inherited calcrete textures within the silcrete, however, suggest that much of the silcrete and cal-silcrete formed via the replacement of a pre-existing micritic calcrete. The uppermost calcrete is suggested to have developed on top of this silcrete and post-dates the silicification process. This is evidenced by brecciation of the uppermost silcrete by calcite, fretting of the margins of brecciated silcrete fragments, and the presence of vertically-oriented strings of sparite crystals along cracks and late-stage calcite void fills within the silcrete. Nash et al. (2004) suggest that the initial replacement of calcrete was by groundwater silicification mechanisms, most likely beneath a former valley floor prior to incision of the Okwa. This was followed by a further phase (or phases) of non-pedogenic calcrete development, accompanied by the gravitational precipitation of calcite within cracks and voids to produce cal-silcretes.

Cal-silcretes, sil-calcretes and cal-ferricretes have been described in the flanks of the fossil valleys that converge around Letlhakeng (Boocock and van Straten, 1962; Shaw and de Vries, 1988; Nash et al., 1994a; Ringrose et al., 2002; Kampunzu et al., 2007). These valleys form the southeast part of the Okwa-Mmone drainage system, rising at the Kalahari-Limpopo watershed and flowing northwards towards the Makgadikgadi sub-basin (Nash and Eckardt, 2016). Silcretes and sil-calcretes are exposed extensively along the Goatlhabogwe-Moshaweng valley north and east of Letlhakeng; Nash et al. (1994a) have described the nature of outcrops along the main valley flanks and Ringrose et al. (2002) sequences within lower (sub-rim) valley surfaces. The thickness of the duricrust sequence is ~18.5 m (Gwosdz and Modisi, 1983), and, taking outcrops on both valley flanks into consideration, the total length of duricrust exposure exceeds 80 km (Nash et al., 1994a). Ringrose et al. (2002) report that duricrusts can be identified in three distinct levels: an upper level containing abundant sil-calcrete; an intermediate level in which sil-calcrete underlies nodular calcrete; and a lowest level where sil-calcrete and calcrete are interbedded. However, systematic profile mapping by Nash et al. (1994a) indicates that the situation may be more complex.

The environmental conditions required to generate the suite of duricrusts around Letlhakeng remain only partly understood. Ringrose et al. (2002) proposed that early calcrete formation in the area was initiated during wet periods when abundant Ca^{++}-rich groundwater flowed along the structurally aligned valley systems to converge at Letlhakeng. During subsequent drier periods, water table fluctuations led to the precipitation of nodular calcretes. For reasons unknown, the geochemistry of the valley hydraulic system then changed and became increasingly saline, leading to the preferential silicification of the nodular calcrete deposits to form sil-calcretes. Kampunzu et al. (2007) used trace element data to constrain the pH associated with silicification to between pH 6.5 and 8 under alternating wetter and drier environments. However, the patchy distribution of silcrete and sil-calcrete along the Goatlhabogwe-Moshaweng valley (Nash et al., 1994a) implies that pH must also have varied spatially. Little consideration has been given to changing environmental conditions as the valleys incised over time and regional groundwater systems were increasingly focussed towards the Letlhakeng area.

The most recent analyses of silcrete-calcrete intergrade crusts come from the palaeo-estuary of the Boteti River where it enters the Makgadikgadi sub-basin. Using examples from the proximal and distal palaeo-estuary, Ringrose et al. (2014) provide insights into the pre-cursor environmental conditions required for the formation of silcrete-calcrete intergrade crusts, with particular attention paid to those crusts where SiO_2 and $CaCO_3$ cements appear to have formed penecontemporaneously. The study again highlights the importance of cyclical freshwater inflows into saline depressions, at timescales from seasonal to centennial, to trigger changes in groundwater pH and hence silica precipitation in carbonate-rich settings. The most interesting insight from the analyses, however, is the importance of micro-fossils in providing a source of more soluble silica and carbonate. Intergrade crusts comprising irregular zones of siliceous sediment formed within otherwise calcareous deposits are suggested to relate to the irregular occurrence of biogenic silica in the source sediments, inferring a source for local mobilisation of silica.

Taken as a whole, these studies illustrate the crucial role of groundwater salinity/pH and the relative height of the groundwater table in controlling if and where the replacement of silica and $CaCO_3$ cements takes place to generate intergrade duricrusts. Equivalent studies of the silicification of limestone (e.g. in the Paris Basin; Thiry, 1999) indicate that there is a strong relationship between voids and silicification. This also appears to be the case for sil-calcrete development, where joints and other structural features within the pre-cursor calcrete act as foci for local or more pervasive silicification. What is now needed is a greater understanding of the causes of spatial variations in groundwater pH that lead to the patchy silicification of calcrete (or calcretisation of silcrete). Could it be, for example, that changes in pH associated with the wetting/drying of sediments beneath relatively short-lived pools are required, as proposed by Ringrose et al. (2002) for the formation of sil-calcretes at Sua Pan? Or maybe the periodic flushing of saline groundwater systems by infiltrating floodwaters, as discussed by Shaw and Nash (1998) in relation to silcretes in the Boteti River? Or the presence of amorphous biogenic silica in the host sediments, as discussed for the Boteti palaeo-estuary (Ringrose et al., 2014)? Botswana, with its substantial outcrops of intergrade duricrusts, offers a natural laboratory to address these questions in the future.

X.5. Determining the age of Kalahari duricrusts

Determining the timing of calcrete and silcrete formation in the Botswana Kalahari is not easy. No radiometric dating techniques are available to ascertain the age of silcrete. Mallick et al. (1981, pp.25-26) suggested that duricrusts in Botswana could be divided into two broad groups. The first, which they termed ‘older’ duricrusts, are mostly found in peri-Kalahari locations and include the calcretes that outcrop high up the flanks of drainage systems such as the Molopo, Auob, Nossop and Okwa-Mmone (Shaw and de Vries, 1988; Nash et al., 1994a; Ringrose et al., 2002). Pedogenic calcretes in intervening areas may also fall into this ‘older’ grouping. ‘Younger’ calcrete duricrusts occur on the floors or as low terraces towards the centre of drainage lines below these older calcrete cliffs.

The ages of the ‘older’ duricrusts remain unknown. Silcretes and calcretes found at depth within the Kalahari Group are suggested on the basis of stratigraphic correlation to be of mid-Miocene age (Haddon and McCarthy, 2005). Linol et al. (2015) use lithostratigraphic comparisons with the 'Polymorph Sandstones' at the base of the Kalahari Group in the Congo Basin to argue that the Nxau-Nxau Calcrete Formation may even be Eocene in age. However, attempts at correlation are complicated. Calcretes and silcretes necessarily develop within pre-existing bodies of sediment and therefore make poor stratigraphic markers. Further, while pedogenic calcretes form in association with palaeosurfaces, groundwater calcretes and silcretes can, in theory, develop at any depth, since cementation is linked to the position of the water table (Netterberg, 1969b; Nash and Smith, 1998; Basile-Doelsch et al., 2005). Duricrusts have, nonetheless been used as markers in some stratigraphic schemes for the Kalahari Group in Botswana (e.g. du Plessis, 1993) and adjoining areas of South Africa (e.g. Thomas, 1981). Bulk samples from 'younger' surface calcrete outcrops have been radiocarbon dated to the late Pleistocene (e.g. Cooke and Verhagen, 1977; Cooke, 1984; Shaw et al., 1992). Such dates can only be regarded as minimum age estimates, however, given that calcretes commonly contain multiple generations of carbonate cement that build up within sediment pore-spaces over time.

X.6. Conclusions

This chapter has provided an overview of the development of calcrete, silcrete and related intergrade duricrusts in Botswana. It is apparent from the text that the processes responsible for the formation of many silcrete and calcrete sub-types are well understood. There are, however, areas where future investigations in Botswana could help address globally-significant research questions. For example, the formation of non-pedogenic calcretes and silcretes is less well understood compared with their pedogenic cousins. Detailed petrographic and geochemical analyses of silcretes in and around the Makgadikgadi basin, for example, could not only shed new light on pan/lacustrine silcrete formation but also provide a window on processes of basin evolution over time. Studies of calcretes found in association with Kalahari pans could yield similar insights for smaller evaporitic basins. The widespread exposure of duricrusts in Botswana offers real potential for understanding the factors influencing calcrete and silcrete distribution at a landscape scale. However, to answer this question, much better mapping of duricrusts sub-types is needed at a national and, ideally, regional level. At present, our understanding of the distribution of silcrete and calcrete sub-types is limited to 'joining the dots' between outcrops in published studies.

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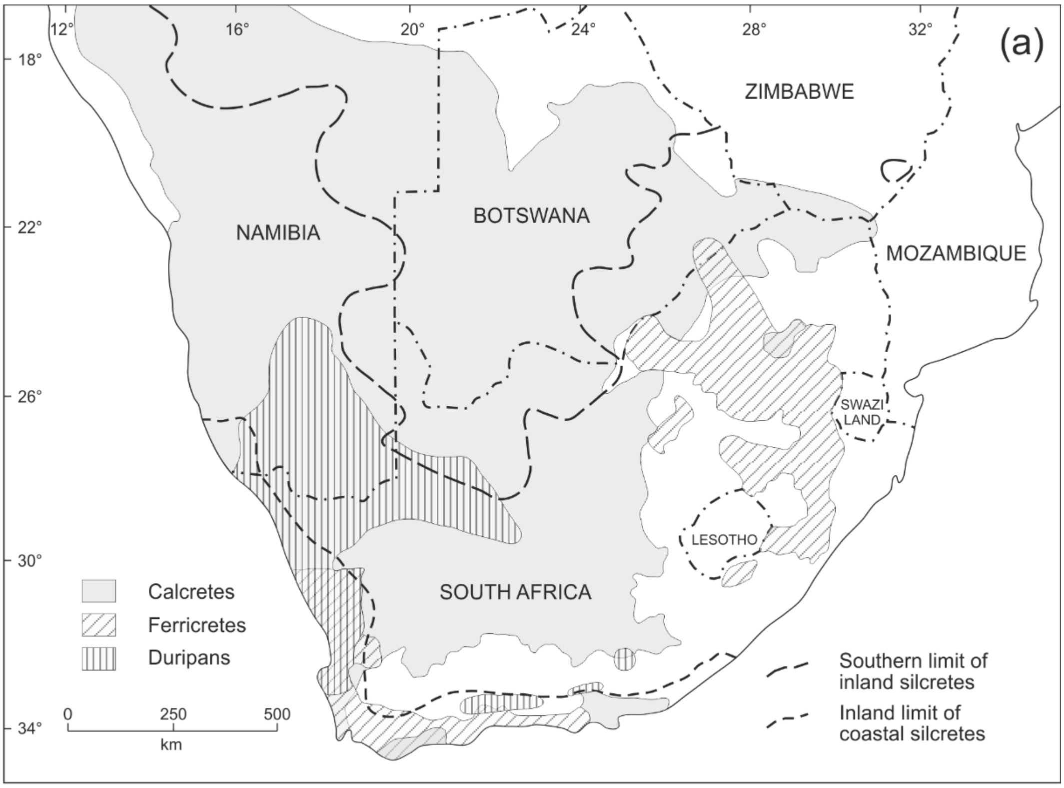

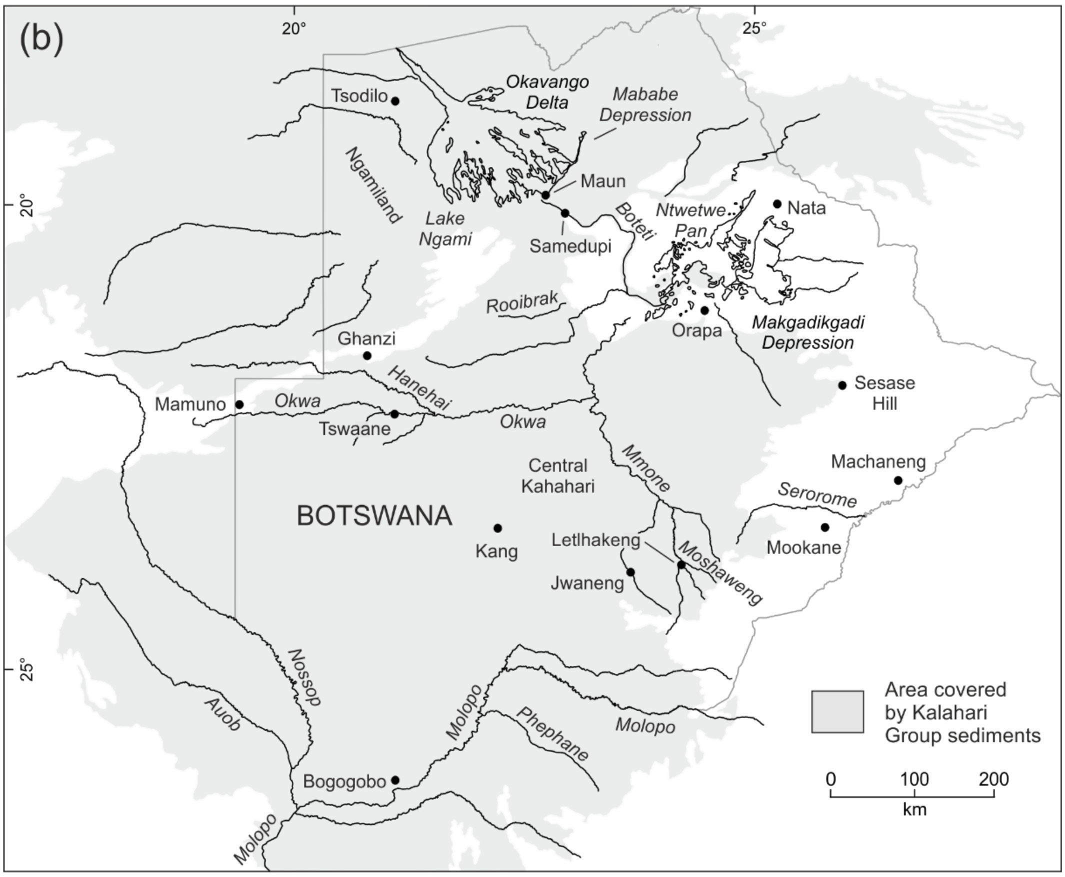

Figure X.1: (a) General distribution of pedogenic duricrusts in southern Africa (after du Toit, 1954; Weinert, 1980; Ellis and Schloms, 1984; Schloms and Ellis, 1984; Netterberg, 1985; Partridge, 1997; Botha, 2000; Fey, 2010; Nash, 2012); (b) Main areas and locations mentioned in the text.

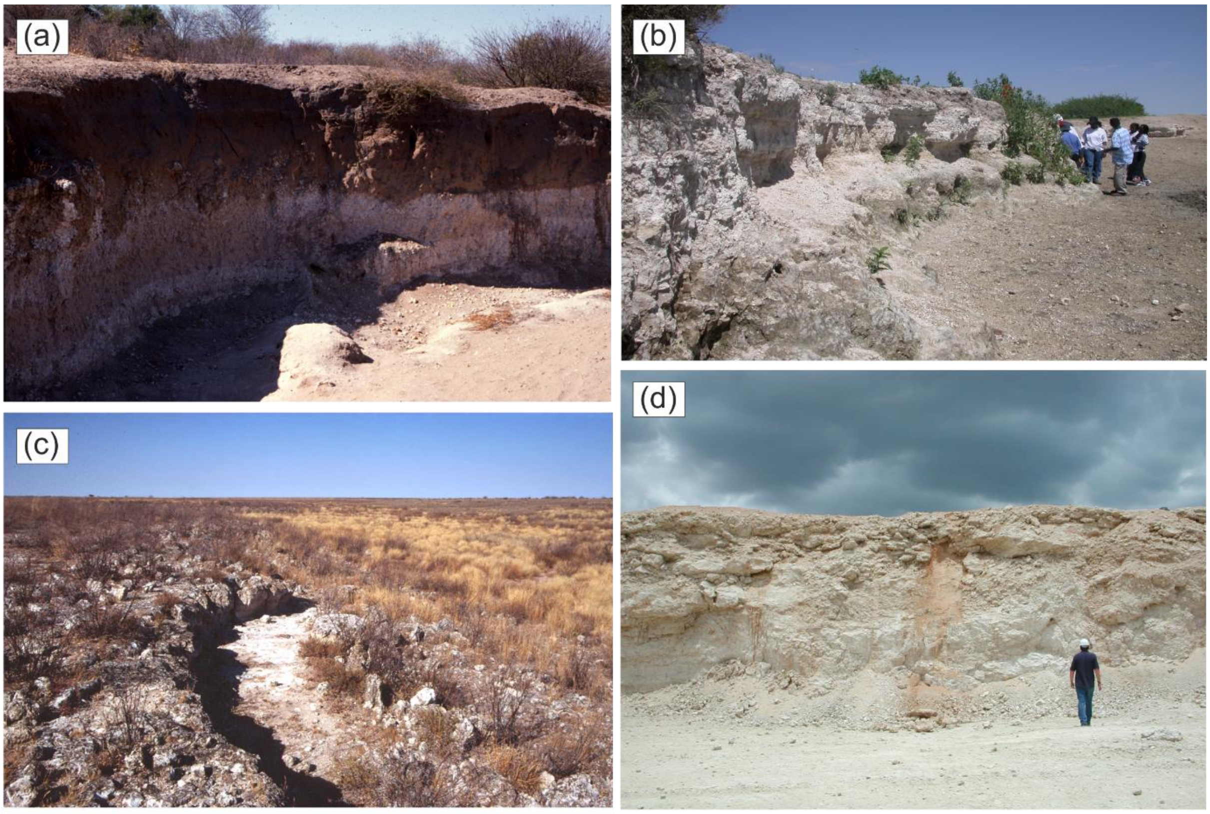

Figure X.2: Examples of pedogenic and non-pedogenic calcrete profiles in Botswana: (a) Powdery to nodular pedogenic calcrete exposed near New Hanehai (image © David Nash); Calcrete profile exposed around the margin of a pan near Tshono, southeast of Jwaneng (image © Frank Eckardt); (c) Valley calcrete exposed within a river terrace in the floor of the Okwa Valley (image © David Nash); (d) Thick pedogenic calcrete exposure close to Orapa (image © Frank Eckardt)

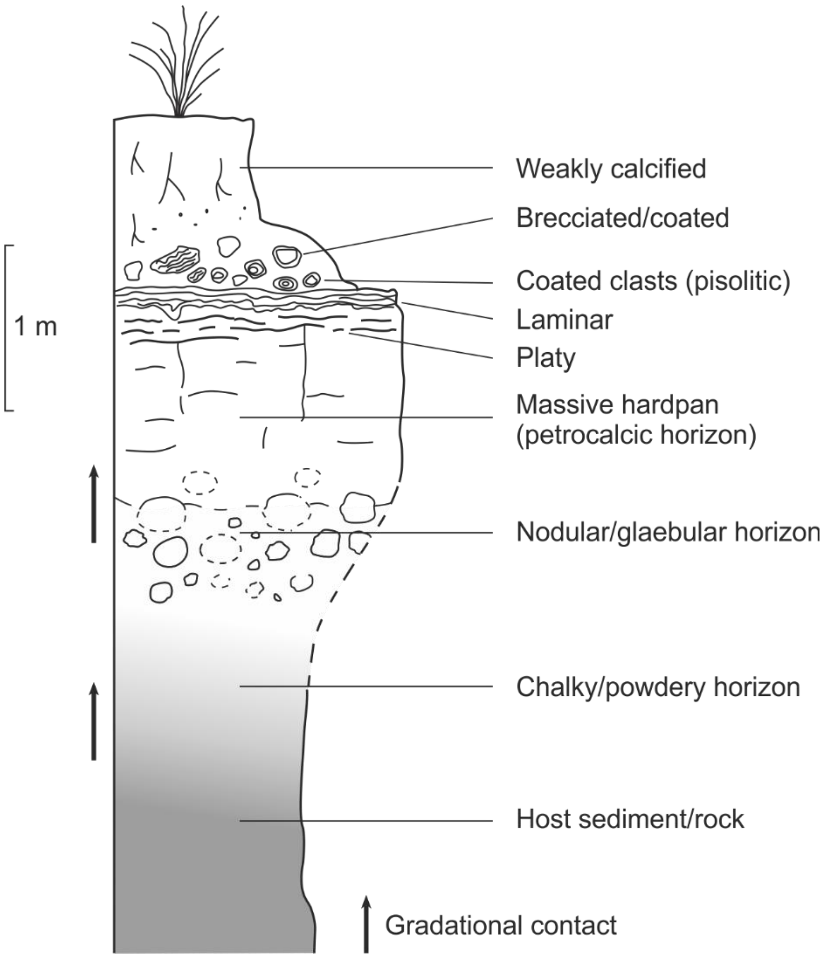

Figure X.3: Idealised pedogenic calcrete profile showing a range of macroforms (after Wright, 2007; Nash, 2012).

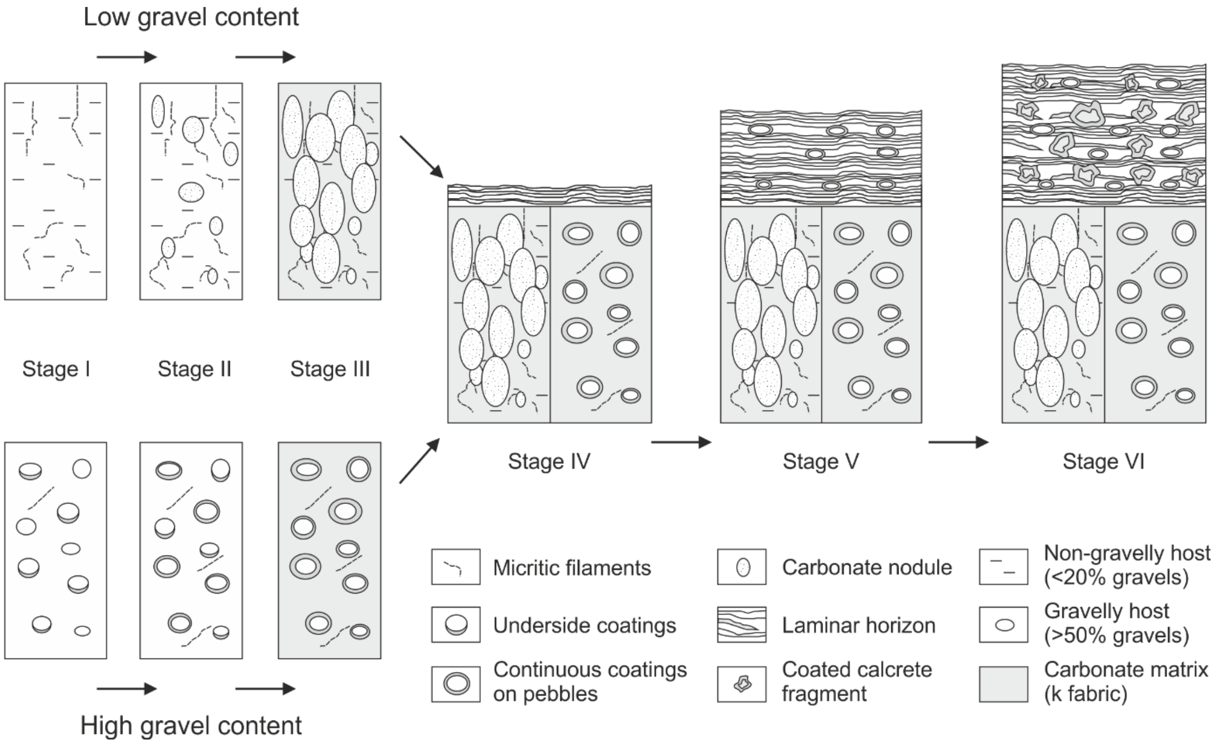

Figure X.4: Stages in the development of a typical pedogenic calcrete profile formed in gravel-poor and gravel-rich sediments (based on Machette, 1985; Alonso-Zarza, 2003). The low gravel content genetic sequence is most relevant in the context of the sand-dominated Kalahari Group sediments, but calcretised gravels have been described in the Letlhakeng area of Botswana (e.g. Nash et al., 1994a).

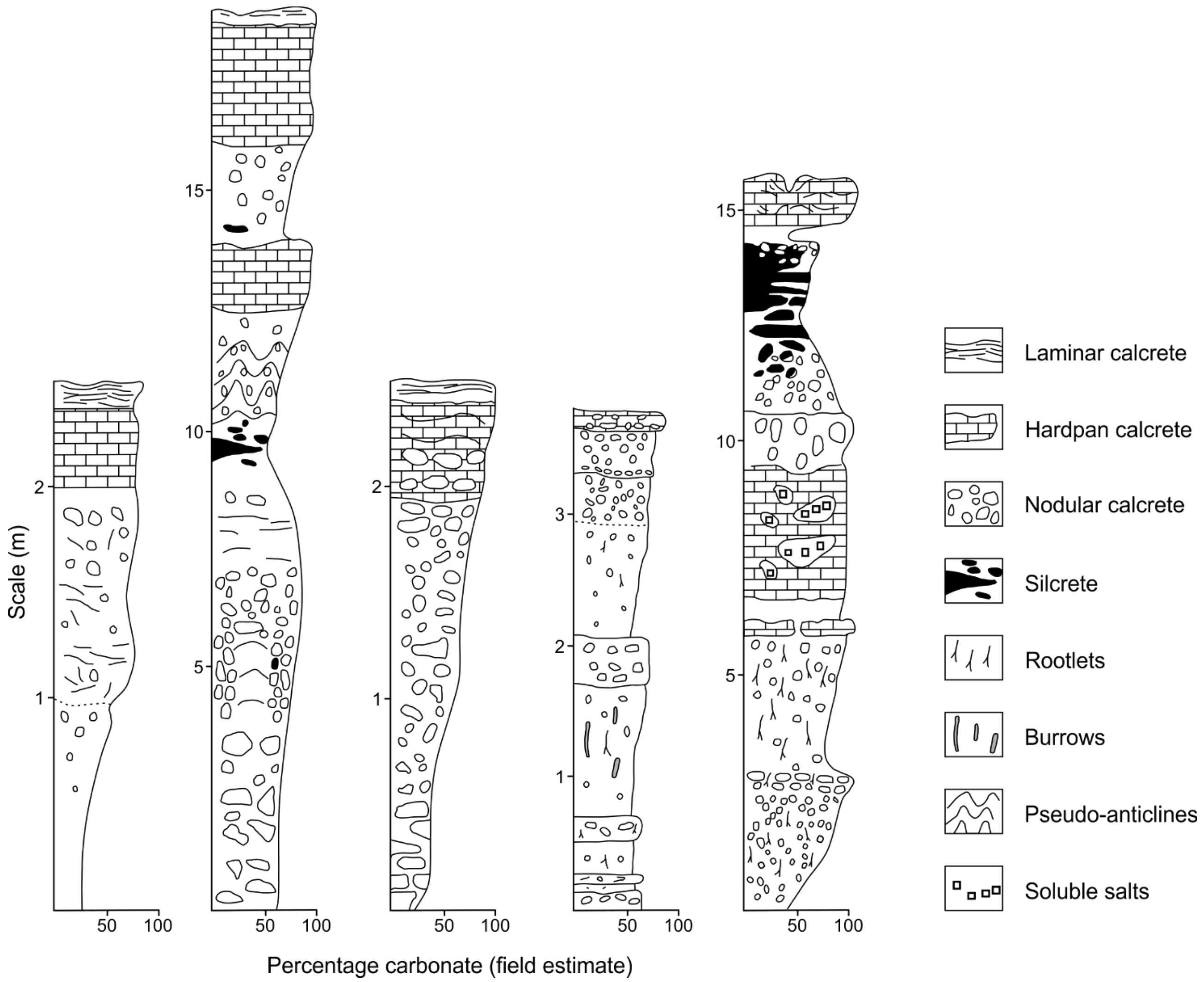

Figure X.5: Simple and composite logged pedogenic calcrete profiles from the southern Kalahari along the Botswana-South Africa border (after Watts, 1980): (1) borrow pit in the Phephane valley just south of the confluence with the Molopo valley; (2-5) cliff exposures on the south side of the Molopo valley near Bogogobo.

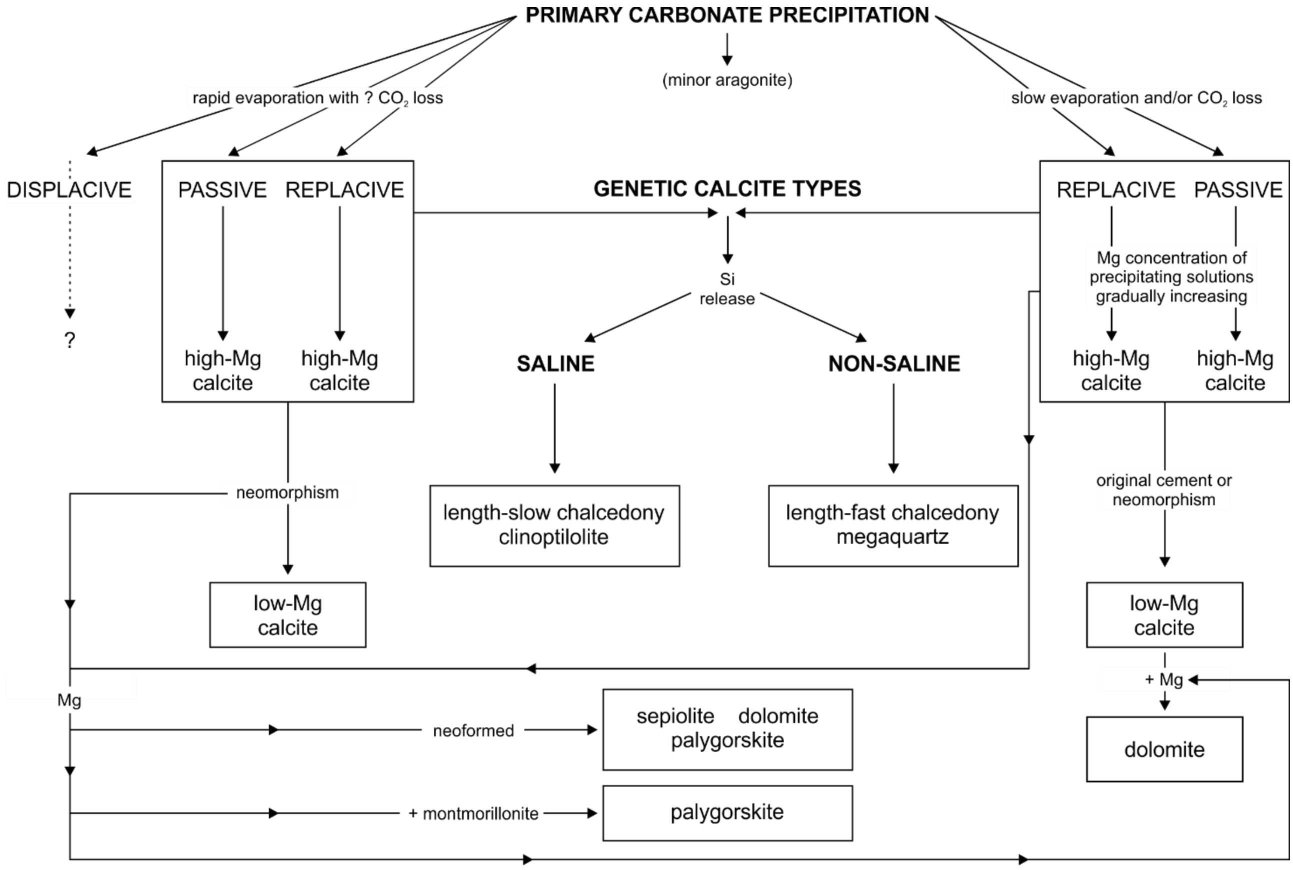

Figure X.6: Schematic flow diagram summarising the major pedogenic and diagenetic processes within pedogenic calcretes in the Kalahari (modified after Watts, 1980).

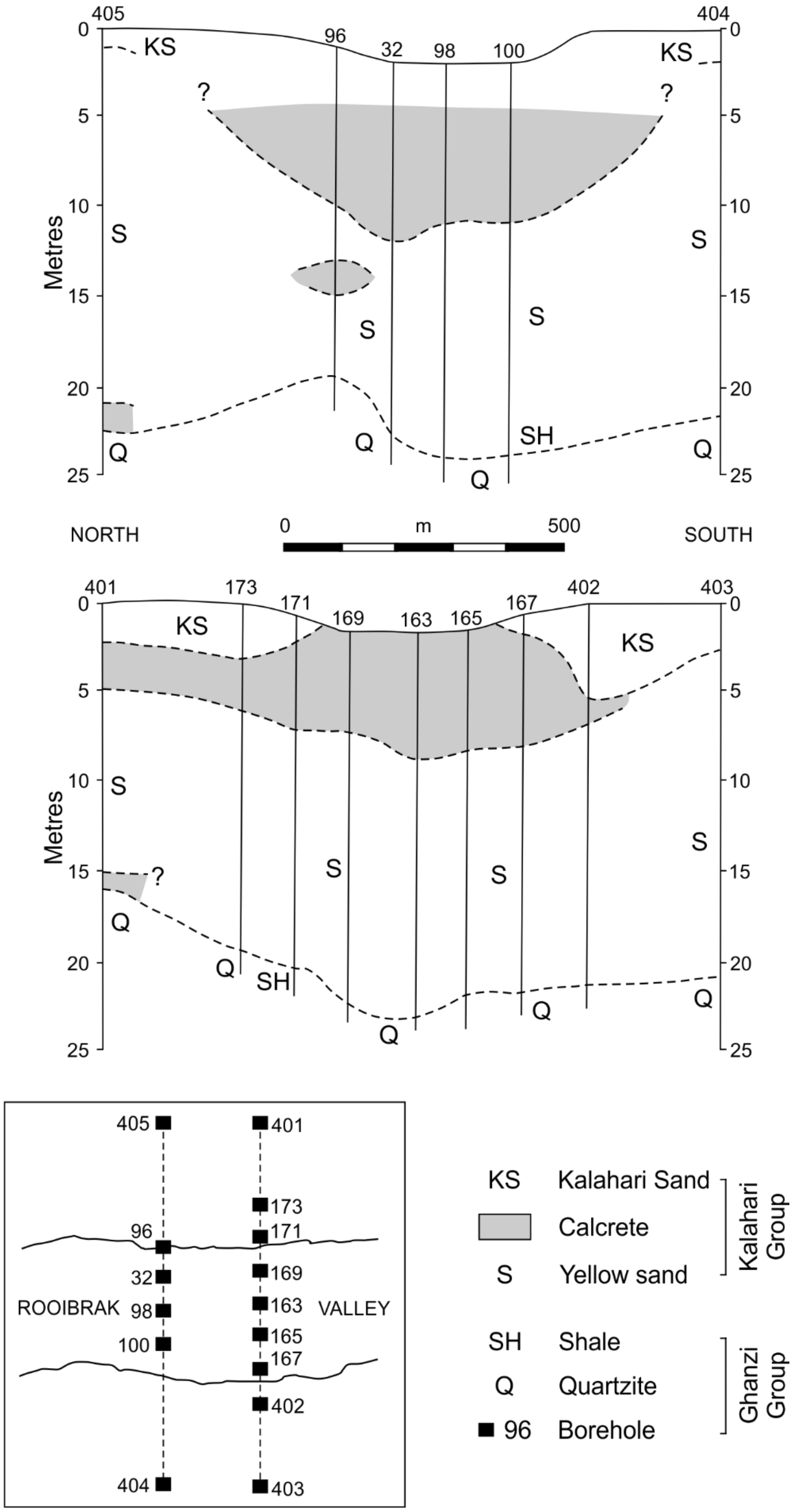

Figure X.7: Variability in thickness of valley calcrete development beneath the Rooibrak Valley identified from boreholes drilled during uranium prospecting by Union Carbide (after Nash et al., 1994a).

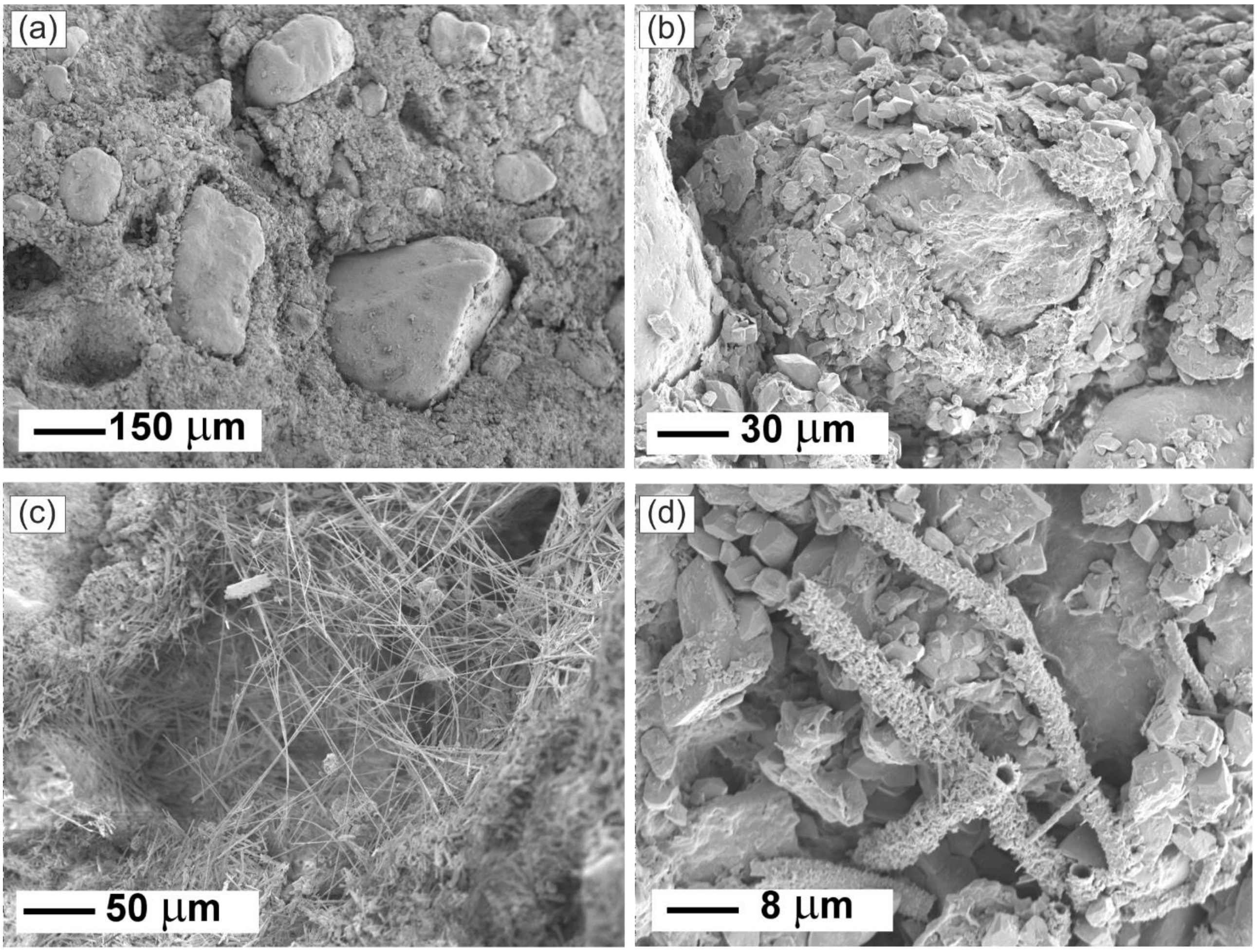

Figure X.8: Scanning electron microscope images of samples from non-pedogenic valley calcretes exposed in the Okwa and Hanehai valleys: (a) rounded quartz grains and minor shell fragments cemented by microcrystalline calcite (micrite); (b) quartz grain coated by micrite and microspar cement; (c) needle-fibre and calcified fungal filaments (plus possible fruiting spores) lining a void with needle-fibres crossing the void; (d) hollow fungal filaments encrusted with micrite and small bladed and acicular calcite crystals. Images (a) and (b) represent typical cements developed under evaporitic conditions whilst (c) and (d) suggest organic activity under vadose conditions (after Nash and McLaren, 2003).

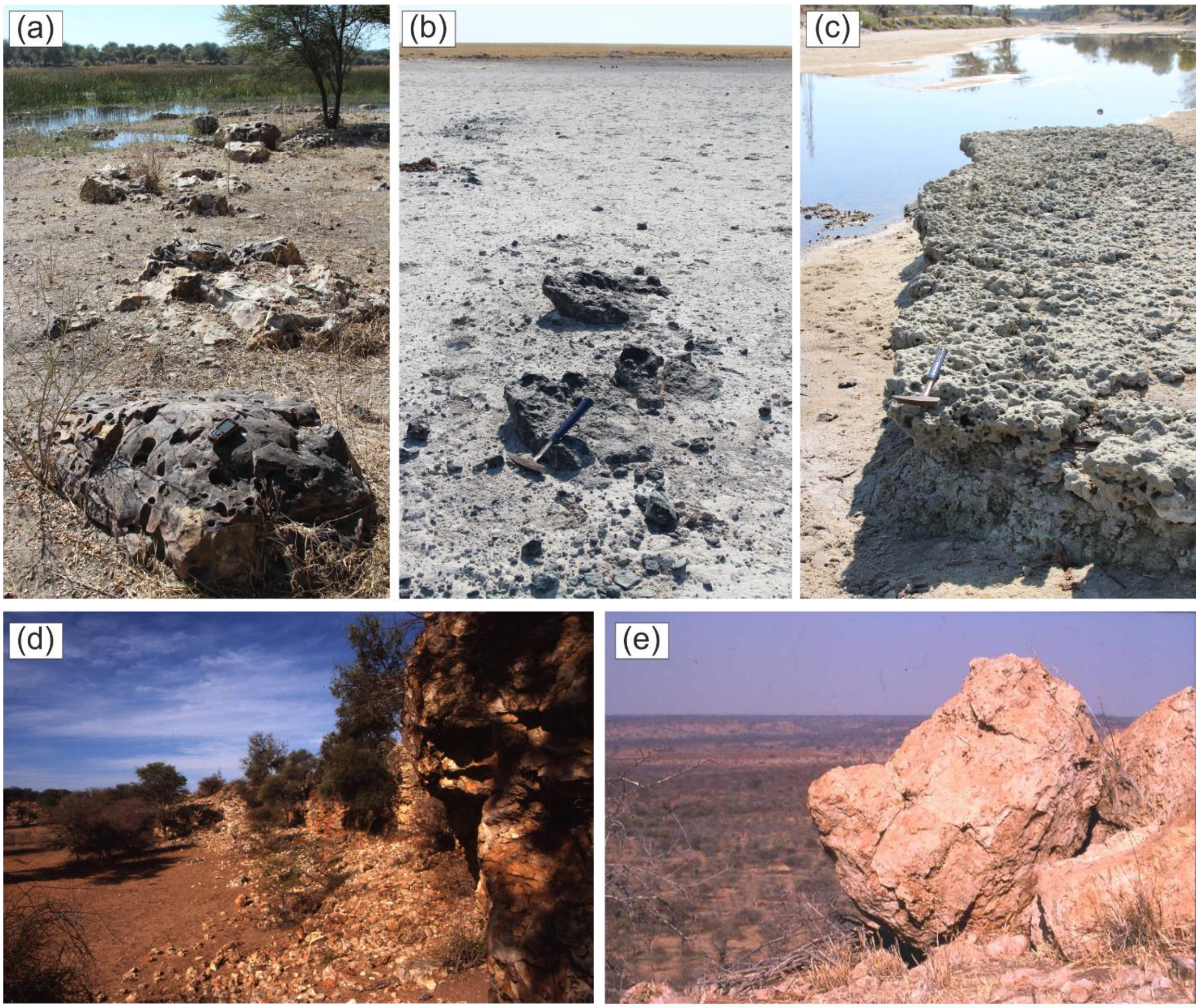

Figure X.9: Examples of silcrete outcrops in Botswana: (a) Massive drainage-line silcrete at Samedupi Drift at the margin of the Boteti River; (b) Massive to blocky pan/lacustrine silcrete from the southern margin of Ntwetwe Pan; (c) Nodular drainage-line silcrete in the bed of the Nata River downstream of Nata village; (d) Massive drainage-line silcrete outcropping in the flanks of the Moshaweng Valley, southeast of Letlhakeng; (e) Massive silcrete caprock overlying basalt at the eastern margin of the Kalahari Group sediments, Sesase Hill. All images © David Nash.

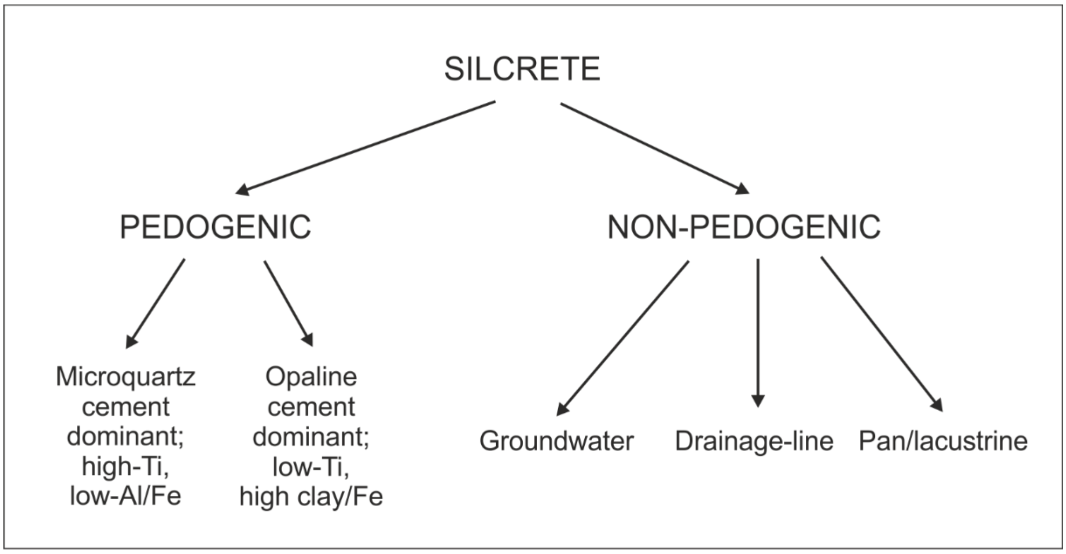

Figure X.10: Geomorphological classification of silcrete (after Nash and Ullyott, 2007).

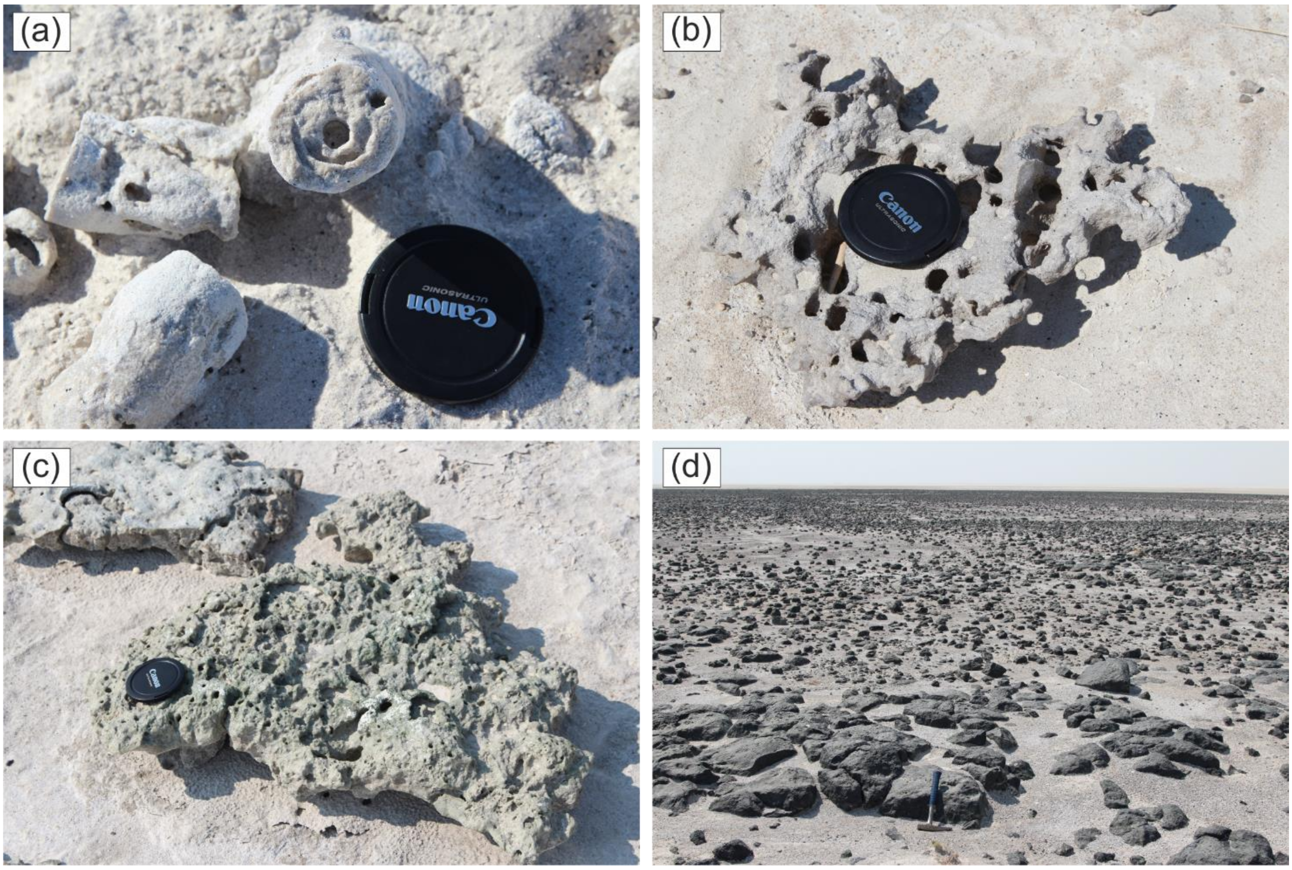

Figure X.11: Variations in silcrete morphology across Ntwetwe Pan: (a) Silicified tube-like structures suggestive of former roots; (b) thin 'honeycomb' silcrete sheet formed by the merger of individual silcrete nodules; (c) decimetre-scale sheet-like silcrete with vertical hollows; (d) massive outcrops of black silcrete surrounded by a lag of black silcrete fragments. (a-c) North-central Ntwetwe Pan, (d) south-central Ntwetwe Pan. All images © David Nash.

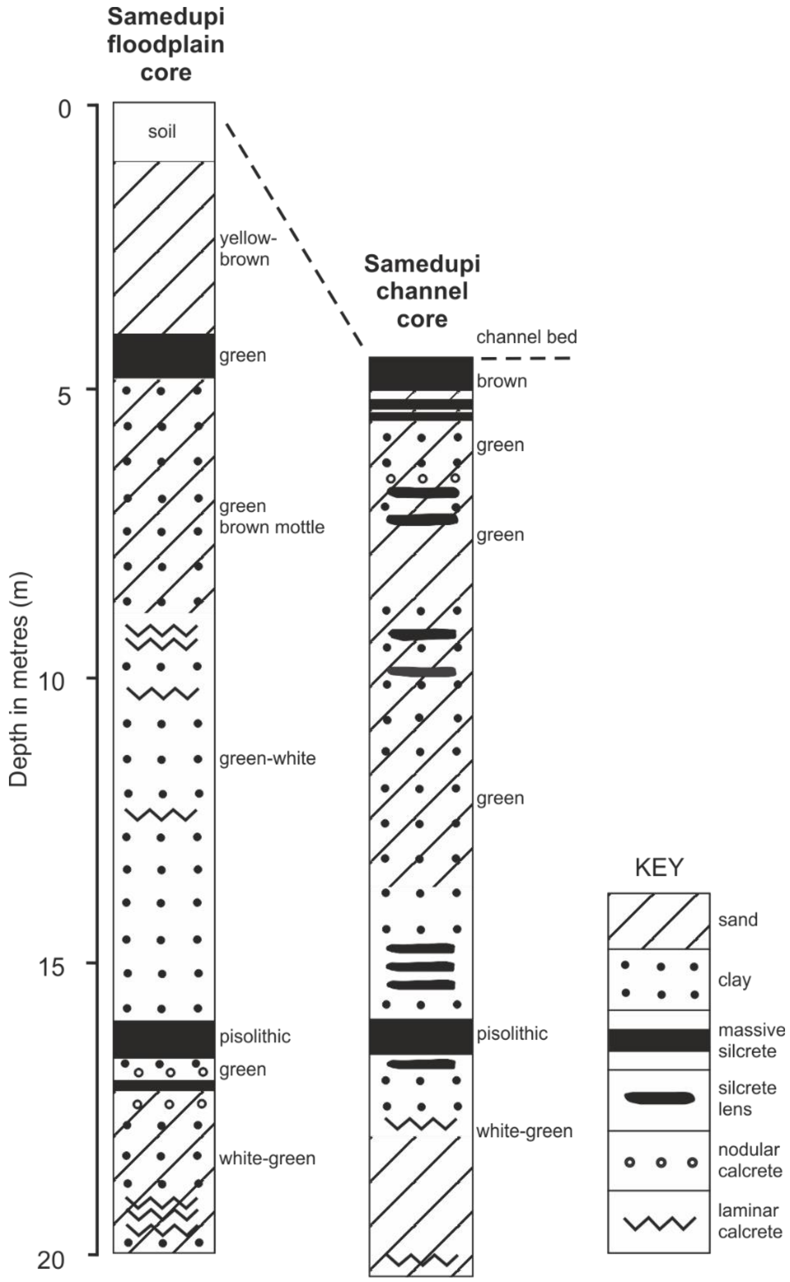

Figure X.12: Cores extracted from the bed of the Boteti River at Samedupi Drift, showing a range of geochemical sediments developed beneath the channel floor, including massive and pisolithic drainage-line silcretes (after Shaw and Nash, 1998).

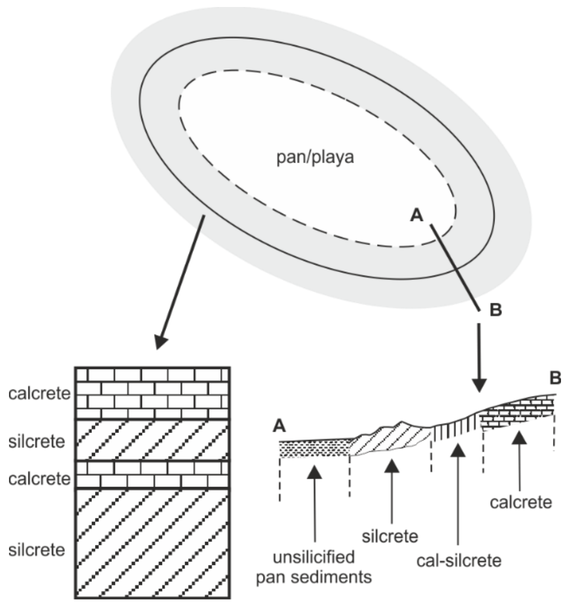

Figure X.13: Schematic representation of geochemical sedimentation patterns in the vicinity of a pan or ephemeral lake (after Summerfield, 1982).

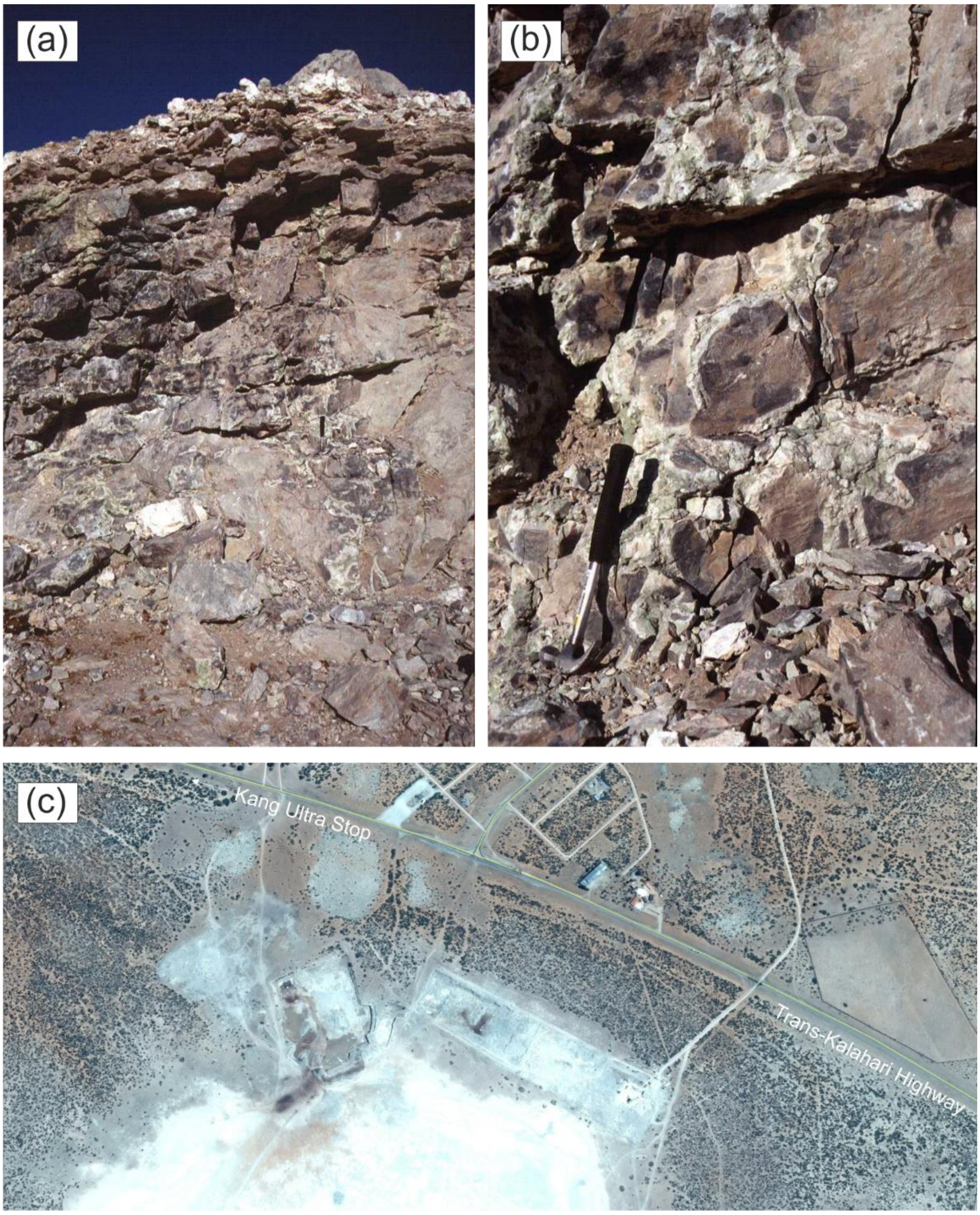

Figure X.14: Views of the aggregate quarry cut into the northern rim of Kang Pan: (a) Overview of the 5.5 m sequence of silcrete, calcrete and silcrete-calcrete intergrade duricrusts; (b) Close-up showing patchy silicification and alteration of pre-existing calcrete. (c) Aerial view of the quarry, showing its proximity to the Trans-Kalahari Highway. Images (a) and (b) © David Nash. Image (c) courtesy of Google Earth (date of image, 12 June 2016).

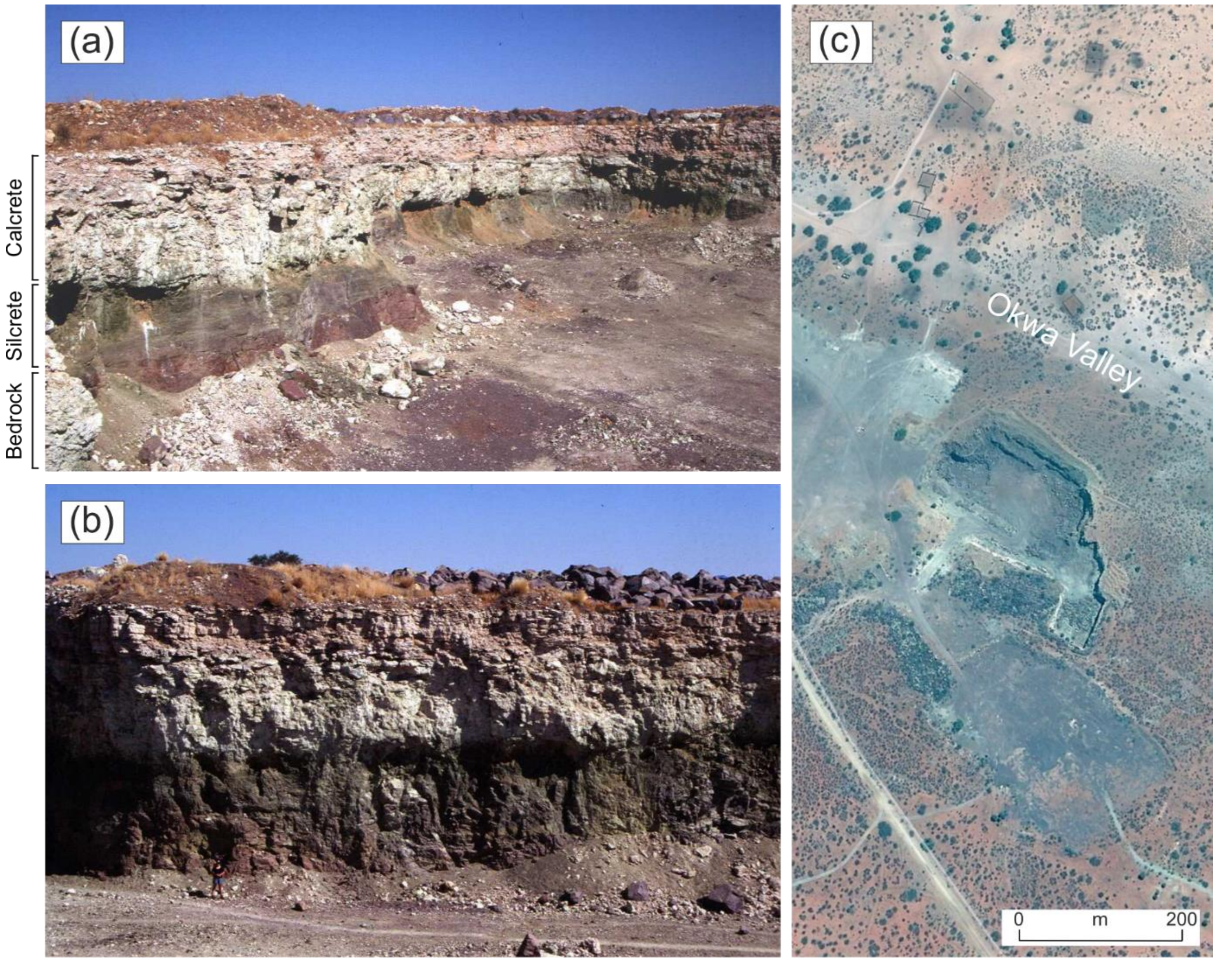

Figure X.15: Views of the (a) eastern and (b) northern face of the aggregate quarry at Tswaane on the Okwa Valley, 12 km east of the Trans-Kalahari Highway, where a complex sequence of calcrete, silcrete and silcrete-calcrete intergrade duricrusts are exposed above weathered Precambrian bedrock. Note figure for scale, bottom left of image (b). (c) Aerial view of the quarry, showing its proximity to the Okwa Valley. Images (a) and (b) © David Nash. Image (c) courtesy of Google Earth (date of image, 11 February 2006).

TABLES

Table X.1: A classification of calcrete types (Carlisle, 1983).

Calcrete classification	**Incorporated calcrete types**
Pedogenic calcrete	Caliche; Kunkar; Nari
Non-pedogenic superficial calcrete	Laminar crusts; Case hardening
Non-pedogenic gravitational zone calcrete	Gravitational zone calcrete
Non-pedogenic groundwater calcrete	Valley calcrete; Channel calcrete; Deltaic calcrete; Alluvial fan calcrete
Non-pedogenic detrital and reconstituted calcrete	Recemented transported calcrete; Brecciated and recemented calcretes

Table X.2: Stages in the morphogenetic sequence of carbonate deposition during calcrete formation (Bachman and Machette, 1977).

Stage	**Diagnostic carbonate morphology**
I	Filaments or faint carbonate coatings, including thin discontinuous coatings on the underside of pebbles
II	Firm carbonate nodules few to common but isolated from one another. The matrix between nodules may include friable interstitial carbonate accumulations. Continuous pebble coatings present.
III	Coalesced nodules in disseminated carbonate matrix.
IV	Platy, massive indurated matrix, with relict nodules visible in places. The profile may be completely plugged with weak incipient laminar carbonate coatings on upper surfaces. Case hardening is common on vertical exposures.
V	Platy to tabular, dense and firmly cemented. Well-developed laminar layer on upper surfaces. Scattered incipient pisoliths may be present in the laminar zone. Case hardening common.
VI	Massive, multilaminar and brecciated profile, with pisoliths common. Case hardening common.