Comparison of stable isotope values of Quaternary calcretes from Adana and Mersin provinces: implications on controlling factors

Muhsin EREN1*, Meryem YEŞİLOT KAPLAN2, Selahattin KADİR3, Selim KAPUR4

1Department of Geological Engineering, Faculty of Engineering, Mersin University, Çiftlikköy, Mersin, Turkey
2Department of Petroleum and Natural Gas Engineering, Faculty of Engineering, İskenderun Technical University, İskenderun, Hatay, Turkey
3Department of Geological Engineering, Faculty of Engineering and Architecture, Eskişehir Osmangazi University, Meşelik, Eskişehir, Turkey
4Department of Soil Science and Plant Nutrition, Faculty of Agriculture, Çukurova University, Balcalı, Adana, Turkey

Abstract: Calcretes are widespread in Adana and Mersin provinces and form under different morphologies. Most calcrete profiles comprise a hard laminated crust/hardpan at the top, gradually intergrading into the nodular and/or tubular/columnar horizon with depth. This study compares the $\delta^{18}$O and $\delta^{13}$C values of calcretes from both provinces and discusses the controlling factors and environmental conditions. The $\delta^{18}$O and $\delta^{13}$C values are characteristic for the pedogenic calcretes. The Adana calcrete mean $\delta^{18}$O values of the hardpan, nodules and tubes, and fractures-infills are 0.69‰, 0.77‰, and 1.04‰ PDB heavier than those of the Mersin calcretes, respectively. The overall difference between the two groups is 0.78‰ PDB. The differences are related to the high evaporation rate in Adana province in respect to Mersin province under similar climatic conditions, except for the evaporation rate. The high evaporation rate in Adana province is due to higher ventilation. The $\delta^{13}$C values of both provinces are almost the same, reflecting calcrete formation in soil with abundant C$_3$ vegetation similar to contemporary vegetation. In addition, the mean $\delta^{18}$O values of the hardpan calcretes slightly differ from those of the columnar horizon, showing a depletion in heavy isotopes. The depletion in the mean $\delta^{18}$O values of hard laminated crust in respect to the columnar horizon is 0.09‰ PDB for Adana calcretes and 0.12‰ PDB for Mersin calcretes. This is related to the relatively thick water film from which the calcretes formed by precipitation and displacive replacement processes. The difference in the mean $\delta^{13}$C values is 0.32‰ PDB for the Adana calcretes and 0.11‰ PDB for the Mersin calcretes, and the depletion in $\delta^{13}$C values of the hard laminated crust reflects proximity of the bioactive horizon in the soil.

Key words: Calcrete, stable isotope, hard laminated crust, columnar horizon, southern Turkey

1. Introduction

The calcretes are terrestrial carbonates (predominantly CaCO$_3$) that accumulate and/or replace the host materials in near-surface settings and occur in a variety of morphologies (Wright and Tucker, 1991; Kelly et al., 2000; Alonso-Zarza and Wright, 2010). They are often associated with authigenic clays as a minor constituent, generally including palygorskite and sepiolite (Wang et al., 1994; Verrecchia and Le Coustumer, 1996; Garcia-Romero et al., 2004; Silva et al., 2018; Elidrissi et al., 2018). There are two major groups of calcretes regarding their origin: (i) the pedogenic calcretes, generated by soil-forming processes and characterized by abundant $\beta$-fabric (biogenic) features (Klappa, 1983; Shankar and Achyuthan, 2007; Singh et al., 2007; Zamanian et al., 2016; Eren et al., 2018), and (ii) the groundwater or nonpedogenic calcretes, precipitated from groundwater by evaporation in the capillary zone (Goudie, 1973; Nash and McLaren, 2003) or in the phreatic zone (Mann and Horwitz, 1979). Calcretes are widely accepted as indicators of arid and semiarid climates (Anand et al., 1997; Alonso-Zarza and Wright, 2010; Achyuthan et al., 2012). A great number of studies exist on the different aspects of calcretes in the world and also in Turkey, including isotopic studies (e.g., Cerling, 1984; Andrews et al., 1998; Chiquet et al., 2000; Leone et al., 2000; Srivastava, 2001; Achyuthan, 2003; Nash and McLaren, 2003; Dworkin et al., 2005; Durand et al., 2006; Kovda et al., 2006; Achyuthan et al., 2007; Zhou and Chafetz, 2009; Gallala et al., 2010; Meléndez et al., 2011; Horn et al., 2013; Mortazavi et al., 2013; Elidrissi et al., 2017; literature from

* Correspondence: m_eren@yahoo.com

Received: 21.02.2019 • Accepted/Published Online: 01.07.2019 • Final Version: 04.09.2019

This work is licensed under a Creative Commons Attribution 4.0 International License.
Turkey given in Table 1). However, comparative isotopic studies on calcretes are very limited and include worldwide comparisons (Salomons et al., 1978; Talma and Netterberg, 1983; Eren, 2011). The isotope values of Quaternary calcretes from both Adana and Mersin provinces were previously studied by Kaplan et al. (2014) and Eren et al. (2008). This study aims to compare isotopic compositions of calcretes in these provinces and also attempts to discuss the climatic controlling factors and environmental conditions affecting the formation of “calcrete profiles” (term first used by Meléndez et al. (2011) for the Ebro Basin calcretes and Eren et al. (2018) for the Adana and Mersin calcretes), which has not been undertaken to date. Furthermore, these new regional isotopic comparisons and interpretations will guide future investigations of similar geographic settings concerning paleoclimate and the environmental conditions in the Mediterranean and worldwide.

2. Geological setting
This study concerns the Neogene Adana basin developed within the central Taurides of SE Turkey and comprises two sampling sites in Adana and Mersin provinces (Figure 1). The basin infill contains Tertiary and Quaternary sedimentary rocks and sediments unconformably overlying the pre-Miocene basement rocks of clastics, carbonates,

### Table 1. Literature summary of the calcretes in Turkey.

| Reference            | Subject                                                                 | Location            |
|----------------------|-------------------------------------------------------------------------|---------------------|
| Kapur et al., 1987   | Soil-calcrete (caliche) and its relationship with geomorphology         | Adana               |
| Özer et al., 1989    | ESR and TL age determination of caliche nodules                          | Çukurova/Adana      |
| Kapur et al., 1990   | Geomorphology and pedogenic evolution of Quaternary calcretes           | Adana               |
| Kapur et al., 1993   | Soil stratigraphy and Quaternary caliche                                 | Misis/Adana         |
| Atalay, 1996         | Paleosols as indicators of the climatic changes                          | South Anatolia      |
| Atabey et al., 1998  | Sedimentology of caliche (calcrete) occurrences                          | Kırşehir            |
| Kapur et al., 2000   | Carbonate pools in soils                                                | Mediterranean area   |
| Eren, 2007           | Genesis of tepees in the Quaternary hardpan calcretes                   | Mersin              |
| Eren et al., 2008    | Quaternary Calcrete Development                                          | Mersin              |
| Kadir and Eren, 2008 | Genesis of clay minerals in Quaternary caliches                          | Mersin              |
| Kadir et al., 2010   | Dolocretes and associated palygorskite                                   | Çanakkale           |
| Eren and Hatipoğlu-Baçı, 2010 | Karst surface features of the hard laminated crust (caliche hardpan) | Mersin              |
| Eren, 2011           | Stable isotope geochemistry of Quaternary calcretes                     | Mersin              |
| Küçükuysal et al., 2011 | ESR dating of calcrete nodules                                          | Bala/Ankara         |
| Kaplan et al., 2013  | Mineralogical, geochemical, and isotopic characteristics of Quaternary calcretes | Adana               |
| Kadir et al., 2014   | Genesis of Late Miocene-Pliocene lacustrine palygorskite and calcretes  | Kırşehir            |
| Kaplan et al., 2014  | Pedogenic palygorskite associated with Quaternary calcretes              | Adana               |
| Küçükuysal et al., 2013 | Multiproxy evidence of Mid-Pleistocene dry climates in calcretes        | Ankara              |
| Küçükuysal and Kapur, 2014 | Mineralogical, geochemical, and micromorphological evaluation of the Plio-Quaternary paleosols and calcretes | Karahamzahi/Ankara |
| Küçükuysal, 2016     | Mineralogical, micromorphological, geochemical, and stable isotopic compositions, and radiocarbon ages of the Late Pleistocene calcretes | Gölbabağı Basin/Central Anatolia |
| Gürel and Özcan, 2016 | Paleosol and dolocrete associated clay mineral                          | Tuzköy/Ankara       |
| Kadir et al., 2018   | Genesis of palygorskite and calcrete in Pliocene Basin                  | Eskişehir           |
| Eren et al., 2018    | Biogenic (β-fabric) features in the hard laminated crusts                | Adana, Mersin       |

Modified from Eren et al. (2018).
and ophiolites (Figures 2 and 3; Schmidt, 1961; Yalçın and Görür, 1983; Yetiş, 1988; Yetiş et al., 1995; Darbaş et al., 2008). The Tertiary units are mainly represented by the Kuzgun and Handere Formations in Mersin and Adana provinces, respectively. The Kuzgun Formation, deposited during the late Miocene (Tortonian), comprises predominantly shallow marine mudstones and sandstones at the lower to middle part and fluvial deposits consisting mainly of reddish-brown mudstones of overbank deposits intercalated with cross-bedded sandstones of point bar and channel deposits at the upper part (Eren et al., 2008). The Handere Formation of the Messinian to Pliocene age is made up of predominantly mudstones associated with conglomerates, sandstones, and gypsum lenses of lagoonal, shallow marine, and fluvial environments (Yetiş et al., 1995; Gürbüz, 1999). The Quaternary covers recent alluvium, alluvial terraces, colluvial red soils, and/or red soils and hardpan calcretes.

Calcretes are widely available on and/or within layers of the Kuzgun and Handere Formations in Mersin and Adana provinces, respectively (Figure 4; Eren et al., 2008; Kaplan et al., 2013). They have also been recognized in/on the Pleistocene glaci (mass flow or mud flow) terraces (Kapur et al., 1993; Kaplan et al., 2013) of Adana province and the Quaternary colluvial red soils of Mersin province (Eren et al., 2008). The Pleistocene ages of the calcretes of the area dated from 250 to 782 ka BP were determined by Özer et al. (1989), whereas the early Holocene to Pleistocene ages were based on the field observations of Erol (1981, 1984), Atalay (1996), Eren et al. (2008), and Kaplan et al. (2013) studies. Furthermore, Küçüküysal et al. (2011) and Küçüküysal (2016) provided Middle to Late Pleistocene age for calcretes determined by ESR and radiocarbon techniques in the Bala and Gölbasi Basin/Ankara regions of central Turkey, respectively.

Calcrete profiles often reflect maturation in the soil profile development and consist mainly of the hard laminated crust with a thickness of about 1.5 m at the top, gradually intergrading with depth into the 1.5–2 m thick nodular and/or tubular/columnar (term first used by Kapur et al., 1990) horizon (Figure 4; Eren et al., 2008; Kaplan et al., 2013). In some cases, fracture infills are also observed in the nodular-tubular horizons. The hard laminated crust spreads in large areas unconformably overlying the different layers of the Handere and Kuzgun Formations and outcrops as an undulating crust on the small ridges and highs in low-lying areas (20 to 250 m). The nodular and/or tubular/columnar horizon has developed predominantly within the mudstones of the Kuzgun and Handere Formations as scattered/discreet white mottlings associated with fracture infills.

3. Materials and methods
A total of 164 calcrete samples were collected from 24 measured sections in Adana and Mersin provinces. For isotope analysis, 24 calcrete samples were selected from the hard laminated crust (n = 25) and nodular and/or tubular/columnar horizon (n = 19). Isotopic measurements were
Figure 2. Geological maps of the studied areas: (a) the Adana region (modified from Yetiş, 1988); (b) the Mersin area (Eren et al., 2004).
made on carbon dioxide (CO₂) released after the reaction of approximately 5 mg of powder samples with 100% phosphoric acid (H₃PO₄) at 50 °C using a Finnigan MAT 252 mass spectrometer at ISO Analytical Laboratories (Cheshire, UK). The mass spectrometer was calibrated using NBS 18 and NBS 19 standards. The isotopic results were reported as δ values in parts per mil relative to the Pee Dee Belemnite (PDB) standard. Analytical detection limits at laboratory conditions were ±0.05‰ for δ₁⁸O and ± 0.02‰ for δ₁³C.

The analytical results were cross-plotted as δ₁⁸O versus δ₁³C and analyzed using multivariate statistical analysis to illustrate separation in the samples. Hierarchical clustering analysis (HCA) methods were used for all samples, and the Ward method revealed more meaningful cluster structures (Ward, 1963). The dendrograms were drawn over the statistical application and the Ward method in turn minimizing intracluster differences yielded the correct results. The two-dimensional Pythagorean theorem of the Euclidean distance was used for the calculations (Kaufman and Rousseeuw, 2009).

4. Results
Isotope values of the calcrites are listed in Table 2, where samples of the Mersin calcrites have δ₁⁸O and δ₁³C values ranging from −4.31‰ to −5.84‰ and from −8.40‰ to −7.82‰.
–9.65‰ PDB, respectively. The Adana calcretes have PDB values of δ¹⁸O ranging from −3.76‰ to −5.74‰ and of δ¹³C ranging from −7.71‰ to −10.01‰. In this context, the δ¹⁸O values of calcretes vary in a wide range in respect to the δ¹³C values in the Mersin area, whereas the Adana calcretes have δ¹⁸O and δ¹³C values varying almost in the same range (Figure 5). Within this scope, both cross-plot and hierarchical cluster analyses of δ¹⁸O and δ¹³C values show two distinct calcrete groups referring to Adana and Mersin provinces (Figures 5 and 6). Consequently, the hierarchical cluster analysis revealed that the fracture infills, separately sampled in the field, are associated with and appear to be a subgroup of the calcrete nodules/tubes of the columnar horizon (Figure 6).

Figure 4. Typical calcrete profiles: (a) Kılıç village, Adana; (b) Mersin University campus area, Mersin, showing the hard laminated crust (H) at the upper part of the profile gradually intergrading downward into the nodular (nd) and tubular (tb) horizon (black arrow). In (a), the hard laminated crust shows an upward buckling, which is the cross-section of dome-lime surface morphologies called tepee structure (Eren, 2007).

5. Discussion
The isotope values of the calcrete samples collected from the hard laminated crust and the nodular and/or tubular horizon, including the fracture infills, are in the range of δ¹⁸O and δ¹³C for the pedogenic calcretes (Alonso-Zarza, 2003; Bajnóczi et al., 2006; Eren, 2011; Küçükuysal, 2016). Eren (2011) and Küçükuysal (2016) provided worldwide and mainly regional isotopic comparisons of calcretes, respectively. These δ¹⁸O and δ¹³C values reflect calcrete development under the influence of meteoric water and soil-forming processes, respectively (Purvis and Wright, 1991; Strong et al., 1992; Leone et al., 2000; Alonso-Zarza, 2003; Alonso-Zarza and Arenas, 2004; Eren, 2011). The oxygen isotopic fractionation during inorganic calcite precipitation depends mainly on temperature; therefore, δ¹⁸O values reflect the temperature of water from which calcite was precipitated (Friedman and O’Neil, 1977; Talbot and Kelts, 1990; Bar-Matthews et al., 2003; Dietzel et al., 2009), whereas the δ¹³C values of the pedogenic carbonates are directly related to the soil-derived CO₂ and infer the plant types living at the surface during formation of the calcretes. There are two major plant photosynthetic pathways, C₃ and C₄, where each pathway fractionates carbon to a different extent (Alonso-Zarza, 2003; Tanner, 2010). Moreover, comparisons of the isotopic results using the cross-plot and hierarchical cluster analysis exhibit two distinct groups of Adana and Mersin provinces (Figures 5 and 6). The Adana calcrete samples exhibit an enrichment in δ¹⁸O values compared to the values of the Mersin calcrete samples. These enrichments in the mean δ¹⁸O values of the hard laminated crust, calcrete nodules and tubes, and fracture infills are 0.69, 0.77, and 1.04, respectively. The enrichment is clearer in the fracture infill samples. The overall enrichment in mean δ¹⁸O values of the two groups is 0.78‰ PDB. The oxygen isotopes of the calcretes are sensitive to climatic conditions and mainly reflect the composition of meteoric water (Talma and Netterberg, 1983; Alonso-Zarza, 2003). The enrichment in the δ¹³C values of the Adana region was related to the high evaporation rate in comparison to the Mersin area, despite similar climatic conditions (Table 3). The high evaporation rate of the Adana region is due to probable higher ventilation rates of the area that resulted in removal of moisture in the air and consequently enhanced the evaporation rate under the same annual average temperature conditions as the Mersin area. High mean δ¹⁸O values in the samples of fracture infills are due to the appropriate connection of the fractures with the air spaces with respect to the soils and their high moisture rates. The almost identical δ¹³C values, together with the abundant β-fabric (biogenic) features in the hard laminated crust (Eren et al., 2008, 2018; Kaplan et al., 2013) of both provinces are indicators...
Similarities in δ\(^{13}\)C values between the two groups also reflect the development of calcretes under the same vegetation cover. Small variations in the δ\(^{13}\)C values are due to the soil respiration rate in local areas (Cerling, 1984; Andrews et al., 1998). The δ\(^{13}\)C values suggest the influence of dense C\(_3\) vegetation on calcrete development (Lee, 1999; Bar-Matthews et al., 2003; McDermott, 2004; Candy et al., 2012; Alçıçek and Alçıçek, 2014). Moreover, similarities in the contemporary and past climatic conditions.

### Table 2. Isotopes of the calcretes from the Adana and Mersin provinces.

| Sample | δ\(^{18}\)O (‰ PDB) | δ\(^{13}\)C (‰ PDB) |
|--------|-----------------|-----------------|
| Hard laminated crust Adana province | | |
| Y-6    | -3.76           | -10.01          |
| O-9    | -4.64           | -8.55           |
| YY-5   | -4.50           | -9.09           |
| CKK    | -5.74           | -8.86           |
| B-3    | -3.95           | -8.41           |
| K-1    | -4.61           | -8.41           |
| M-4    | -3.91           | -8.75           |
| KA-2   | -5.13           | -9.15           |
| SA-5   | -4.35           | -8.27           |
| AK-2   | -4.91           | -8.34           |
| Mean   | -4.55           | -8.78           |
| Nodule and tube Adana province | | |
| Y-5    | -3.87           | -9.38           |
| O-2    | -4.44           | -8.63           |
| O-3    | -4.53           | -8.77           |
| YY-9   | -4.22           | -8.35           |
| B-1    | -4.13           | -8.38           |
| K-3    | -4.30           | -8.25           |
| K-5    | -4.56           | -8.11           |
| M-2    | -3.87           | -8.24           |
| KA-1   | -4.69           | -8.71           |
| SA-2   | -4.66           | -7.94           |
| SA-3   | -4.68           | -8.22           |
| S-5    | -4.04           | -8.53           |
| AK-1   | -4.77           | -8.49           |
| Mean   | -4.36           | -8.46           |
| Fracture infill Adana province | | |
| KCD    | -4.05           | -7.71           |
| YY-2   | -4.06           | -8.51           |
| YY-6   | -4.04           | -8.26           |
| Mean   | -4.05           | -8.16           |

| Sample | δ\(^{18}\)O (‰ PDB) | δ\(^{13}\)C (‰ PDB) |
|--------|-----------------|-----------------|
| Hard laminated crust Mersin province | | |
| H-1    | -5.26           | -9.00           |
| H-3    | -4.92           | -8.89           |
| H-4    | -4.89           | -8.66           |
| H-5    | -4.97           | -9.03           |
| H-8    | -5.25           | -9.07           |
| H-9    | -5.25           | -8.90           |
| E-4    | -5.47           | -8.49           |
| E-13   | -5.84           | -8.91           |
| E-66   | -5.31           | -8.56           |
| Mean   | -5.24           | -8.83           |
| Nodule and tube Mersin province | | |
| 7-A    | -5.13           | -8.70           |
| 11-B   | -5.39           | -8.79           |
| O-2    | -5.07           | -8.61           |
| E-18   | -5.58           | -8.63           |
| E-32   | -5.59           | -8.40           |
| 12     | -5.43           | -8.66           |
| 12     | -5.43           | -8.66           |
| Mean   | -5.13           | -8.73           |
| Fracture infill Mersin province | | |
| E-23   | -5.00           | -8.54           |
| K-1    | -5.18           | -8.74           |
| Mean   | -5.09           | -8.64           |

See Figure 2 for sample locations.
Figure 5. A cross-plot of stable isotope values ($\delta^{18}$O and $\delta^{13}$C) of the calcretes showing the two distinct groups of Adana and Mersin provinces.

Figure 6. Cluster analysis showing two groups of samples of Adana and Mersin provinces where the fracture infills appear as a subgroup of the nodular-tubular horizon.
conditions suggest the availability of similar contemporary vegetation represented by the Mediterranean crops on the appropriate land surfaces, namely olives (*Olea europaea*) and carob (*Ceratonia siliqua*), including other shrubby vegetation. The end-member δ¹³C values of soil carbonates formed under 100% C₄ and C₃ ecosystems are about 0‰ to +3‰ and −12‰ to −13‰ PDB, respectively (Cerling, 1984; Cerling et al., 1989; Zamanian et al., 2016).

The δ¹⁸O and δ¹³C values of the hardpans also differ slightly from those of the nodular and/or tubular horizons. The hard laminated crust shows a slight depletion in the δ¹⁸O values regarding those of the calcrete nodules and tubes. These values are 0.19‰ PDB for the Adana calcretes and 0.11‰ PDB for the Mersin calcretes. The depletion in the δ¹⁸O values is due to leaching soil water along pore channels, from or in which calcite forms by precipitation and displacive replacement processes. During the early stages of calcrete profile development, the nodular and tubular features form from the vertically leaching, relatively thin soil-water cover, reducing the permeability of rocks and sediments, in turn causing the development of sheet-like laminar calcrites on the impermeable horizon from laterally moving, relatively thick soil-water (Figure 7; Wright et al., 1988, 1995; Eren et al., 2008; Kaplan et al., 2014). This assumption is also supported by the existence of palygorskite in the samples of calcrete nodules and tubes, and its absence in the hard laminated crust. Palygorskite precipitation requires high pH values (pH » 9; Verrecchia and Le Coustumer, 1996; Bouza et al., 2007) or more evaporative conditions with respect to calcite (Eren et al., 2008, 2018; Kaplan et al., 2013, 2018). A slight difference is present between the average values of the hard laminated crust and nodular and/or tubular horizon regarding the δ¹⁳C values. This difference is 0.32‰ PDB for the Adana calcretes and 0.10‰ PDB for the Mersin calcretes. The hard laminated crust exhibits a depletion in the δ¹³C values related to proximity to the bioactive horizon in the soil (Gong et al., 2005). The nodular and/or tubular horizon develops below the bioactive soil horizon where water is leached vertically in a vadose zone from which calcite precipitates or replaces the host material, creating impermeable/water plugged conditions. This characterizes the early stage of the calcrete profile development in the region (Eren et al., 2008, 2018; Kaplan et al., 2013). The advanced stage most likely occurred over this nodular

| Data                        | Adana | Mersin |
|-----------------------------|-------|--------|
| *Mean annual temperature (°C)* | 18.9  | 19.1   |
| *Mean annual precipitation (mm)* | 646.6 | 634    |
| **Mean annual evaporation (mm)** | 1555.3 | 1262.2 |
| **Mean annual humidity (%)** | 65.54 | 60.78  |

* From 1927 to 2017; ** from 2007 to 2017.

---

**Table 3.** Climatic properties for Adana and Mersin provinces from the Turkish State Meteorological Service (https://www.mgm.gov.tr/).

---

Figure 7. Schematic presentation of the calcrete development exhibiting two major stages: (i) early stage characterized by calcrete mottling, and (ii) late stage characterized by lamination (modified from Eren et al., 2018).
and/or tubular horizon close to the bioactive soil horizon where the static soil water probably rested laterally over the impermeable column horizon. This consequently increased the residence time of water in the bioactive layer and most likely influenced the soil light carbon isotopes (Figure 7).

6. Conclusion
The oxygen and carbon isotopes of the calcretes in Adana and Mersin provinces indicate a pedogenic origin similar to calcretes in other parts of the world. The enrichment of $\delta^{18}O$ values of the calcretes in Adana province in respect to those in Mersin caused by the high evaporation rate in the Adana region is bound to higher ventilation of the land surface. The $\delta^{13}C$ values suggest that calcrete formation in the soil is associated with extensive C$_3$ vegetation similar to contemporary Mediterranean-type vegetation. Isotopic difference is also present between the hardpan and nodular and/or tubular/columnar horizon. The hardpan exhibits a slight depletion in the $\delta^{18}O$ and $\delta^{13}C$ values with respect to those of the nodular and/or tubular/columnar horizon. This is most likely due to the amount of leaching soil water from which calcretes form during the pedogenic processes, as well as the proximity to the bioactive soil layer.

References

Achyuthan H (2003). Petrologic analysis and geochemistry of the Late Neogene-Early Quaternary hardpan calcretes of western Rajasthan, India. Quaternary International 106-107: 3-10.

Achyuthan H, Quade J, Roe L, Placzek C (2007). Stable isotopic composition of pedogenic carbonates from the eastern margin of the Thar Desert, Rajasthan, India. Quaternary International 162-163: 50-60.

Achyuthan H, Shankar N, Braida M, Ahmad SM (2012). Geochemistry of calcretes (calcic palaeosols and hardpan), Coimbatore, Southern India: formation and paleoenvironment. Quaternary International 265: 155-169.

Alçiçek H, Alçiçek MC (2014). Palustrine carbonates and pedogenic calcretes in the Çal basin of SW Anatolia: implications for the Plio-Pleistocene regional climatic pattern in the eastern Mediterranean. Catena 112: 48-55.

Alonso-Zarza AM (2003). Palaeoenvironmental significance of palustrine carbonates and calcretes in the geological record. Earth Science Reviews 60: 261-298.

Alonso-Zarza AM, Arenas C (2004). Cenozoic calcretes from the Teruel Graben, Spain: microstructure, stable isotope geochemistry and environmental significance. Sedimentary Geology 167: 91-108.

Alonso-Zarza AM, Wright VP (2010). Calcretes. In: Alonso-Zarza AM, Tanner LH (editors). Carbonates in Continental Settings: Facies, Environment, and Processes. Developments in Sedimentology 61: 225-267.

Anand RR, Phang C, Wildman JE, Lintern MJ (1997). Genesis of some calcretes in the southern Yilgarn Craton, Western Australia: implications for mineral exploration. Australian Journal of Earth Sciences 44: 87-103.

Andrews JE, Singhvi AK, Kailath AJ, Kuhn R, Dennis PF et al. (1998). Do stable isotope data from calcrete record late Pleistocene Monsoonal climate variation in the Thar Desert of India? Quaternary Research 50: 240-251.

Atabey E, Atabey N, Kara H (1998). Sedimentology of caliche (calcrete) occurrences of the Kirşehir region. Bulletin of the Mineral Research and Exploration 120: 69-80.

Atalay İ (1996). Palaeosols as indicators of the climatic changes during the Quaternary period in S Anatolia. Journal of Arid Environments 32: 23-35.

Bajnóczi B, Horváth Z, Demény A, Mindszenty A (2006). Stable isotope geochemistry of calcrete nodules and septarian concretions in a Quaternary ”red clay” paleovertisol from Hungary. Isotopes in Environmental and Health Studies 42: 335-350.

Bar-Matthews M, Ayalon A, Gilmour M, Matthews A, Hawkesworth CJ (2003). Sea-land oxygen isotopic relationships from planktonic foraminifera and speleothems in the Eastern Mediterranean region and their implication for paleorainfall during interglacial intervals. Geochimica et Cosmochimica Acta 67: 3181-3199.

Bouza PJ, Simón M, Aguilar J, del Valle H, Rostagno M (2007). Fibrous-clay mineral formation and soil evolution in aridisols of northeastern Patagonia, Argentina. Geoderma 139: 38-50.

Candy I, Adamson K, Gallant CE, Whitfield E, Pope R (2012). Oxygen and carbon isotopic composition of Quaternary meteoric carbonates from western and southern Europe: their role in palaeoenvironmental reconstruction. Palaeogeography, Palaeoclimatology, Palaeoecology 326-328: 1-11.

Cerling TE (1984). The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth and Planetary Science Letters 71: 229-240.

Cerling TE, Quade J, Wang Y, Bowman JR (1989). Carbon isotopes in soils and paleosols as ecology and paleoecology indicators. Nature 341: 138-139.

Chiquet A, Colin F, Hamelin B, Michard A, Nahon D (2000). Chemical mass balance of calcrete genesis on the Toledo granite (Spain). Chemical Geology 170: 19-35.
Darbaş G, Nazik A, Temel A, Gürbüz K (2008). A paleoenvironmental test of the Messinian Salinity Crisis using Miocene-Pliocene clays in the Adana Basin, southern Turkey. Applied Clay Science 40: 108-118.

Dietzel M, Tang J, Leis A, Köhler SJ (2009). Oxygen isotopic fractionation during inorganic calcite precipitation – effects of temperature, precipitation rate and pH. Chemical Geology 268: 107-115.

Durand N, Gunnell Y, Curmi P, Ahmad SM (2006). Pathways of calcrete development on weathered silicate rocks in Tamil Nadu, India: mineralogy, chemistry and paleoenvironmental implications. Sedimentary Geology 192: 1-18.

Dworkin SI, Nordt L, Atchley S (2005). Determining terrestrial paleotemperatures using the oxygen isotopic composition of pedogenic carbonate. Earth and Planetary Science Letters 237: 56-68.

Elidrissi S, Daoudi L, Fagel N (2018). Palygorskite occurrences and genesis in the Al Haouz area, Central Morocco: characterization and environmental significance. Catena 149: 331-340.

Elidrissi S, Daoudi L, Fagel N (2017). Development of quaternary calcrete in the Tensift Al Haouz area, Central Morocco: characterization and environmental significance. Catena 149: 331-340.

Elidrissi S, Daoudi L, Fagel N (2018). Palygorskite occurrences and genesis in Calcisol and groundwater carbonates of the Tensift Al Haouz area, Central Morocco. Geoderma 316: 78-88.

Eren M (2007). Genesis of tepees in the Quaternary hardpan calcretes, Mersin, S Turkey. Carbonates Evaporites 22: 123-134.

Eren M (2011). Stable isotope geochemistry of Quaternary calcretes, Mersin, S Turkey. Earth and Planetary Science Letters 237: 1-18.

Eren M (1981). Quaternary pluvial and interpluvial conditions in Anatolia and environmental changes in south-central Anatolia since the last glaciation. In: Prey W, Uarpmann HP (editors). Contributions to the Environmental History of South Asia. Beihefte zum Tübinger Atlas des Vorderen Orients. Tübingen, Germany: University of Tübingen, pp. 101-109.

Erol O (1984). Neogene and Quaternary continental formation and their significance for soil formation. In: Proceedings of the 1st National Clay Symposium, Adana, Turkey, pp. 24-28 (in Turkish).

Friedman I, O’Neill JR (1977). Compilation of stable isotope factors of geochemical interest. In: Fleischer M (editor). Data of Geochemistry. Professional Paper 440-KK. Reston, VA, USA: United States Geological Survey, pp. 1-12.

Gallala W, Gaied ME, Essefi E, Montacer M (2010). Pleistocene calcretes from eastern Tunisia: the stratigraphy, the microstructure and the environmental significance. African Journal of Earth Sciences 58: 445-456.

Garcia-Romero E, Barrios MS, Revuelta MAB (2004). Characteristics of a Mg-palygorskite in Miocene rocks, Madrid Basin (Spain). Clays and Clay Minerals 52: 484-494.

Gong SY, Mi HS, Wei KY, Horng CS, You CF et al. (2005). Dry climate near the western Pacific warm pool: Pleistocene caliches of the Nansha Islands, South China Sea. Palaeogeography, Palaeoclimatology, Palaeoecology 226: 205-213.

Goudie AS (1973). Duricrusts in Tropical Landscapes. Oxford, UK: Clarendon Press.

Gürbüz K (1999). Regional implications of structural and eustatic controls in the evolution of submarine fans: an example from the Miocene Adana Basin, southern Turkey. Geological Magazine 136: 311-319.

Gürel A, Özcân S (2016). Paleosol and dolocrete associated clay mineral occurrences in siliciclastic red sediments of the Late Miocene Kömişini Formation of the Tuzgölü basin in central Turkey. Catena 143: 102-113.

Horn BLD, Pereira VP, Schultz CL (2013). Calcretes of the Santa Maria supersequence, Middle Triassic, Rio Grande do Sul, Brazil: classification, genesis and paleoclimatic implications. Palaeogeography, Palaeoclimatology, Palaeoecology 376: 39-47.

Kadir S, Eren M (2008). The occurrence and genesis of clay minerals associated with Quaternary caliches in the Mersin area, southern Turkey. Clays and Clay Minerals 56: 244-258.

Kadir S, Eren M, Atabay E (2010). Dolocretes and associated palygorskite occurrences in siliciclastic red mudstones of the Sariyer formation (Middle Miocene), southeastern side of the Çanakkale strait, Turkey. Clays and Clay Minerals 58: 205-219.

Kadir S, Eren M, Külah T, Erkoyun H, Huggett J et al. (2018). Genesis of palygorskite and calcretes in Pliocene Eskişehir Basin, west central Anatolia, Turkey. Catena 168: 62-78.

Kadir S, Eren M, Külah T, Önalgil N, Cesur M et al. (2014). Genesis of Late Miocene-Pliocene lacustrine palygorskite and calcretes from Kırşehir, central Anatolia, Turkey. Clay Minerals 49: 433-454.

Kaplan MY, Eren M, Kadir S, Kapur S (2013). Mineralogical, geochemical and isotopic characteristics of Quaternary calcretes in the Adana region, southern Turkey: implications on their origin. Catena 101: 164-177.

Kaplan MY, Eren M, Kadir S, Kapur S, Huggett J (2014). A microscopic approach to the pedogenic formation of palygorskite associated with Quaternary calcretes of the Adana area, southern Turkey. Turkish Journal of Earth Sciences 23: 559-574.

Kapur S, Çavuşgil VS, FitzPatrick EA (1987). Soil-calcrete (caliche) relationship on a Quaternary surface of the Cukurova Region, Adana (Turkey). In: Federoff N, Bresson LM, Courty MA (editors). Soil Micromorphology. Paris, France: Association Française pour L’Etude du sol, pp. 597-603.
Kapur S, Çavuşgil VS, Şenol M, Gurel N, FitzPatrick EA (1990). Geomorphology and pedogenic evolution of Quaternary calcretes in the northern Adana Basin of southern Turkey. Zeitschrift für Geomorphologie 34: 49-59.

Kapur S, Saydam C, Akça E, Çavuşgil VS, Karaman C et al. (2000). Carbonate pools in soil of the Mediterranean: a case study from Anatolia. In: Lal R, Kimble JM, Eswaran H, Stewart BA (editors). Global Climate Change and Pedogenic Carbonates. Boca Raton, FL, USA: Lewis Publishers, pp. 187-212.

Kapur S, Yaman S, Gökçen SL, Yetiş C (1993). Soil stratigraphy and Quaternary caliche in the Misis area of the Adana Basin, southern Turkey. Catena 20: 431-445.

Kaufman L, Rousseau RJ (2009). Finding Groups in Data: An Introduction to Cluster Analysis. Hoboken, NJ, USA: John Wiley & Sons.

Kelly M, Black S, Rowan JS (2000). A calcite-based U/Th chronology for landform evolution in the Sorbas basin, southeast Spain. Quaternary Science Reviews 19: 995-1010.

Klappa CF (1983). A process-response model for the formation of pedogenic calcretes. In: Wilson RCL (editor). Residual Deposits: Surface Related Weathering Processes and Materials. London, UK: Geological Society of London Special Publications, pp. 211-220.

Kovda I, Mora CI, Wilding LP (2006). Stable isotope compositions of pedogenic carbonates and soil organic matter in a temperate climate vertisol with gilgai, southern Russia. Geoderma 136: 423-435.

Küçükuysal C (2016). Late Pleistocene calcretes from central Anatolia (Lake Eymir and Mogan, Gölbasi Basin): comparison to Quaternary calcretes from Turkey. Journal of Earth Science 27: 874-882.

Küçükuysal C, Engin B, Türkmenoğlu AG, Aydaş C (2011). ESR dating of calcite nodules from Bala, Ankara (Turkey): preliminary results. Applied Radiation and Isotopes 69: 492-499.

Küçükuysal C, Kapur S (2014). Mineralogical, geochemical and micromorphological evaluation of the Plio-Quaternary paleosols and calcretes from Karahamzalı, Ankara (central Turkey). Geologica Carpathica 65: 241-253.

Küçükuysal C, Türkmenoğlu AG, Kapur S (2013). Multi-proxy evidence of Mid-Pleistocene dry climates observed in calcretes in central Turkey. Turkish Journal of Earth Sciences 22: 463-483.

Lee YI (1999). Stable isotopic composition of calcic paleosols of the Early Cretaceous Hasandong Formation, southeastern Korea. Palaeogeography, Palaeoclimatology, Palaeoecology 150: 123-133.

Leone G, Bonadonna F, Zanchetta G (2000). Stable isotope record in Mollusca and pedogenic carbonate from Late Pliocene soils of Central Italy. Palaeogeography, Palaeoclimatology, Palaeoecology 163: 115-131.

Mann AW, Horwitz RC (1979). Groundwater calcrete deposits in Australia some observations from Western Australia. Journal of the Geological Society of Australia 26: 293-303.

McDermott F (2004). Palaeo-climate reconstruction from stable isotope variations in speleothems: a review. Quaternary Science Reviews 23: 901-918.

Meléndez A, Alonso-Zarza AM, Sancho C (2011). Multi-storey calcrete profiles developed during the initial stages of the configuration of the Ebro Basin’s exorheic fluvial network. Geomorphology 134: 232-248.

Mortazavi M, Moussavi-Harami R, Brenner RL, Mahboubi A, Nadjafi M (2013). Stable isotope record in pedogenic carbonates in northeast Iran: implications for Early Cretaceous (Berriasian–Barremian) paleovegetation and paleoatmospheric P(CO₂) levels. Geoderma 211-212: 85-97.

Nash DJ, McLaren SJ (2003). Kalahari valley calcretes: their nature, origins, and environmental significance. Quaternary International 111: 3-22.

Özer AM, Wieser A, Göksu HY, Müller P, Regulla DF et al. (1989). ESR and TL age determination of caliche nodules. International Journal of Radiation Applications and Instrumentation Part A 40: 1159-1162.

Purvis K, Wright VP (1991). Calcretes related to phreatophytic vegetation from the Middle Triassic Otter Sandstone of south west England. Sedimentology 38: 539-551.

Salomons W, Goudie A, Mook WG (1978). Isotopic composition of calcite deposits from Europe, Africa and India. Earth Surface Processes 3: 43-57.

Schmidt GC (1961). Stratigraphic nomenclature for the Adana region petroleum district VII. Petroleum Administration Bulletin 6: 47-63.

Shankar N, Achyuthan H (2007). Genesis of calcic and petrocalcic horizons from Coimbatore, Tamil Nadu: micromorphology and geochemical studies. Quaternary International 175: 140-154.

Silva ML, Batezelli A, Ladeira FSB (2018). Genesis and paleoclimatic significance of palygorskite in the cretaceous paleosols of the Bauru Basin, Brazil. Catena 168: 110-128.

Singh BP, Lee YI, Pawar JS, Charak RS (2007). Biogenic features in calcrites developed on mudstone: examples from Paleogene sequences of the Himalaya, India. Sedimentary Geology 201: 49-156.

Srivistava P (2001). Paleoclimatic implications of pedogenic carbonates in Holocene soils of the Gangetic plains, India. Palaeogeography, Palaeoclimatology, Palaeoecology 172: 207-222.

Strong GE, Giles JRA, Wright VP (1992). A Holocene calcrete from North Yorkshire, England: implications for interpreting palaeclimates using calcrites. Sedimentology 39: 333-347.
Talbot MR, Kelts K (1990). Paleolimnological signatures from carbon and oxygen isotopic ratios in carbonates from organic carbon-rich lacustrine sediments. In: Katz BJ (editor). Lacustrine Basin Exploration: Case Studies and Modern Analogs. Tulsa, OK, USA: American Association of Petroleum Geologists, pp. 88-112.

Talma AS, Netterberg F (1983). Stable isotope abundances in calcretes. In: Wilson RCL (editor). Residual Deposits: Surface Related Weathering Processes and Materials. London, UK: Geological Society of London Special Publications, pp. 221-233.

Tanner LH (2010). Continental carbonates as indicators of paleoclimate. Developments in Sedimentology 62: 179-214.

Verrecchia EP, Le Coustumer MN (1996). Occurrence and genesis of palygorskite and associated clay minerals in a Pleistocene calcrete complex, Sde Boqer, Negev desert, Israel. Clay Minerals 31: 183-202.

Wang Y, Nahon D, Merino E (1994). Dynamic model of the genesis of calcretes replacing silicate rocks in semi-arid regions. Geochimica et Cosmochimica Acta 58: 5131-5145.

Ward JH (1963). Hierarchical grouping to optimize an objective function. Journal of American Statistical Association 69: 236-244.

Wright VP, Platt NH, Marriott SB, Beck VH (1995). A classification of rhizogenic (root-formed) calcretes, with examples from the Upper Jurassic–Lower Cretaceous of Spain and Upper Cretaceous of southern France. Sedimentary Geology 100: 143-158.

Wright VP, Platt NH, Wimbledon WA (1988). Biogenic laminar calcretes: evidence of calcified root-mat horizons in paleosols. Sedimentology 35: 603-620.

Wright VP, Tucker ME (1991). Calcretes. Oxford, UK: Blackwell Scientific Publications.

Yağış MN, Göürür N (1983). Sedimentological evolution of the Adana Basin. In: Tekeli O, Göncüoğlu MC (editors). Geology of the Taurus Belt. Proceedings of International Tauride Symposium. Ankara, Turkey: Mineral Research and Exploration Institute of Turkey (MTA) Publications, pp. 165-172.

Yetiş C (1988). Reorganization of the Tertiary stratigraphy in the Adana Basin, southern Turkey. Newsletters on Stratigraphy 20: 43-58.

Yetiş C, Kelling G, Gökçen SL, Baroz F (1995). A revised stratigraphic framework for later Cenozoic sequences in the northeastern Mediterranean region. Geologische Rundschau 84: 794-812.

Zamanian K, Pustovoytov K, Kuzyakov Y (2016). Pedogenic carbonates: Forms and formation processes. Earth Science Reviews 157: 1-17.

Zhou J, Chaletz HS (2009). Biogenic caliches in Texas: the role of organisms and effect of climate. Sedimentary Geology 222: 207-225.