

Origin of calcrete and dolocrete in the carbonate mantle of St Vincent Basin, southern South Australia

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Abstract

Calcrete profiles developed in a toposequence in the carbonate mantle covering the landscape in the St Vincent Basin South Australia are examined. Strong trends in morphology, chemistry and mineralogy are observed from higher to lower profile and topographic locations. Carbonate profiles are dominated by calcrete in both higher profile and toposequence locations while dolocrete dominates in lower profile and toposequence locations. These changes are accompanied by progressive increases in dolomite abundance and decreasing calcite abundance and reflected in decreasing Ca/Mg ratios with depth and decreasing toposequence elevation. Observed trends are explained in terms of profile leaching and groundwater drainage.

Key words: Calcrete, dolocrete, carbonate mantle, South Australia

INTRODUCTION

Dolomite has long been recognised as an important component of the carbonate mantle that is extensively developed over landscapes in southern Australia. The origin of the veneer, which is several metres thick in places, and includes a range of minerals, is attributed to a combination of geological and pedological processes. Early studies identified Pleistocene beach and dune calcarenites as sources of calcareous sediment, and suggested that fine materials were winnowed from these sediments and transported inland on the wind and there deposited. Pedological processes acted to form a mantle of calcareous calcrite that takes various forms including calcic and petrocalcic horizons (CROCKER, 1946; see also NETTERBERG, 1980; MILNES and HUTTON, 1983). This general concept is widely accepted. MILNES and HUTTON (1983) used the term calcrite in its broadest sense to refer to the range of materials encompassed by the carbonate mantle. They described its distribution, relationships, form and characteristics.

NORRISH and PICKERING (1977) examined the mineralogy of various carbonate accumulations, finding that the concentration of dolomite increased relative to calcite with depth and that dolomite was the only carbonate mineral present in the lower parts of some profiles. HUTTON and DIXON (1981) studied the mineralogy and chemistry of calcrites from Yorke Peninsula and the Murray Basin of southern South Australia. In profiles consisting typically of an upper indurated caprock, an underlying nodular horizon and a lower zone of calcareous fine earth, they also identified a consistent progressive enrichment of dolomite relative to calcite with depth. Palygorskite and sepioli-

ite were found in association with dolomite in some profiles. MILNES and HUTTON (1983) and MILNES et al. (1987) extended these studies, again concentrating on assessments of the detailed chemical and mineralogical variations within vertical profiles through the mantle.

PHILLIPS and MILNES (1988), on the other hand, analysed systematic changes in both the mineralogical composition and the morphology of the carbonate in vertical profiles from the St Vincent Basin south of Adelaide. They also mapped lateral changes in the morphology of the calcrites and related these changes to local geomorphic influences. However, they did not link vertical and lateral changes in dolomite to the distribution of dolomite within the regional carbonate mantle. Yet such situations provide the opportunity to study the distribution of dolomite relative to calcite in the carbonate mantle in relation to macro morphological features and topography. In the following synthesis an origin is suggested for the dolomite, its spatial distribution, and implications for the formation of dolomite in the carbonate mantle of St Vincent Basin.

REGIONAL SETTING

Field relationships in the study area south of Adelaide South Australia have been described in detail by PHILLIPS and MILNES (1988). In general terms, the carbonate mantle is well exposed in coastal cliffs forming the eastern margin of Gulf St Vincent, and in various road and railroad cuttings behind the coast (figure 1). Although the carbonate mantle contains a variety of materials, there is typically a systematic arrangement of morphological forms or horizons. For example, unconsolidated "silt" or "fine earth" is typical of many horizons at the base of the mantle. Carbonate-indurated nodules may occur in

the silt and commonly increase in abundance upwards. In fact, horizons composed largely of such nodules or clasts coated by concentric carbonate lamellae form conspicuous horizons between the unconsolidated “silt” and

indurated pans of various types which form caprocks. The upper surfaces of such pans are characteristically coated by thin deposits of laminar carbonate.



Fig.1. Location of the Lonsdale, South Australia, study area.

The mantle overlies Pleistocene sediments of fluvial origin (PHILLIPS and MILNES 1988). These are typically clay-rich with some sand intervals and form part of an extensive sequence marking the close of sedimentation in the Tertiary St Vincent Basin and its various local sub-basins and embayments (WARD, 1965, 1966; TAYLOR, et al. 1974; DAILY et al. 1976). Uplift due to faulting in combination with receding seas, has exposed most of the Pleistocene succession as well as the underlying marine Tertiary sequence.

THE STUDY SITE

The study site is located in a railway cutting between Hallett Cove and Lonsdale southeast of Adelaide (figure 1) where an extensive outcrop of the carbonate mantle and associated non-carbonate sediments is exposed. The carbonate mantle is overlain by a thin surface soil. Several types of calcrete are present within the mantle. On topographic highs the calcrete is dominated by weakly cemented hardpan 1.0-1.5m in thickness, overlain by a discontinuous layer of strongly indurated nodules and pisoliths. On the flanks of slopes the thickness of the hardpan calcrete increases and displays an irregular upper surface resulting from groundwater dissolution. Depressions in the surface of the hardpan are filled with calcareous sands and silts containing abundant strongly indurated nodular calcrete. The base of the weakly indurated hardpan calcrete unit is poorly defined and is characterised by the presence of discontinuous carbonate patches in a reddish non-calcareous sand.

Beneath the complex surface calcrete unit is a unit dominated by sand, clay and

some gravel which unconformably overlies Permian age glacial clays (PHILLIPS and MILNES, 1988). The sandy sediments occupy channels within the clay and are equivalent to the Ngalinga Formation of PHILLIPS and MILNES (1988). A series of thin carbonate layers is developed within the sand beneath the surface calcrete. They presumably represent former periods of carbonate mantle deposition and calcrete formation. Like the surface calcrete they display marked lateral variation in morphology.

METHODS

Samples were collected at 10 cm intervals from trenches cut down the face of the exposed railway cutting sections (figure 2). The trenches were spaced at irregular intervals along the sections, depending partly on the ease of access but also in order to include clearly recognisable macro-morphological features.

In the laboratory, unconsolidated samples were sieved through a 2mm mesh, retaining both the clasts and the fine fraction. Consolidated samples were gently ground using a steel mortar and pestle. All sub-samples were finely ground in alcohol in a Sibtechnik ring and puck mill, using a Cr-steel vessel and the resulting powder was dried at 105 °C in a bench oven. This technique was adopted in order to minimise damage to the carbonate crystal structure during fine grinding.

Selected samples were treated with dilute HCl to remove the carbonate minerals. The residual fraction was dispersed and allowed to settle in a water column in order to separate the <2 µm fraction for analysis. The clay was concentrated by centrifugation, washed repeatedly in distilled water, and dried to a

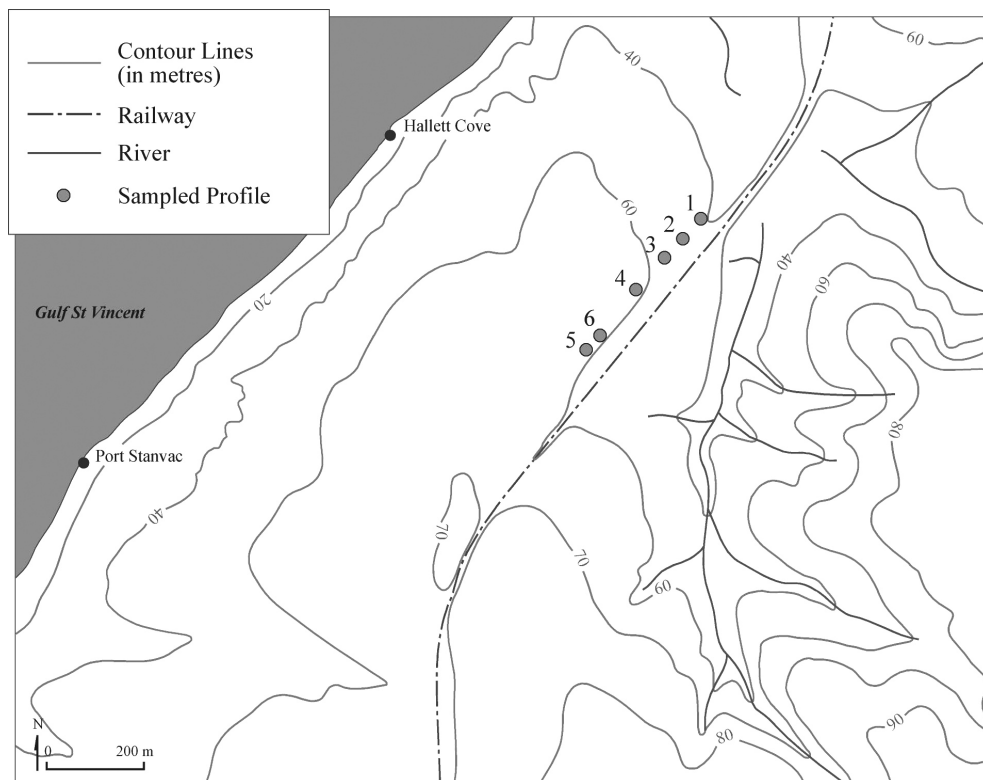


Fig. 2. Location of the carbonate profiles in the Lonsdale toposequence.

powder form at 105 °C. Randomly oriented samples of the powders were prepared for XRD analysis as above. Sub samples of the powders were re-dispersed in distilled water and sucked on to ceramic plates under vacuum to prepare oriented samples. One of the oriented samples was saturated with Mg (using 1N MgCl₂) and glycerol for identification of the layer silicate clay minerals by XRD; the other was saturated with Ba (using 1N BaCl₂) for measurement of cation exchange capacity and chemical composition using XRF.

The dried powders were packed randomly into aluminum sample holders for

XRD analysis. The instrument used was a micro-processor controlled Phillips PW1710 diffractometer with CoK α radiation, automatic divergence slits and a graphite monochromator. XRD patterns were collected in digital mode (step scan at 0.5 degrees 2 theta, 0.5 second sampling time at each step) and were logged to permanent files on an IBM PC/XT computer. Analysis of the data was carried out using the software package XPLOT.

Chemical analyses of the same samples for major element composition were carried out on a Phillips PW1400 micro-processor controlled x-ray fluorescence spectrometer.

Approximately 0.28 g of each finely ground sample was accurately weighed into glass vials with about 1.5 g of lithium tetraborate-lanthanum oxide flux (NORRISH and HUTTON, 1969). The mixture was fused into a homogeneous glass in a Pt-Au crucible using an oxy-propane flame at a temperature of 1050°C and the molten material was quenched between a graphite mold and an aluminum plunger.

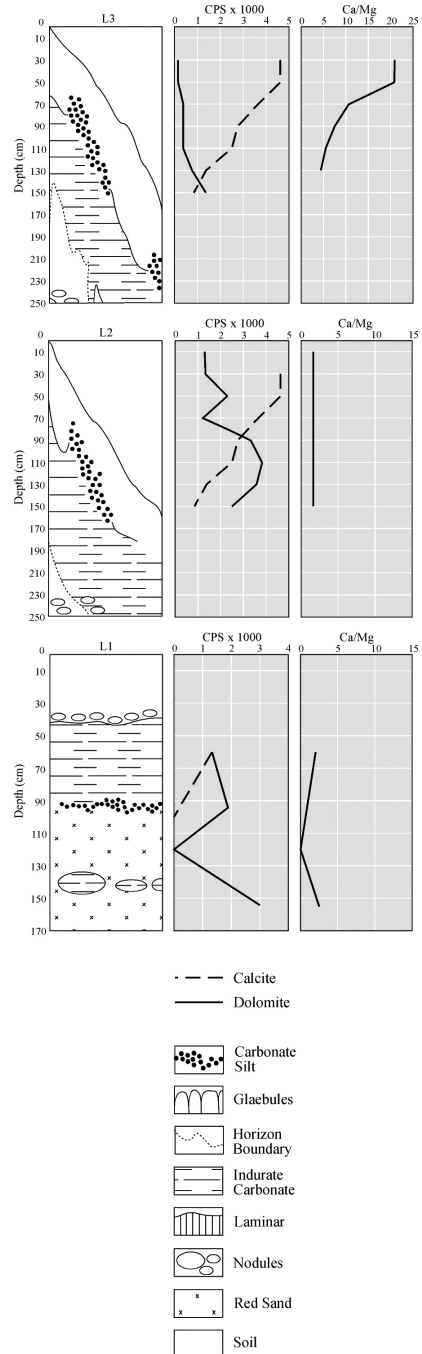
RESULTS

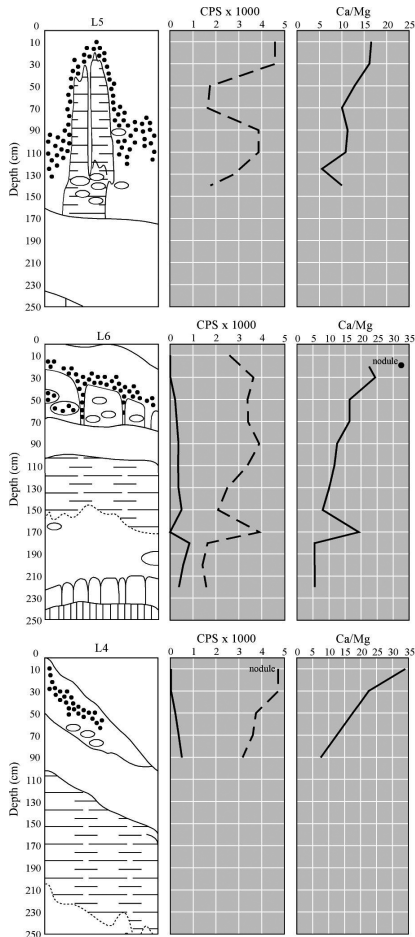
Carbonate mineralogy

The sediment consists of rounded pelletal grains of calcite, dolomite and older calcrete. The primary quartz-rich, carbonates have been pedogenically modified by solution, translocation and precipitation of calcite and dolomite.

Distinct lateral and vertical trends in carbonate mineralogy are observed within the carbonate profiles from the study site at Lonsdale (L1—L6 in figure 3). The profile at the highest elevation (L5) is dominated by calcite throughout its entire thickness. Calcite abundances are variable in the upper 100 cm of the profile, but below that depth there is a progressive decrease in calcite abundances as the underlying non-calcareous sediment is approached. No dolomite was found within the profile.

Some 60 m down slope from L5 (L6 in figures 2 and 3), calcite dominates the carbonate profile, but dolomite first appears in the calcrete in small quantities with a slight, but progressive increase in abundance with depth. There is also a slight decrease in the abundance of calcite. At no location in the profile, however, does the abundance of dolomite exceed that of calcite. Nodules sam-





pled from the upper part of the profile are composed entirely of calcite.

The third profile (L4 in figures 2 and 3) in the Lonsdale toposequence is located a further 80 m downslope from the L6 profile. At this site dolomite and calcite abundances are similar to those found in the L6 profile. However, there is a substantially stronger vertical trend in the distribution of the two minerals. Throughout the greater thickness of the profile the occurrence of calcite dominates dolomite. With increasing depth in the profile the abundance of dolomite increases while that of calcite decreases.

In the profiles on the lower slopes of the Lonsdale toposequence the pattern of distribution and relative abundances of the carbonate minerals changes substantially. Three profiles were sampled along this portion of the railroad cut. The first profile (L3 in Figs. 2 and 3) is approximately 30 m downslope from profile L4. Vertical trends in both dolomite and calcite are similar to those observed in profiles higher in the toposequence. Dolomite shows a progressive increase in abundance with depth and this is accompanied by a progressive decrease in calcite. Two differences are observed in

Fig. 3. Carbonate toposequence profiles showing systematic changes in morphology, mineralogy, and chemistry from higher (L5) to lower (L1) topographic positions. Note that thickness and degree of induration generally increases from higher to lower topographic positions. Carbonate mineral abundances are shown by the peak heights from X-ray spectra (CPS x 1000). Profile L5 is dominated exclusively by calcite (dashed line) while profile L1 is dominated by dolomite (solid line). Intervening profiles display progressive increases in dolomite abundance with both depth and downslope. Changes in carbonate chemistry are indicated by the Ca/Mg ratio. This ratio shows progressive decreases in depth and downslope from profile L5—L1 as abundance of calcite decreases and dolomite increases.

profile L3 compared to those higher in the toposequence. The overall abundance of dolomite is greater in this profile than those described previously (L4-L6 in figure 3) and at the base of profile L3 the abundance of dolomite exceeds that of calcite.

A further 10 m downslope from profile L3, at profile L2 (figure 3) vertical trends in both dolomite and calcite are similar to those observed in profiles higher in the toposequence. Dolomite shows a progressive increase in abundance with depth and this is accompanied by a progressive decrease in calcite. The pattern of increase in dolomite abundance with depth is not as regular as that for calcite. Two substantial differences are observed in patterns of dolomite and calcite distribution and abundances in this profile (L2 in figure 3) compared to those higher in the toposequence. First, dolomite abundances are substantially greater in this profile than in any of those at higher elevations and calcite abundances are substantially lower. Second, with the exception of the upper 30 cm of the profile, dolomite abundances exceed those of calcite. Strongly indurated nodules analysed down the profile are more dolomitic than the weakly indurated hardpan calcrete in which they are embedded. In the upper part of the profile the nodules consist of approximately equal amounts of calcite and dolomite. Nodules from the lower parts of the profile are exclusively dolomitic in composition.

A profile some 20 m further downslope from L2 (L1 in figure 3) was sampled and analysed by PHILLIPS (1988). Significantly this profile is more abundant in dolomite than the L2 profile and in the lower half of the profile dolomite is the only carbonate mineral present.

Non-carbonate mineralogy

The non-carbonate mineralogy of the calcretes is dominated by quartz, with trace amounts of feldspar. The clay fraction of the carbonates is dominated by illite, kaolinite and randomly interstratified minerals. In contrast to the carbonate mineralogy, the non-carbonate mineralogy displays weak vertical and lateral trends. However, clay mineral abundances appear to vary slightly with calcrete type.

Illite is the most abundant clay mineral identified in the insoluble fractions of the calcrete and ranges from 40-55%. Its abundance in the one silt sample analysed was slightly less at 40%. Abundances in the profile in the lowest topographic position are slightly greater than those higher in the toposequence.

Randomly interstratified clays and smectite are the next most abundant clay mineral assemblage ranging in abundance from 25-40%. The greatest abundance occurs in the carbonate silt sample. Greatest abundances are observed in the profile at the top of the toposequence and lowest abundances are observed at the bottom of the toposequence. Abundances remain relatively uniform down the profile.

Kaolinite ranges in abundance from 20-30%, with the smallest abundance occurring in the silt at the top of the profile at the top of the toposequence. There is a slight tendency for abundances to be higher at the top of hardpan profiles. No lateral variations were observed.

Carbonate Chemistry

The chemistry of the carbonates is dominated by three elements which together ac-

count for well over 70% by weight. In all profiles analysed Mg, expressed as MgO, is the least abundant metal oxide, i.e. generally less than 10%. While overall values are low there is a tendency for MgO to show a progressive increase in abundance with increasing depth. Magnesium abundances show marked contrasts between higher toposequence profiles and those in lower topographic positions. Generally speaking, MgO abundances in profiles L6, L5, and L4 are less than 2.5% while the magnesium content of the lowest three profiles is greater than 2.5% with site L2 containing between 6-10% MgO.

Calcium, expressed as CaO, is present in abundances that are an order of magnitude greater than those of MgO. In general, Ca decreases with depth as the degree of carbonate induration increases. Similarly the abundance of Ca tends to decrease down the toposequence.

Ca/Mg ratios, which reflect the relative amounts of these elements in the carbonates and also reflect the relative abundances of the dominant carbonate minerals. Several distinct trends are observed. Ca/Mg ratios decrease with increasing depth in the profile and commonly display an order of magnitude change (figure 3). This is especially observed in profiles L6, L4, and L3 (figure 3). The other notable trend is the marked decrease in the ratio in lower toposequence profiles compared to higher profiles. Profiles high in the toposequence (L4, L5, and L6 in figure 3) display ratios that are an order of magnitude greater than those in profiles lower in the profile (L1, L2, and L3 in figure 3). In their investigation of secondary soil carbonates, ST ARNAUD and HERBILLON (1973) showed that secondary CaCO₃ contain at least 5% MgCO₃ in the calcite structure. This corresponds to a Ca/Mg weight

ratio of 26 for calcite and 1.7 for dolomite. The carbonates in this study are clearly mixtures of calcite and dolomite as these ratios tend to be higher than either of the ideal ratios. However, the observed trends clearly indicate that the upper parts of the profiles are calcite dominated by contrast with the lower parts of the profile and toposequence which are dolomite dominated.

DISCUSSION

The carbonate mantle

In the study area, as with most of the calcretes forming in the mantle, there is a recurring pattern of arrangement of calcrete morphologies, which represent successive stages of development (WRIGHT, 2007). Calcrete profiles typically display a lower unconsolidated horizon of calcareous silt or powder calcrete. Above this horizon is one dominated by calcareous nodules, grading upward into massive hardpan calcrete, which incorporates weakly to strongly cemented nodules and pisoliths. The surface of the hardpan unit commonly displays a thin carapace of laminar calcrete with accompanying solutional features (NETTERBERG, 1967, 1980; GOUDIE, 1983). It is not uncommon for this sequence to be repeated several times within a sediment package (DIXON, 1978, 1994; MILNES and HUTTON, 1983; PHILLIPS and MILNES, 1988; DIXON and McLAREN, 2009). At the Lonsdale site, profiles L5 and L6 display a modern surface soil with carbonate silt and embedded nodules overlying a discontinuous horizon of moderately indurated hardpan calcrete. Profile L4 consists of a modern surface soil over a horizon of coated clasts which sit on top of a moderately indurated

hardpan calcrete. Profiles L2 and L3 comprise a modern surface soil with incorporated nodules over a moderately indurated hardpan with an underling nodular zone. Profile L1 consists of a surface soil with nodular layer at its base sitting over a moderately indurated hardpan layer. Beneath the hardpan layer is a powdered silt unit. This pattern of arrangement is generally interpreted to represent illuviation of carbonate saturated waters and progressive induration (GILE et al., 1965, 1966; GOUDIE, 1983). Precipitation of calcite and dolomite in the carbonate mantle may also be partially facilitated by biological processes (PHILLIPS et al., 1987; PHILLIPS and SELF, 1987). Where present, laminar forms on the surface of hardpan layers may also be related to biomineralisation processes (KLAPPA, 1979; VERRECCHIA et al., 1995)

Changes in calcrete morphology are also strongly expressed laterally. On topographic highs the hardpan layer is relatively thin and discontinuous. Down the toposequence, however, the hardpan layer becomes thicker, more strongly indurated and more continuous. It also displays more strongly karstified surface features. In addition, such as at site L4, there is strong suggestion of downslope movement and accumulation of carbonate cobbles. These lateral variations, together with the vertical trends discussed above, reflect a combination of both vertical and lateral soil water and groundwater migration controlled by gravity and topography.

Dolomitisation of the carbonate mantle

The presence of dolomite in calcretes is widely recognised (WATTS, 1977; MANN and HORWITZ, 1979; KHALAF, 1990, 2007; DIXON, 1994; WRIGHT, 2007) and

the tendency for its distribution to be concentrated in the lower parts of the profile widely reported (HUTTON and DIXON, 1981; MILNES and HUTTON, 1983; WRIGHT and TUCKER, 1991; DIXON, 1994; DIXON and McLAREN, 2009). However, in some instances dolomite has been observed to be the dominant cementing agent of hardpans at the top of indurated profiles (MILNES, 1992; KHALAF, 1990). Where dolomite is the principal cementing and/or replacement agent of the primary sediment or soil, it is most appropriate to refer to these carbonate materials as dolocretes (GOUDIE, 1973; KHALAF, 1990, 2007).

In the case of the indurated carbonates at Lonsdale this study identified the occurrence of dolomite and its concentration lower in the profile. The systematic increase in dolomite and accompanying decrease in calcite down profile together with systematic decreases in Ca/Mg ratios, suggests that calcite is being progressively replaced by dolomite. Induration of the dolomite results in the formation of dolocrete (ARAKEL, 1986; COLSON and COJAN, 1996; SCHMID et al., 2006). The systematic lateral increase in dolomite abundance and an accompanying decrease in calcite, accompanied by progressive decreases in Ca/Mg ratios, suggests progressive downslope replacement of calcite by dolomite (KHALAF, 1990). Explanation of the development of dolomite in calcrete must account for both of these patterns observed in a landscape setting.

The original carbonate mantle of the Gulf St Vincent region is generally considered to have been an aeolian silt derived from the winnowing of extensive Pleistocene dune fields that consisted of a spatially variable mixture of calcite, dolomite, quartz and

clay minerals. The work of DIXON (1978, 1994) and HUTTON and DIXON (1981) in the Murray Basin demonstrated that at some sites the primary carbonate mantle consists entirely of dolomite.

In order to explain the pattern of calcite and dolomite distribution in most profiles a leaching model is proposed (HUTTON and DIXON, 1981). Soil and groundwater becomes enriched in Ca and Mg as it percolates through the carbonate mantle. As the water becomes saturated, calcite is precipitated first (ARAKEL, 1986; MORGAN, 1993) locally cementing the carbonate silt. As calcite is precipitated, groundwater is progressively enriched in Mg relative to Ca resulting in preferential precipitation of dolomite at depth (WATTS, 1977). Such a model fits the data obtained in this study with Ca/Mg ratios in carbonate profiles decreasing systematically with depth, with dolomite abundances increasing systematically down profile, and with the presence of dolomite crystals intergrowing with calcite and lining voids (see also PHILLIPS and MILNES, 1988).

The lateral variations in dolomite abundance observed at the Lonsdale toposequence are consistent with downslope patterns of water movement and mantle induration. As groundwaters flow downslope through the carbonate mantle they evolve chemically with Ca/Mg ratios gradually decreasing. Once these waters become saturated they begin to precipitate calcite making the remaining water enriched in Mg relative to Ca. This increase in Mg/Ca ultimately results in the precipitation of dolomite rather than calcite and the associated formation of dolocrete (ARAKEL, 1986; COLSON and COJAN, 1996; SCHMID et al., 2006; KHALAF, 2007; WRIGHT, 2007). This process

is also consistent with the observed morphological changes observed laterally with thickening, hardening and stronger lateral continuity of the hardpan layer.

CONCLUSIONS

Thus, it is interpreted that the formation of the calcretes and dolocretes in the aeolian carbonate mantle of the St Vincents Basin is the result of profile and landscape controlled patterns of soil and groundwater movement. Changes in water chemistry associated with leaching of a mixed Ca/Mg-dominated sediment account for the pattern of distribution of calcrete and dolocrete. The process of induration is a combination of both dolomitisation at depth and downslope, as well as de-dolomitisation of the original sediments higher in the profile and in the landscape (KHALAF and ABDAL, 1993). This study represents a contribution to the understanding of the pattern of dolocrete occurrence in the landscape in the eastern St Vincent Basin.

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