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Mechanism of calcrete formation in the Lower Cretaceous (Neocomian) fluvial deposits, northeastern Iran based on petrographic, geochemical data

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ABSTRACT

The Kopet-Dagh basin of northeastern Iran was formed during the Middle Triassic orogeny. From Jurassic through Miocene time, sedimentation was relatively continuous in this basin. The Shurijeh Formation (Neocomian), which consists of red bed siliciclastic sediments that were deposited in fluvial depositional settings, crops out in the southeastern part of the Kopet-Dagh basin. In addition to clastic lithofacies, non-clastic facies in the form of calcrete paleosols, were identified in this formation. The calcrete host rocks are mainly sandstone, pebbly sandstone. The calcrete in middle unit in the Shurijeh Formation consists of, from bottom to top: incipient calcrete, nodular calcrete, massive calcrete horizons. The maturity pattern of these calcrete gradationally increases from bottom to top in this unit. Lack of organo-sedimentary structure (mainly plant roots), diversity of calcite fabric, suggest that the studied calcretes have a multi-phase development: a short vadose phase followed by a long phreatic phase. These calcretes are neither pedogenic nor groundwater calcretes. Petrographic studies show that they are composed of micritic textures with a variety of calcite fabrics, microsparitic/sparitic veins, displacive, replacive fabrics, quartz, hematite grains. Cathodoluminescence images, trace elemental analysis (Fe, Mn increased, Na, Sr decreased) of calcrete samples show the effects of meteoric waters during the calcrete formation when water tables were variable. In this study, we conclude that evaporation, degassing of carbon dioxide are the two main factors in the formation of non-pedogenic or groundwater calcrete. The sources of carbonate were probably parent materials, surface waters, ground waters, eolian dusts, numerous outcrops of limestones that have been exposed in the source area during Neocomian time.

1. Introduction

Paleosols can provide information about climate, sedimentation rate, evolution patterns of flood plains in fluvial systems, have been considered by geologists, geochemists for a long time (Miall, 1996; De La Horra et al., 2008). Paleosols have been identified on the basis of color, texture, mineralogy (Duchaufour, 1982; Wright and Tucker, 1991; Miall, 1996; Wright and Marriott, 1996; Khadkikar, 2005; Therrien, 2005; De La Horra et al., 2008). Calcrete, calcic soil are common features of arid, semi-arid, sub-humid landscapes wherein they form either within the soil profile or through evaporative precipitation from groundwater in phreatic, capillary-fringe zones (Alonso-Zarza, 2003; Huerta and Armenteros, 2005; Khadkikar, 2005; Schmid et al., 2006; Durand et al., 2007; Khalaf, 2007). These materials are also referred to caliche, nari, kunkar, etc. (Goudie, 1983). Calcrete development is mainly controlled by three factors: the nature of host sediment, availability of carbonate-rich solution, climatic conditions. The suitable climate for calcrete formation is enough precipitation for translocation of carbonate, temperatures that facilitate a high evaporation rate (Khalaf, 2007). However, calcrete usually develops during arid to semi-arid intervals that follow humid climatic intervals. Calcrete is commonly developed within the vadose zone; however, its formation within the phreatic zone is not uncommon. Vadose or pedogenic calcrete is predominantly rhizoconcretionary (Khalaf, 2007). While phreatic or groundwater calcrete occurs as thin sheets formed by precipitation of carbonate from the laterally moving solution within the zone of capillary rise just above the water table (Miall, 1996; Pimentel et al., 1996). However, most calcrete profiles are polygenetic, where different processes may act during their evolution leading to fabric transformation, facies superimposition (Durand et al., 2007; Khalaf, 2007).

Accumulations of calcium carbonate in soils, weathering profiles are particularly widespread in arid, semi-arid regions receiving rainfall between 400, 600 mm/yr, both on calcareous, non-

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calcareous rocks (Goudie, 1983; Wright and Tucker, 1991). Given that calcium carbonate accumulation requires sufficiently wet conditions for the release of calcium from primary minerals but also sufficiently dry conditions to ensure subsequent precipitation of CaCO3 one would expect that the conditions leading to the weathering of rocks, those leading to the precipitation of CaCO3 are best fulfilled by semi-arid conditions as these involve seasonal alternations of rainfall, drought (Wang et al., 1994; Durand et al., 2007).

This study investigated the mode of occurrence, textural, mineralogical characteristics of calcretes hosted within the Lower Cretaceous fluviatile sequence in northeastern Iran. The role of movements, characteristics of groundwaters in the formation of these paleosols, influence of meteoric waters in calcrete occurrence are discussed.

2. Geological setting

The Kopet-Dagh is an intracontinental basin located in northeastern Iran. This basin formed after the closure of the Hercynian Ocean following the Middle Triassic Orogeny (Berberian and King, 1981; Ruttner, 1993; Alavi et al., 1997). From the Jurassic through the Miocene time, relatively continuous sedimentation recorded by five major transgressive-regressive sequences that took place in the eastern Kopet-Dagh basin (Moussavi-Harami and Brenner, 1992). The study area is located in the southeastern part of this basin between 35° 44′, 36° 48′ N, 60°13′, 60° 17′ E. In this part of the Kopet-Dagh basin, climate varies from arid to semi-arid conditions, means annual precipitation is 39 mm/yr. The Lower Cretaceous red beds of the Shurijeh Formation crop out within a northwest-southeast plunging syncline (Fig. 1). These siliciclastic rocks have been deposited in a variety of fluvial depositional systems through most part of the Neocomian Time (Moussavi-Harami, 1986; Moussavi-Harami and Brenner, 1990; Moussavi-Harami and Brenner, 1993).

2.1. Shurijeh Formation

In this study, three sections of Shurijeh Formation were measured at Senjedak, Razmgah-e-Paein, Gargesh (Fig. 1). Thicknesses of formation in these sections are 165, 166, 310 meters, respectively. In this region, the Shurijeh Formation overlies the Kashafrud Formation with fault-related, gradational contacts with Tirgan Formation at the top (Fig. 2). The Shurijeh Formation is composed of a lower conglomeratic unit, a middle sandstone unit, an upper conglomeratic-sandstone unit. A few layers of mudstone, calcrete nodules, horizons have been observed in the middle unit.

Based on texture, sedimentary structures, three clastic lithofacies including gravely (Gcm, Gp, Gh), sandy (Sm, Sp, St, Sh), muddy (Fm), one nonclastic facies paleosol (P) have been identified. On the basis of facies changes, unimodal sedimentary structures (planar, trough cross-bedding), presence of fining-upward cycles, their lower erosional contacts, siliciclastic sediments of Shurijeh Formation have been interpreted to be deposited in fluvial depositional systems (Moussavi-Harami and Brenner, 1990). Thick gravely, sandy facies, absence of lateral accretion beds, low frequency of fine grain flood plain deposits, paleocurrent analysis suggest that deposition may have taken place in low sinuosity proximal channels (e.g. Huerta and Armenteros, 2005). Therefore, Neocomian siliciclastic rocks can be deposited in proximal braided rivers with gravely bed load (Fig. 3). Paleocurrent analysis is shown that this river has been flowed toward the northwest of the study area during the Neocomian Time.

Petrographic data (mineralogical composition), field studies, paleocurrent analysis, regional geology indicate that the source area for these siliciclastic sediments was probably the paleotethys rocks that are cropped out in southeast of the study area (Moussavi-Harami and Brenner, 1990).

Diagenetic processes operated on the siliciclastic sediments of the Shurijeh Formation are compaction (physical, chemical), cementation (iron oxide, calcite, silica), dolomitization, alteration, dissolution, fracturing. Our study shows that these processes have taken place during three stages: eogenesis, mesogenesis, telogenesis.

3. Material, methods

We used a database of 150 samples collected from three measured stratigraphic sections through the Shurijeh Formation (Fig. 4). Thin sections were stained with an Alizarin Red S, Potassium Ferricyanide mixture (Dickson, 1966) to differentiate nonferroan from ferroan calcite. 45 polished thin sections with

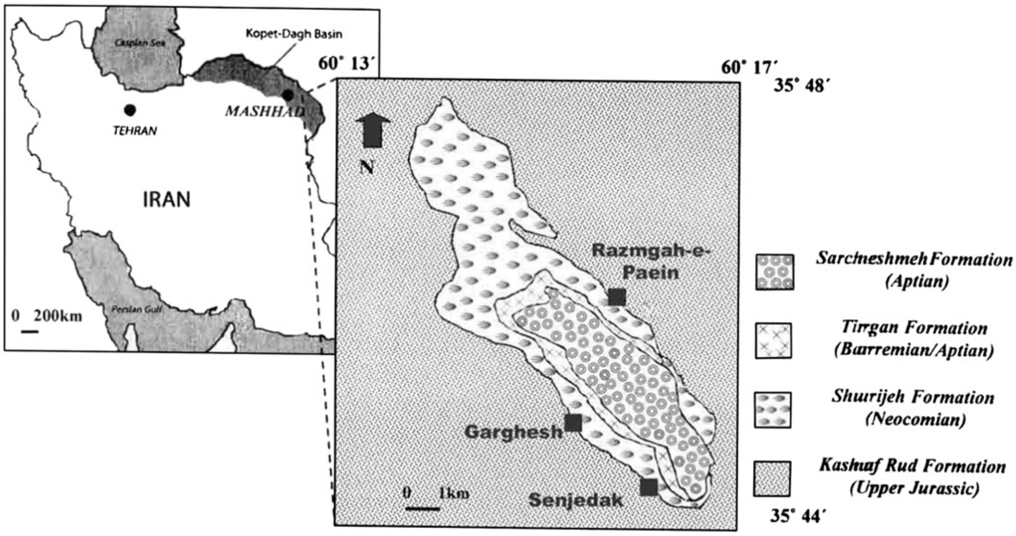

Fig. 1. Simplified geological map of the study area in NE Iran; inset box shows the location of measured stratigraphic sections: Senjedak; Razmgah-e-Paein; Garghesh (modified from Ghaemi and Hosseini, 1999).

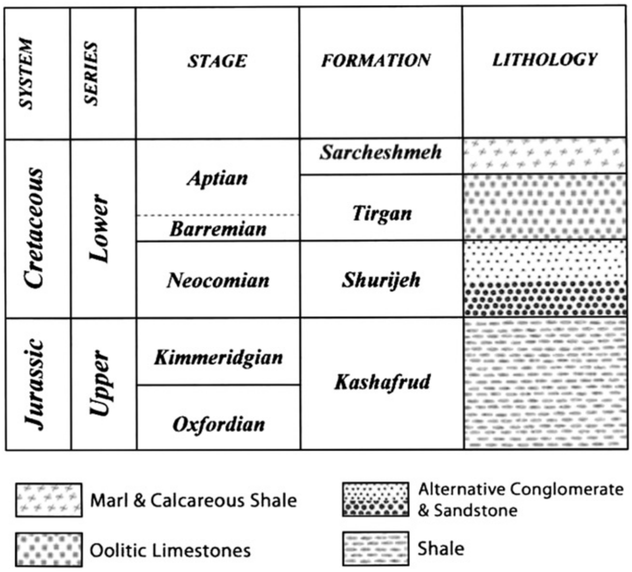

Fig. 2. General stratigraphic column of Lower Cretaceous strata in the southeast Kopet-Dagh basin, NE Iran (modified from Kalantary, 1987).

thicknesses of 80–100 μm were studied by cathodoluminescence microscopy. Cathodoluminescence studies were performed using a Technosyn Cold Cl (Model 8200 Mk3) at 12 KV, 160–195 μA with an automatic camera. In addition, 15 samples of calcretes were analyzed by Atomic Absorption Spectrophotometry to determine their Ca, Mg, Sr, Na, Mn, Fe contents (e.g. Winefield et al., 1996). Elemental analysis carried out using a Shimatzu AA-670/670G in Geochemistry Lab at the Ferdowsi University of Mashhad.

4. Results

4.1. *Mode of calcrete occurrence*

4.1.1. *Host rocks*

Microscopic investigation supported by lithofacies analysis of host rocks (Fig. 5) indicated the occurrence of two textural classes. They are medium to coarse grain sandstones (Fig. 6a), pebbly sandstones (Fig. 6b). These sandstones are commonly massive with no obvious macroscopic pedogenic features. They are composed of moderately to poorly-sorted siliciclastic framework grains bounded by or floating in carbonate cement. The framework grains are mainly represented by quartz (monocrystalline, polycrystalline), feldspars, chert rock fragments.

4.2. *Macroscopic features of calcretes*

4.2.1. *Incipient calcrete*

Description: This type of calcrete (calcareous patches) is usually seen in the medium grain sandstones of middle unit of the Shurijeh Formation. The shape of these calcareous patches are subhydral to unhydral, their size varies from <1 to >10 cm. Color of incipient calcretes is pale yellow (5Y 9/2), their distribution in the lower part of middle unit are more than other parts. There are no fossil root traces in these paleosols.

Interpretation: This type of calcrete represents the very early stage of calcretization, where calcite is precipitated within the intergranular pores of the matrix of host sediment (Fig. 6c), forming a pale yellow calcareous patches that grew in size by displacing, then replacing the matrix material (Fig. 6d). Calcite precipitation resulted from evaporation or degassing of CO_2 (e.g. Khadkikar et al., 2000).

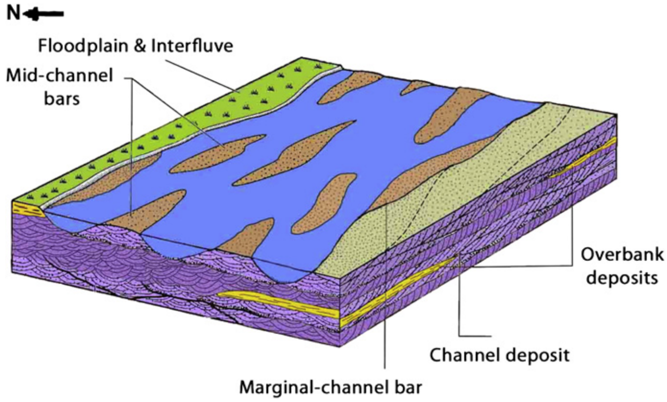

Fig. 3. Schematic diagram showing depositional model of Shurijeh Formation.

4.2.2. *Nodular calcrete*

Description: Nodular calcrete is composed of abundant hard, dense calcrete nodules scattered in the host rock, mostly in the red massive medium-grained sandstones. Calcrete nodules are cream (5Y 7/2) in color, range in size from 3 to 40 cm (Fig. 6e). These calcretes are spheroidal to elliptical in shape. Frequency of nodules in the middle unit decreases upward. No apparent orientation of nodules was observed.

Interpretation: This type of calcrete represents an early stage of calcretization, where authigenic calcite partially replaced some of the siliciclastic framework grains. However, calcite nodule formation can be largely dependent on evaporation processes and/or microenvironmental changes in pH, CO2 partial pressure (e.g. Achyuthan et al., 2007).

4.2.3. *Massive calcrete horizons*

Description: The color of massive calcrete horizons is changed from pale yellow (5y 5/2) to pale gray (5G 8/2.5) with brown- red mottles (10R 4/6) in the various sections (Fig. 6g,h). These calcretes commonly are found in the upper part of middle unit of the Shurijeh Formation. Thickness of the horizons is changed from 20 to 50 cm. Despite some of the horizons are continuous part of them is not extended. A massive mudstone layer covered the calcrete horizons, their host rocks. Plant traces were not found anywhere in massive calcrete horizons.

Interpretation: Color of calcrete horizons may confirm relative Fe, Mn concentrations in matrix that in most cases are controlled by palaeoclimate, palaeoenvironmental conditions (Atchley et al., 2004). Duchaufour (1982) believed that gray soils are formed near the water table, under reduced conditions. Brown to red mottles is created by Fe transfer in soil profiles while alternation of reduction-oxidation conditions shows water table fluctuations (e.g. Vepraskas and Wilding, 1994). This type of calcrete is generally formed as a massive calcite groundmass with scattered poorly sorted quartz grains. The distribution pattern of quartz grains indicates that calcretization is responsible for complete replacement of the host sediment matrix, displacement, partial replacement of framework grains. The calcitic groundmass does not have a uniform texture (e.g. Durand et al., 2007).

4.3. *Microscopic features of calcretes*

The calcretes of the Shurijeh Formation are shown various microscopic features. These microfabrics have been described individually, their genesis explained below.

4.3.1. *Micritic textures*

Dense accumulations of equal microcrystalline calcite <4 μm are observed in most thin sections. The micrite is most commonly light

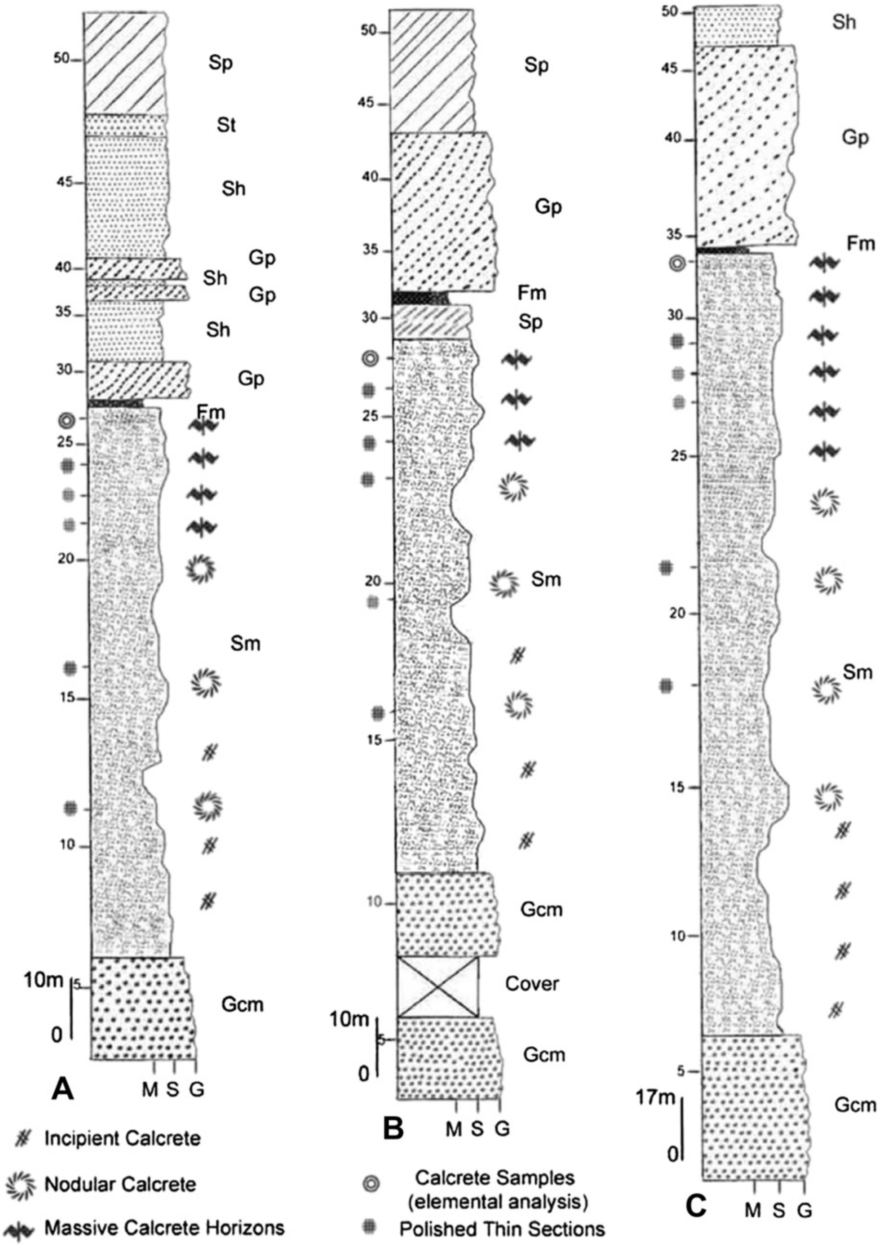

Fig. 4. Lithofacies, position of calcretes for Shurijeh Formation. A, Senjedak, B, Razmgah-e-Paein, C, Garghesh.

brown in color. In some places, microsparitic growth was common, these occur as irregularly distributed patches. The micrite is subhydral to anhydral, in some samples forms the bulk of the thin section. This microfabric has been reported from other parts of the world in both Pleistocene, ancient calcretes (Khadkikar, 2005). The micritic texture forms through the simultaneous growth of closely spaced nuclei or crystallites, which in turn depends on the super saturation threshold. The predominance of micrite may be due to rapid carbon dioxide degassing mediated through evaporative processes (Fig. 7A, B).

4.3.2. *Calcite cement fabrics*

Calcite cement fabrics including granular, drusy mosaic, blocky cements are the most abundant fabrics observed in the Shurijeh Formation (Fig. 7A, B, C). Crystal size of drusy calcite varies from 0.04 to 0.2 mm at the margin of micritic textures. Maximum size of drusy calcite crystals is 0.9 mm. The blocky calcite crystals range between 0.5 to 0.7 mm in diameter. Different calcite fabrics are light red color in stained thin sections, showing the lack of Fe in the calcite structure (Fig. 7D). These calcrete samples may also contain hematite (e.g. Jimenez-Espinosa and Jimeneze-Millan, 2003). No plant fragments are seen in these samples. Calcite cements form after the passage of meteoric waters through the sediment by evaporation, carbon dioxide degassing.

4.3.3. *Microsparitic/sparitic veins*

Veins of calcite cut across randomly in all thin sections. These veins are filled with sparite or microsparitie, are directly linked with the width of the veins (Fig. 7A, D) (e.g. Khadkikar et al., 2000). The sparitic/microsparitic veins appear to be shrinkage planes that have subsequently been cemented by the pore-filling sparite, microsparite. Through successive wet-dry cycles, shrinkage cracks are formed which ultimately caused spar/microspar filled veins (e.g. Khadkikar et al., 2000).

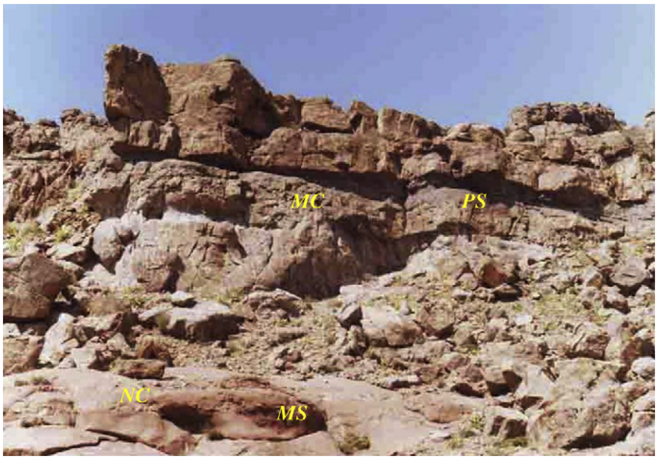

Fig. 5. Field photo of host rocks of calcretes within the Shurijeh Formation: (MS) medium to coarse grain sandstone, (PS) pebbly sandstone, (MC) massive calcrete horizons, (NC) nodular calcretes.

4.3.4. *Displacive, replacive fabrics*

Most siliciclastic grains show evidence of etching on their margins. Some siliciclastics contain a network of calcite veins cutting across the mineral grain (Fig. 6b). Due to undersaturation of the pore fluids with respect to silica, the interaction of such waters with grains causes dissolution. Evaporative processes resulted in displacive growth in the vadose zone. This mechanism began with the withdrawal of pore waters from grain surfaces, segregation within intergranular boundaries along cleavage planes, intergrain contacts (Khadkikar et al., 2000).

Although the three types of calcrete have similar mineralogical composition, significant differences in relative abundance of authigenic calcite, detrital minerals were recognized. These differences reflect the magnitude of calcretization. The average relative abundance of the siliciclastic components decreases from 77% in the incipient calcrete to 45% in the nodular calcrete, 20% in the massive calcrete horizons, while that of authigenic calcite increases from 23% in incipient calcrete to 55% in the nodular calcrete, 80% in the massive calcrete horizons.

4.4. *Geochemical analysis*

4.4.1. *Cathodoluminescence studies of calcretes*

Cathodoluminescence studies of calcrete samples of the Shurijeh Formation revealed distinct zoning (Fig. 7F, H). CL zoning consists of non-luminescent (dark), slightly luminescent (dull) to strongly luminescent (bright) black-to-ochre-to-yellow bands that indicate different reduction-oxidation conditions, reflecting changes in water chemistry (variations of Fe, Mn values) during formation of calcite crystals (e.g. Wilson & Evans, 2002). These characteristics have also been used by De Boever et al. (2006) to interpret the calcite formation under meteoric water influence.

Calcrete samples contain several stages of cementation, may be interpreted as having formed within the fluctuating Eh-pH conditions of a vadose meteoric-to-shallow phreatic zone. Each non-luminescent crystal would have nucleated under relatively oxidizing conditions of the vadose zone. During the early stages (vadose zone), meteoric waters were mostly in oxidizing conditions where Fe, Mn were precipitated, could not be incorporated into the calcite structure. The brightly luminescent rims were formed either during shallow burial or alternately during a rise in the water table, either of which would have created more reducing conditions within a transition to the shallow phreatic zone. Either progressive burial or rising groundwater table, created even more reducing conditions, in which the next stage of brightly luminescent cements formed. This was probably followed by cementation in a more oxidizing setting, caused during a drying out phase, a relative groundwater table fall during which less-luminescent spars were formed. The final stage of brightly luminescent cements may have formed in the phreatic zone. Under reducing conditions, Fe, Mn could have been incorporated into calcite crystals (Parcerisa et al., 2006). Therefore, the Fe/Mn ratio, absolute values of these elements could have controlled the luminescence of carbonate minerals (Shaaban, 2004). As mentioned above, in pedogenic environments in the study area, changes of water table could have been produced reduction, oxidation conditions as calcite crystals formed in varying hydro-chemical environments (e.g. Williams and Krause, 1998). These kinds of studies have been undertaken primarily on marine limestone but in recent decades they are being applied to calcareous paleosols as well (Retallack, 1991).

4.4.2. *Elemental analysis of calcretes*

Sediment geochemistry reflects source area (provenance), chemical weathering, hydraulic sorting, reduction-oxidation conditions; Therefore, calcrete geochemistry produces useful information about physicochemical conditions of soil where the calcretes were formed (Khadkikar, 2005). Shurijeh Formation samples were subjected to elemental analyses to support petrographic studies in the evaluation of the mechanism of the formation of calcretes (samples of massive calcrete horizons are analyzed).

4.4.2.1. Elemental data. Trace elemental data (Ca, Mg, Fe, Mn, Na, Sr) are presented in Table 1. Calcrete samples have relatively high concentrations of Mg (0.209 to 0.428 wt%, mean: 0.273 wt%), Na (0.063 to 0.428 wt%, mean: 0.084 wt%), Mn (0.053 to 0.113 wt%, mean: 0.095 wt%), Fe (0.133 to 0.199 wt%, mean: 0.161 wt%), relatively low concentrations of Sr (0.024 to 0.035 wt%, mean: 0.029 wt%). The weight percent of Ca in these samples indicate that Insoluble Residue (IR) values of these calcrete samples are less than 5 percent.

4.4.2.2. Interpretation. The chemical composition of carbonate minerals reflect the physicochemical conditions of depositional environments, diagenetic features, therefore elemental data can be used to interpret the nature, history of various processes (Mahboubi et al., 2002). During the early stage, weathering that released different ions into the water often controlled compositions of meteoric water. Climatic changes, vegetation cover, mean annual rainfall, soil temperature control paleosols composition. Generally, control of meteoric water composition performs by allogenic (climatic changes), authigenic (variations of soil temperature, CO2 pressure of soil, weathering rate) factors that occur at regional, local scales (Khadkikar, 2005).

There is a relation between calcite microfabrics, Mg content of paleosol. The main factors that controlled the Mg content in calcite are the rate of crystal growth, solution composition, temperature (Folk, 1974). Variations in Mg values can produce calcite crystals with various fabrics (Khalifa, 2005). During dry periods that are related to either high evaporation rates or rapid CO2 degassing, Mg concentration in meteoric waters increases (Khadkikar et al., 2000). The presence of Mg ions minimizes the size of the calcite crystals, the absence of Mg ions maximizes the size of calcite crystals (Folk, 1974). Micritic textures are formed when meteoric waters get enriched with respect to Mg. Rapid degassing which resulted in high degrees of supersaturation may have driven these crystal types precipitations. Then, at the next stage, when the water table rises, fresh water is capable of leaching Mg ions from calcite crystals

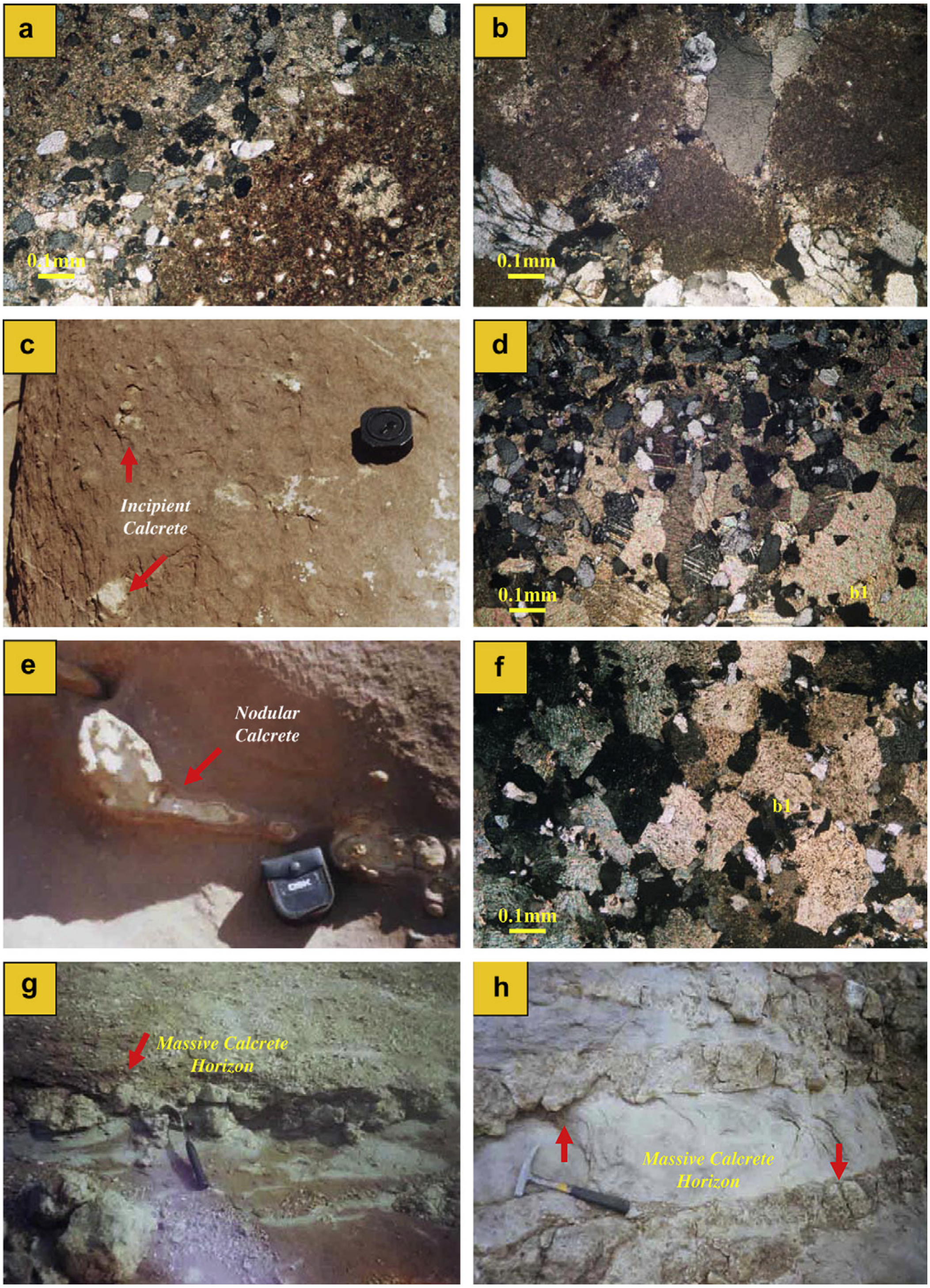

Fig. 6. Field photos, photomicrographs of the calcrete types of the Shurijeh Formation, and their host rocks: a, medium to coarse grain sandstone host rocks; b, pebbly sandstone host rocks, displacive, replacive fabrics (D) can be seen in quartz grains; c, incipient calcrete, d, quartz grains, blocky calcite cement in incipient calcrete; e, nodular calcrete, f, blocky calcite fabric in nodular calcrete with quartz grains; g-h, massive calcrete horizons.

as shown by the coarser calcite grains occurring near micritic textures, granular crystals (e.g. Khadkikar et al., 2000; Khalifa, 2005).

Sr concentration in meteoric waters is typically very low, but during evaporative concentration or rapid crystallization, which again is related to either high evaporation rates or rapid CO2 degassing, Sr values in meteoric waters may increased (Khadkikar et al., 2000). Sr contents of the studied samples were very low (maximum 0.035 wt%) that are specified meteoric water influence. Generally, Na, Sr have low concentrations in the meteoric waters (Veizer, 1983) that led to decreasing these elemental values in calcretes but with water table rise, by increasing of groundwater amounts, Fe, Mn contents were increased in calcrete samples (Brand and Veizer, 1980).

Scattered plots of the studied samples (Fe-Sr, Mg-Fe, Na-Fe, Mg-Mn, Na-Mn, Na-Sr, Sr-Mn, Fe-Mn trends) are shown in Fig. 8. Mg-Fe,

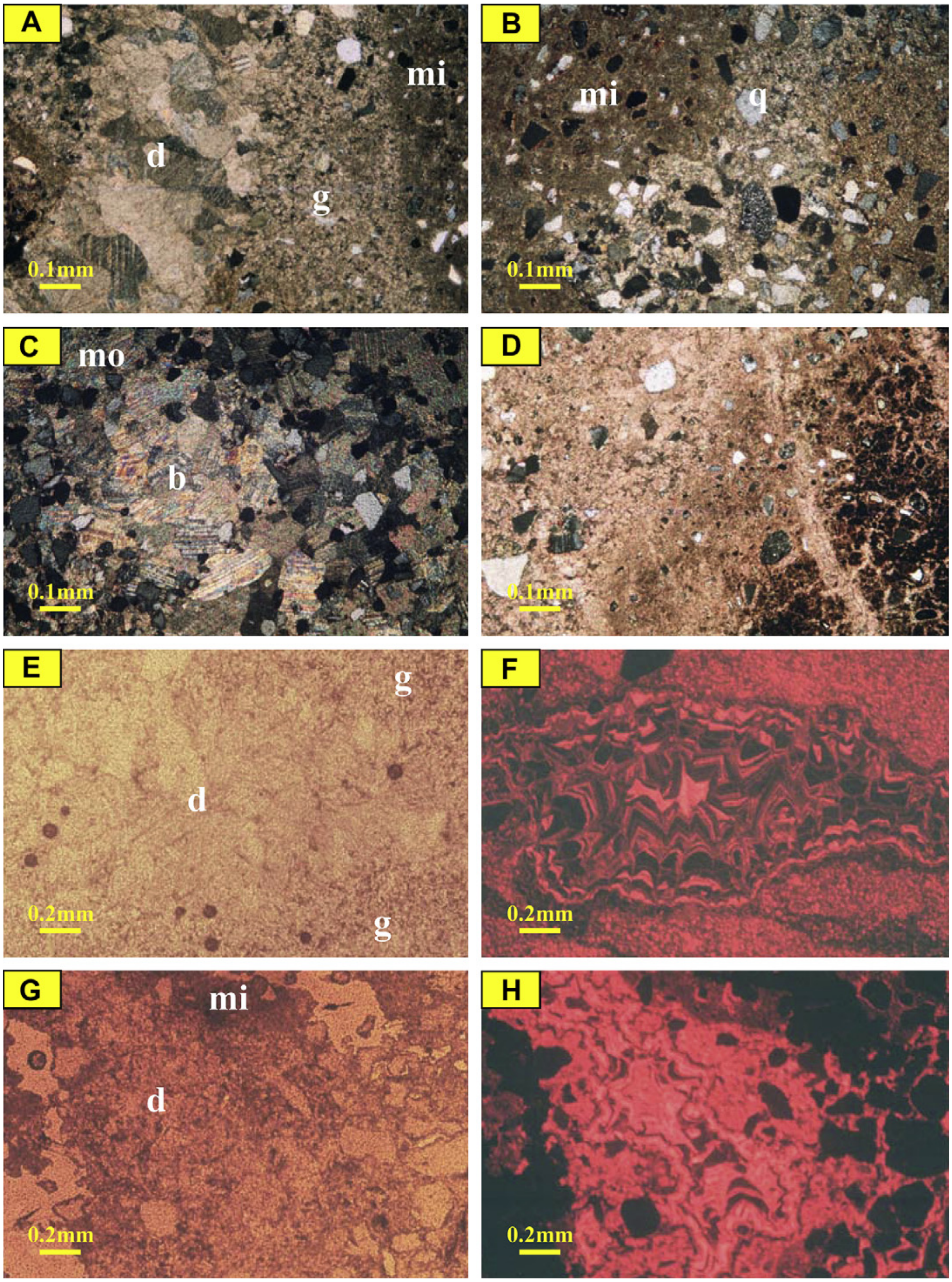

Fig. 7. Photomicrographs (polarized, cathodoluminescence) of various calcite fabrics, other components of paleosols in the Shurijeh Formation. A, Massive calcrete horizon that contains granular (g), drusy mosaic crystals (d), micritic textures (mi) in XPL. B, calcrete with micritic textures (mi), quartz grains (q) (XPL). C, Mosaic (mo), blocky (b) calcite in calcrete (XPL). D, Samples of massive calcrete horizon are stained with Alizarin Red S, Potassium Ferricyanide mixture that are became light red in color, this order of color are confirmed lack of Fe in calcite structure (XPL). E, Granular (g), drusy mosaic (d) calcite (PPL), F, The same view with CL, zoning (dark, bright luminescence) indicates reduction-oxidation conditions during crystal precipitation, G, Micritic textures (mi), drusy mosaic (d) of calcite in paleosol horizons (PPL), H, Same view under CL, variations of luminescence are resulted from changes in water chemistry (Fe, Mn values).

Mg-Mn, Na-Mn, Na-Fe, Sr-Mn, Fe-Sr trends are not directly shown by the compositions of meteoric waters that were introduced by Winefield et al. (1996), whereas detail attention to elemental values reveal that there are two data classes. The first data group that includes calcrete sample numbers of F3-1 to F3-5, that were collected from the Razmgah-e-paein section, are different from the second data group which are calcrete samples collected from the Senjedak, Garghesh sections (samples F1-1 to F2-5). These two groups reveal different phases of calcrete formation (vadose, phreatic samples). As mentioned above, at the early stage (vadose zone), weathering, evaporation, degassing (especially with water table fall during dry periods) are controlled meteoric water elemental composition. Therefore, it is expected that Mg, Na, Sr values in first data group are higher than second data group. The

Table 1
Elemental analysis of paleosol samples from the Shurijeh Formation

Sample Number	Ca Wt%	Mg Wt%	Na Wt%	Sr Wt%	Mn Wt%	Fe Wt%
F1-1	38.34	0.282	0.180	0.034	0.089	0.270
F1-2	36.97	0.279	0.063	0.030	0.071	0.345
F1-3	36.77	0.250	0.102	0.030	0.097	0.311
F1-4	36.12	0.244	0.110	0.023	0.098	0.283
F1-5	37.00	0.276	0.108	0.026	0.097	0.266
F2-1	37.08	0.209	0.082	0.028	0.113	0.333
F2-2	36.85	0.255	0.110	0.034	0.106	0.271
F2-3	36.15	0.264	0.104	0.018	0.087	0.275
F2-4	37.19	0.264	0.114	0.029	0.088	0.185
F2-5	38.09	0.261	0.117	0.030	0.102	0.199
F3-1	36.03	0.413	0.184	0.024	0.057	0.315
F3-2	36.53	0.392	0.224	0.035	0.053	0.331
F3-3	36.00	0.428	0.240	0.029	0.057	0.371
F3-4	37.18	0.411	0.428	0.033	0.053	0.354
F3-5	34.28	0.373	0.260	0.026	0.059	0.350

Mn, Fe contents of first group should be low but the value of Fe is higher than other group that is probably related to high Fe contents in parent materials (silicate minerals) that released high amounts of Fe during weathering processes. As groundwater supply increased, the water table rose, reducing conditions were established; therefore Mn, Fe values of second data group are higher. Due to low evaporation rates, degassing, Mg, Na, Sr contents were decreased in these samples. Calcrete samples of second group reflect the phreatic phase during the time of calcrete formation.

Sedimentologic, petrographic investigation of subsurface Mio-Pleistocene clastic sequence of Kuwait Group in Umm Ghudair water field, Southwest of Kuwait by Khalaf (2007) revealed the occurrence of successive cycles of calcrete profiles. Macroscopic (incipient, nodular, massive calcretes), microscopic (such as various calcite crystal fabrics) characteristics of the Shurijeh calcretes are very similar to the Kuwait calcretes (Khalaf, 2007), except they do not contain many organo-sedimentary materials such as plant roots; therefore we believe these calcretes may have formed under similar conditions.

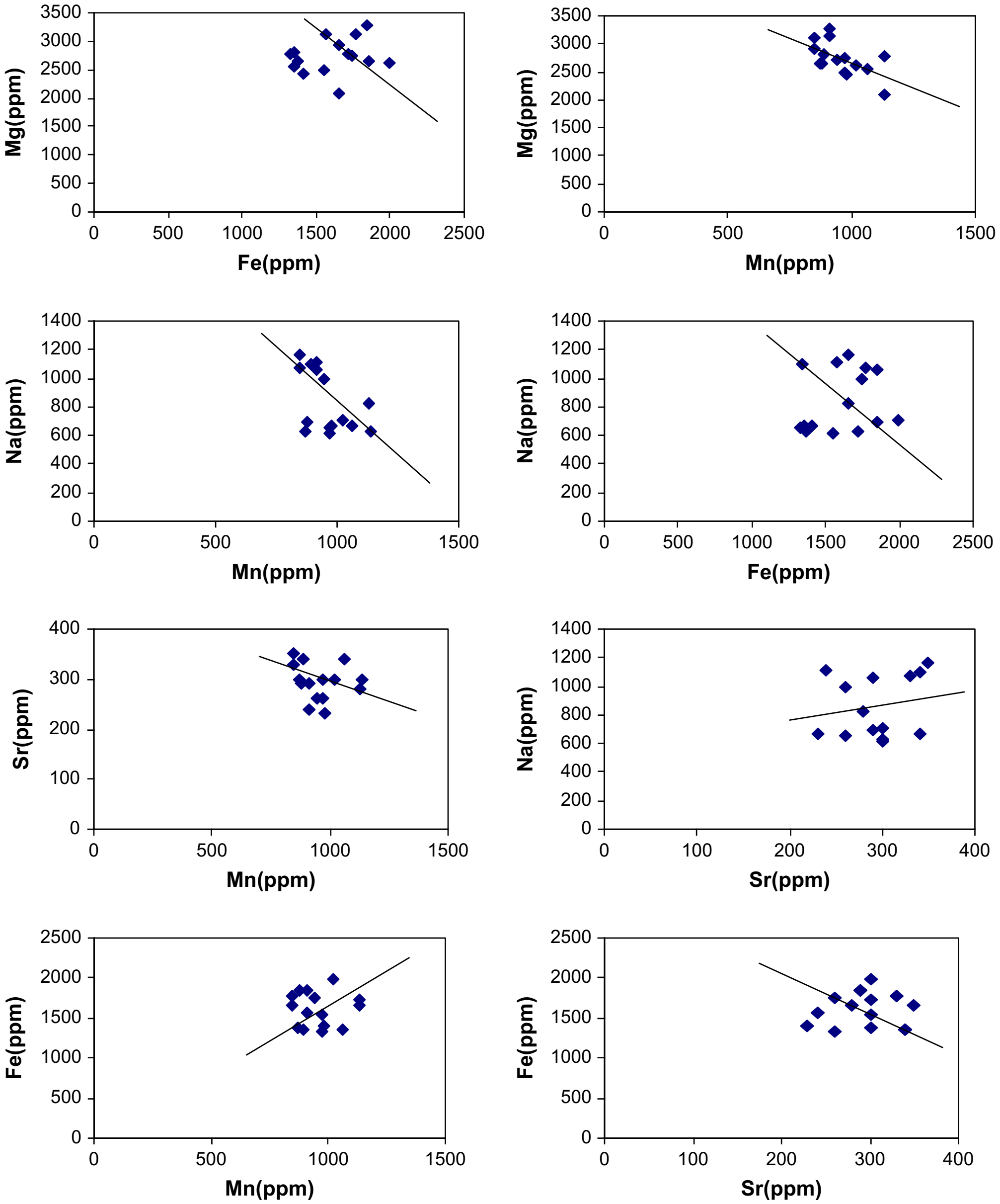

Fig. 8. Elements scattered diagrams of paleosol samples in the study area.

5. Discussion

Generally, calcrete forms either within the soil profile or through evaporative precipitation from groundwater in the phreatic, capillary-fringe zone (pedogenic calcrete versus non-pedogenic calcrete). Pedogenic calcrete contains both alpha, beta fabrics, the extent of each type are mostly depending on climate, hydrologic setting (Wright and Tucker, 1991). Alpha textures include rhombic calcite crystals, dense micritic fabric, floating sediment grains, complex cracks, crystallaria, displacive growth features, exhibit no preserved biogenic features. Beta textures contain features indicating biogenic influence, such as alveolar septal fabric, calcified tubules, microbial coatings, Microcodium. Groundwater calcretes are non-pedogenic in origin, form in the phreatic zone, are typically linear, tabular limestone bodies containing mostly alpha fabrics. These are differentiated from capillary fringe, non-pedogenic calcretes, which form in the vadose zone above the water table, contain beta fabrics that result from phreatophytic plants (Wright and Tucker, 1991; Alonso-Zarza and Tanner, 2006).

The occurrence of calcretes within the studied host rocks indicate that individual calcrete profile has vertical gradational maturity pattern which is manifested by the occurrence of calcretes arranged from bottom to top as follows: non-calcretized host rocks-incipient calcrete- nodular calcrete- massive calcrete horizons (Fig. 4). Lack of beta textures (especially organosedimentary structures), abundance of alpha fabrics suggest that they are non-pedogenic or groundwater calcretes that formed by precipitation of calcium carbonate in the vadose, phreatic zones (e.g. Alonso-Zarza, 2003; Alonso-Zarza and Tanner, 2006). In addition to calcite fabrics that are shown vadose or phreatic non-pedogenic calcretes, geochemical methods (Cathodoluminescence Studies, elemental analysis of calcretes) such as the evaluation of redox-sensitive elements can clarify the position of carbonate accumulation with respect to the water table (e.g. Alonso-Zarza and Tanner, 2006). Calcium carbonate in soils is generally low-Mg calcite, which is stable, resistant to recrystallization. As mentioned in a previous section, Shurijeh calcretes are shown two phases of calcrete genesis (based on geochemical evidence). Generally, the siliciclastic host rocks of the Shurijeh Formation were affected by carbonate cementation processes within both, meteoric vadose, phreatic settings. In these zones, the water table fluctuated periodically (Fig. 9). Thus, we propose that incipient calcretes, calcrete nodules formed within the meteoric vadose zones. The phreatic zone is producing a cumulative cementation on the host lithologies (massive calcrete horizons). Several stages of calcrete cementation that was resulted by varying redox conditions would be caused by a fluctuating water table due to influxes of surficial water by rainfall or channel outflow. The observed pattern of luminescence has been interpreted as characteristic of progressive burial from meteoric to shallow phreatic settings. It is shown that gradual reduction in Eh

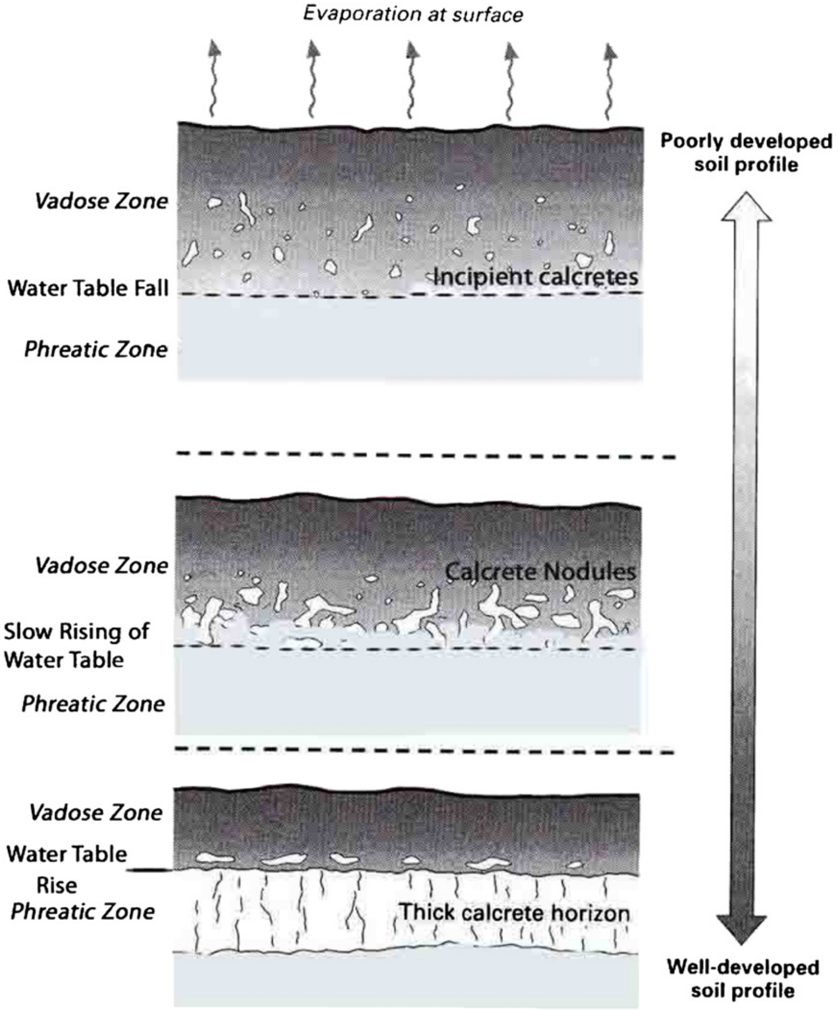

Fig. 9. Multi-phase development of calcrete types. Vadose, phreatic phases, and water table fluctuations are shown. Calcrete maturity increases from top to bottom.

during calcrete formation, is resulted the progressive substitution of first Mn, then Fe ions in the carbonate lattice.

One of the most important variables influencing soil formation is climate (temperature, moisture) (Khadkikar, 2005). Calcium carbonate accumulation requires sufficiently wet conditions for the release of calcium from primary minerals but also sufficiently dry conditions to ensure subsequent precipitation of CaCO3; one would expect that the conditions leading to the precipitation of CaCO3 be best fulfilled by semi-arid conditions as these involve seasonal alternations of rainfall, drought. This same order causes water table fluctuations (Durand et al., 2007).

Micritic textures in calcrete horizons, incipient, nodular calcretes of the Shurijeh Formation was probably developed in the vadose zone within floodplain during periods of low terrigenous supply, hot dry climatic conditions. Instead, calcite cement fabrics (granular, drusy mosaic, blocky cements), microsparitic/sparitic veins, displacive, replacive fabrics were formed in the phreatic zone with rising groundwater table or after flooding episode. In this case, development of vadose calcretes stopped due to high terrigenous supply, calcite cements were slowly precipitated within semi-arid conditions. These results are supported by geochemical analysis (cathodoluminescence, elemental analysis). Then, calcrete types of the Shurijeh Formation had multi-phase development, groundwater evaporation had the most important role in their genesis.

5.1. Source of carbonate

The source of carbonate was variable. It originated mostly from the parent material of the soil including fragments of carbonate rocks. Other sources of carbonate were the surface waters, the eolian dust; in the neighborhood of the studied profiles numerous outcrops of limestones (Mozduran Formation) may have been exposed during deposition of the Shurijeh Formation. The CaCO3-rich dust accumulated at the surface of the soil, then was dissolved by the meteoric water, transported to depth, precipitated at the deeper level (e.g. Williams and Krause, 1998).

6. Conclusion

In this paper, we show how field, petrographic studies, augmented by geochemical examinations (cathodoluminescence, elemental analysis) were used to reveal the calcrete formation mechanism that operated in the Shurijeh Formation. Results of this study are:

1. Three types of calcretes were observed in this formation: incipient calcretes, calcrete nodules, massive calcrete horizons. Calcrete had successive occurrence, presence of them arranged from bottom to top: non-calcretized host rocks-incipient calcrete-nodular calcrete-massive calcrete horizons.
2. Distinctive fabric elements include micritic textures, nodule development, calcite cements, microsparitic/sparitic veins, displacive, replacive fabrics. This suggests that the calcretes formed mostly through evaporation, degassing with no biological activity (alpha type calcretes).
3. Geochemical evidence reveals that water table fluctuated during calcrete~~s~~ formation. Cathodoluminescence features as well as elemental analysis indicate dual phases of calcretization: vadose, phreatic.
4. Calcretization occurred when evaporation exceeded precipitation, caused the upward movement of dissolved materials from the groundwater. At the same time, the movement of rainwater caused a downward movement of the salts. The net result was the deposition of the translocated cations in vadose, phreatic zones by meteoric waters.
5. Calcretes of the Shurijeh Formation were probably formed in arid to semi-arid climatic conditions.
6. The main sources of carbonate for calcrete genesis were parent materials, surface, groundwater, eolian dust, numerous outcrops of limestones in the source area.
7. The nature of the host sediments, the prevailing climatic conditions, the duration, magnitude of the pedogenesis processes, the water table depth, its rising rate, duration of phreatic cementation processes were major factors during formation of different types of calcrete in the Shurijeh Formation. Therefore, hydrogeological, hydrogeochemical settings may have played a significant role in the development of vadose, phreatic or multi-phase calcretes in the sedimentary basin.

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