

OCCURRENCE AND GENESIS OF PALYGORSKITE AND ASSOCIATED CLAY MINERALS IN A PLEISTOCENE CALCRETE COMPLEX, SDE BOQER, NEGEV DESERT, ISRAEL

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ABSTRACT: Palygorskite and associated clay minerals have been studied in a Pleistocene calcrete complex from the Negev desert (Sde Boqer, Israel). This complex is divided into five main parts: the chalky and marly bedrock overlain by its weathered product, a brecciated calcrete hardpan; the laminar crust; loess pockets trapped in the calcrete; and the overlying soft surficial soil. The distribution of clay minerals is directly dependent on the position of the sample in the calcrete complex. Smectite is inherited from the bedrock in the calcrete with an aeolian enrichment in loess pockets and upper soft soil. The source of kaolinite is mainly detrital, related to desert dust. Illite is partly inherited and partly neoformed in loess pockets and desert surficial soil. The origin of palygorskite is clearly related to precipitation processes from soil solutions, Si and Al ions being provided by the slope and detrital grains trapped in the calcrete, with Mg being provided by the parent rock, the slope and aeolian detrital dolomite. This neoformation occurs mainly around detrital grains such as quartz in the hardpan and along textural transitions in loess pockets and is associated with gypsum in the lower part of the toposequence where the evaporation fluxes are the most important. The existence as coatings around grains and the delicate structure of the fibres are incompatible with a detrital origin. Moreover, no evidence was found to support any transformation of smectite into palygorskite in the solid state. Palygorskite is the last step of the cycle of mobile silica and seems to be a product of late diagenesis in Sde Boqer calcrete.

Palygorskite is a common clay mineral of desert soils in the Middle East (Table 1) and is characteristic of soils formed from soft chalk, marl, aeolian desert dust in the semi-arid and arid regions of Israel (Yaalon, 1955; Ravikovitch *et al.*, 1960; Yaalon & Wieder, 1976). Its occurrence is also commonly reported from calcretes, caliches or carbonate-rich soils from the Middle East and from many other calcrete sites in the world (Table 1). Many researchers have shown that the particular alkaline medium constituted by calcrete is favourable to the neoformation of palygorskite (Table 1): a high pH (from 9 to 11), and high Si, Mg and low Al activities in the soil solution are the best conditions for palygorskite precipitation (Weaver & Beck, 1977; Singer, 1979), conditions commonly attained in calcretes. On the other hand, an allochthonous origin of palygorskite is also possible considering the aeolian dynamics in arid deserts

which can transport notable amounts of palygorskite from source areas (Table 1). Consequently, whether inherited from the parent rock, transported by wind from source areas or authigenic in the soil environment, palygorskite genesis can be controversial.

The aim of this paper is to present new data on the occurrence of palygorskite and associated clay minerals in a calcrete complex from Sde Boqer (Northern Negev Desert, Israel), and to discuss a possible polygenic origin of palygorskite in this site.

GEOGRAPHICAL AND GEOLOGICAL SETTINGS

The Sde Boqer site is situated in the Northern Negev Desert, Israel (Fig. 1). This experimental site has been used for 20 years by scientists in an

TABLE 1. Summary of published citations on palygorskite in calcretes and desert soils.

Authors	Region	Geological formation	Proposed sources of palygorskite
Aba-Husayn & Sayegh (1977)	Al-Hasa, Saudi Arabia	Calcareous swamp soils and Mio-Pliocene sediments	Inherited from the parent material.
Abtahi (1977)	Southern Iran	Calcareous Salorthid and Natrixeralf	Very high salinity of solution leads to smectite degradation and palygorskite neoforms from degradation products.
Al-Rawi & Sys (1967)	Mesopotamian floodplain	Soils on Tigris and Euphrates sediments	Pedogenic origin related to arid pedoclimate.
Aqrawi (1993)	Southern Mesopotamia, Iraq	Recent fluvio-lacustrine and deltaic sediments	Palygorskite both detrital (wind and fluvial transportation from source areas) and authigenic (associated with dolomite and gypsum) in origin.
Bachman & Machette (1977)	Southern United States	Quaternary calcic soils and calcretes	Enrichment of Mg in the clayey portion of a calcrete with age. Authigenesis of palygorskite with time. Montmorillonite and montmorillonite-illite can alter to palygorskite.
Barshad <i>et al.</i> (1956)	Israel	Soils developed on various limestones	Palygorskite as a major constituent of acid-insoluble residue of limestone parent material.
Badraoui <i>et al.</i> (1992)	High Chaouia Region, Morocco	Xerochrept soils	Palygorskite inherited from the Cretaceous marl parent material.
Beattie (1970)	Eastern Riverina of New South Wales, Australia	Red and red-brown earth on parna (layered deposit of clay of aeolian origin)	<i>In situ</i> origin from components within a favourable microchemical environment.
Becq-Giraudon & Freytet (1976)	Western France	Tertiary palustrine limestones	Sedimentary and authigenic origin of palygorskite in a confined medium.
Botha & Hughes (1992)	Kalahari basin, northwestern Transvaal, South Africa	Neogene sediments from ephemeral palaeolakes	Soil solutions cause decomposition of smectites and authigenic neoformation of palygorskite.
El-Sherbini & Issa (1989)	Western Desert of Egypt	Quaternary calcrete	Authigenic origin, formed by transformation of smectite.
Elgabaly (1962)	Western Desert of Egypt	Sandy and calcareous desert soils on calcareous sandstone	Palygorskite formed from calcareous argillaceous material associated with salty solutions.
Elloy & Thomas (1981)	NW Algeria (Oran region)	Plio-Pleistocene calcretes	Neoformation of attapulgite.
Elprince <i>et al.</i> (1979)	Alhasa oases, Eastern Saudi Arabia	Soils and palaeosols on dunes and red beds	Pedogenic origin of palygorskite at the expense of smectite.
Eswaran & Barzanji (1974)	Iraq	Soils on alluvial and colluvial deposits	Neoformation of palygorskite preferentially on gypsum grains.
Frye <i>et al.</i> (1974)	Central Eastern New Mexico (USA)	Caliche on Ogallala formation (Quaternary)	Transformation of detrital smectite to palygorskite. High Mg environment, presence of opal.
Gardner (1972)	Clark County, SE Nevada (USA)	Mormon Mesa caliche (Quaternary)	(a) Original detrital constituent of parent sand, (b) airborne dust washed into the profile, (c) chemical precipitation (neoformation) seeming to be the most appropriate to explain the Mg-clay origin.
Gauthier-Lafaye <i>et al.</i> (1993)	Lisboa and Algarve provinces (Portugal), Jbel Rassoul (Morocco)	Weathered profiles on basalt (Portugal). Calcrete in Red Formation (Morocco)	Neoformation during evaporative conditions. Palygorskite formation takes place in more confined conditions than smectite.
Gile <i>et al.</i> (1981)	Desert project, basin and range area of Southern New Mexico	Pleistocene calcic soils and calcretes	Neoformation of palygorskite in the caliche with time.
Hassouba & Shaw (1980)	Coastal plain of Northwest Egypt	Calcrete on Quaternary beach ridge complex	Palygorskite formed authigenically (a) from waters enriched in silica, with high pH and a $Al^{3+}:Mg^{2+}$ ratio of 1, (b) precipitated from highly saline pore waters.

TABLE 1. (contd.)

Authors	Region	Geological formation	Proposed sources of palygorskite
Hay & Wiggins (1980)	Argus Range (California), Wickieup (Arizona), Kile canyon (Nevada), SW USA	Mature calcrete profiles (Quaternary)	Palygorskite as an authigenic mineral formed by reaction and replacement of aluminous detritus or aluminous bedrock.
Heystek & Schmidt (1953)	Springbok Flats, Transvaal, South Africa	Soils on weathered basalt	Weathering of basalt via montmorillonite to attapulgite.
Hutton & Dixon (1981)	South Australia	Quaternary multi-layered calcrete profiles	Precipitation-neoformation of palygorskite in lakes. Contribution of weathered magnesium-rich basic rocks (fragments or bedrock).
Isphording (1973)	Yucatan Platform	Miocene marine clays	Direct precipitation of palygorskite.
Lamouroux <i>et al.</i> (1973)	Lebanon	Soils on sandstone, limestone and basalt	Mineral precipitated from Si, Al, Mg rich soil solutions.
Lang & Pias (1971)	Bamian Basin (central Afghanistan)	Quaternary calcrete	Neoformation of palygorskite when the soil is highly enriched in carbonate.
Lee <i>et al.</i> (1983)	Eastern region of Saudi Arabia	Gypsiorthid and Calciorthid	Palygorskite originates from underlying Mio-Pliocene calcareous bedrock and/or is redistributed by alluvial and aeolian processes.
Mackenzie <i>et al.</i> (1984)	Arabian Peninsula	Salorthid and Torrifuvent	Inheritance and neoformation from soil solutions or from smectite dissolution. Role of soil permeability.
Martin de Vidalès <i>et al.</i> (1986)	Tajo River, Spain	Palaeosols developed on terraces	Formation of palygorskite by dissolution of montmorillonite concomitantly with development of calcic horizons.
Mashhady <i>et al.</i> (1980)	Qasim region, Saudi Arabia	Torrifluents soils	<i>In situ</i> formation from soil solutions (alkaline and calcareous).
McGrawth & Hawley (1987)	Socorro area, New Mexico (USA)	Mid-Pleistocene calcic soils	Mg supplied by degradation of phyllosilicates, volcanish ash and detrital minerals. Neoformation of palygorskite from soil solution precipitations.
McLean <i>et al.</i> (1972)	Southern High Plains, West Texas and Eastern New Mexico, USA	Soils on calcareous lacustrine deposits and their deflation debris	Authigenesis of palygorskite in alkaline lacustrine environments during periods of desiccation. Inherited from the parent rock in soils. Volcanic ash as Si source.
Millot <i>et al.</i> (1957)	Various sites	Continental basins	Neoformed in lacustrine environment from solutions enriched in Si, Mg and Ca by differential leaching of surrounded watersheds.
Millot <i>et al.</i> (1969)	Lower Moulouya (Eastern Morocco)	Quaternary calcretes	Neoformation of pedogenic palygorskite in the hardpan and laminar calcrete.
Monger & Daugherty (1991)	Southern New Mexico (USA)	Petrocalcic horizon in a typical haplargid soil (Pleistocene)	Neoformation of palygorskite. High Mg content and silicate grain dissolution as elements source.
Montenat (1977)	Alicante and Murcie region, SE Spain	Neogene calcretes	Neoformation of attapulgite during calcretization.
Muir (1951)	Syria	Brown desert, grey and brown steppe and saline soils	Palygorskite comes from the underlying limestone.
Nahon <i>et al.</i> (1975)	Thies cliff (Senegal)	Quaternary calcrete on weathered Eocene marls	Palygorskite neoformation associated with quartz neoformation and calcite dissolution from the parent material.
Osmond & Stephen (1957)	Cyprus	Red soils on Pleistocene chalky calcretes (kafkalla)	Palygorskite in soil as a residual mineral from the calcrete and not as a result of pedogenic processes.
Paquet (1983)	Lower Moulouya (Morocco)	Quaternary calcrete	Neoformation of palygorskite before or during calcrete formation, directly from the weathering of Mg silicates and phyllosilicates.
Patil & Surana (1992)	Saswad Niva area, Western Maharashtra (India)	Quaternary calcrete	Alteration of montmorillonite during calcretization of the soil under Mg-rich and high alkaline pH conditions.

TABLE 1. (contd.)

Authors	Region	Geological formation	Proposed sources of palygorskite
Pi-Pujol & Buurman (1987)	SE Ebro Basin, Catalonia, NE Spain	Early Palaeogene palaeosols on fan and playa deposits	Chemical precipitation or transformation of mica. Not pedogenic but sedimentary.
Ravikovitch <i>et al.</i> (1960)	Israel	Mediterranean red earths, Rendzinas, loess and alluvial soils	Palygorskite is mainly inherited from parent rock as soft chalk, marl and aeolian desert dust.
Reeves (1976)	General statement	Caliche	High pH, high Si and Mg concentrations. Palygorskite reflects parent soils or can be formed by alteration of montmorillonite clays.
Regaya (1984)	Matmata loess, Gabes area (Tunisia)	Quaternary calcrete or carbonate accumulations in loessic soils	Neoformation of attapulgite.
Regaya (1992)	Sousse region (Tunisia)	Quaternary calcrete	Attapulgite as weathering clay neoformed during calichification.
Rodas <i>et al.</i> (1994)	Margins of the Duero and Tajo basins (Central Spain)	Calcretes in Lower Paleogene arkosic material	Replacement of trioctahedral smectites or smectites as nucleation sites for palygorskite growth.
Rogers <i>et al.</i> (1954)	Mt. Flinders, Queensland, Australia	Tertiary dolomite from freshwater lake and associated soils	Lacustrine origin. Inherited from the parent material in overlying soils. Can be formed from sepiolite.
Sancho <i>et al.</i> (1992)	East central sector of the Ebro basin (Spain)	Calcretes in lower Pleistocene alluvial formations	Transformation of smectite to palygorskite. Neoformation of palygorskite.
Shadfan & Dixon (1984)	Eastern side of the Jordan valley, Jordan	Upper Cretaceous and Tertiary limestones, Quaternary lacustrine deposits and associated soils	Pedogenic formation of palygorskite associated with inheritance from the parent rocks and transport by wind (detrital origin). Role of high salinity.
Shadfan & Mashhady (1985)	Eastern Saudi Arabia	Torriorthent, Gypsiorthent, Gypsiorthid, Calciorthid	Palygorskite inherited from parent rock or redistributed by alluvial and aeolian processes from Mio-Pliocene sources.
Shadfan <i>et al.</i> (1985a)	Eastern side of the Jordan rift valley	Tertiary hard slightly dolomitic to soft marly limestones and associated Calciorthidic Haploxeroll	<i>In situ</i> formation in marine environment for limestones. Palygorskite is inherited from the parent rock and weathered in solum. Possible transformation of palygorskite into smectite.
Shadfan <i>et al.</i> (1985b)	Western Egypt	Soils on Tertiary limestones	Palygorskite due to inheritance from Tertiary sediments.
Singer (1971)	Yarmouk river terraces, Southern Golan Heights, Israel	Brown calcareous soils on Neogene sediments	Inheritance from the parent material.
Singer (1981)	Rift Valley (Israel)	Neogene lake sediments	Mineral formed by precipitation from solution.
Singer (1984)	World arid zone	Arid soils	Palygorskite precipitated from soil solutions.
Singer (1989)	World arid zone	Pedogenic environment	Palygorskite formed by alteration of precursor minerals or by precipitation from solution.
Singer & Norrish (1974)	Northern Territory (Australia)	Calcareous crust horizon	Pedogenic neoformation from soil waters.
Smith & Whalley (1982)	Northern margin of the Tademaït Plateau (Algeria)	Quaternary duricrust (dolocrete)	Brackish conditions explain the palygorskite formation.
Stephen (1954)	Noss Hill, South Mainland, Shetland Isles	Syenite subjected to hydrothermal alteration	Hydrothermal solutions.
Strakhov (1970)	Kara Kum, Kyzyl Kum (ex USSR)	Pliocene calcareous crust	No explanation. Palygorskite as films and selvages in the lower part of calcareous horizons.
Vanden Heuvel (1966)	Desert project, Las Cricas New Mexico (USA)	Calcareous zone of arid soils	Attapulgite crystallized in the soil during the period of caliche formation and then redistributed in the profile.
Velde (1985)	General statement	Calcrete, caliche	Evaporation of sub-surface waters.

TABLE 1. (contd.)

Authors	Region	Geological formation	Proposed sources of palygorskite
Viani <i>et al.</i> (1983)	Central Saudi Arabia	Mainly Torriorthent and Torrifluent	Palygorskite is detrital, originating from eastern region Tertiary rocks.
Watts (1980)	Kalahari (Southern Africa)	Quaternary calcrete	Authigenic precipitation of palygorskite related to high Mg and to low-Mg calcite transformation and to Si replacement by calcite. Alteration of montmorillonite to palygorskite.
Weaver & Beck (1977)	SE United States	Miocene marine sediments	Smectites alter to palygorskite.
Yaalon (1955)	Israel	Secondary and Tertiary limestones and associated soils	Inherited from the parent rock.
Yaalon & Wieder (1976)	Northern Negev, Israel	Arid brown (calciorthid) soil	Transformation of smectite into palygorskite. Role of transitional layers in soils.

attempt to understand the dynamics of a complex desert ecosystem (Yair & Shachak, 1987). The calcrete complex is at the lower part of the slope above the valley bottom, covering a distance of 15 m.

The study area is composed of three geological formations dated from the Turonian. These forma-

tions are subhorizontal, dipping gently towards NNW. The Drorim member (1 in Figs. 1 and 2), comprising limestone with patches of dolomite, constitutes the bedrock of the lower part of the slope and the main formation of the calcrete complex bedrock. The strata are thin, densely jointed, with chalky and/or marly beds alternating

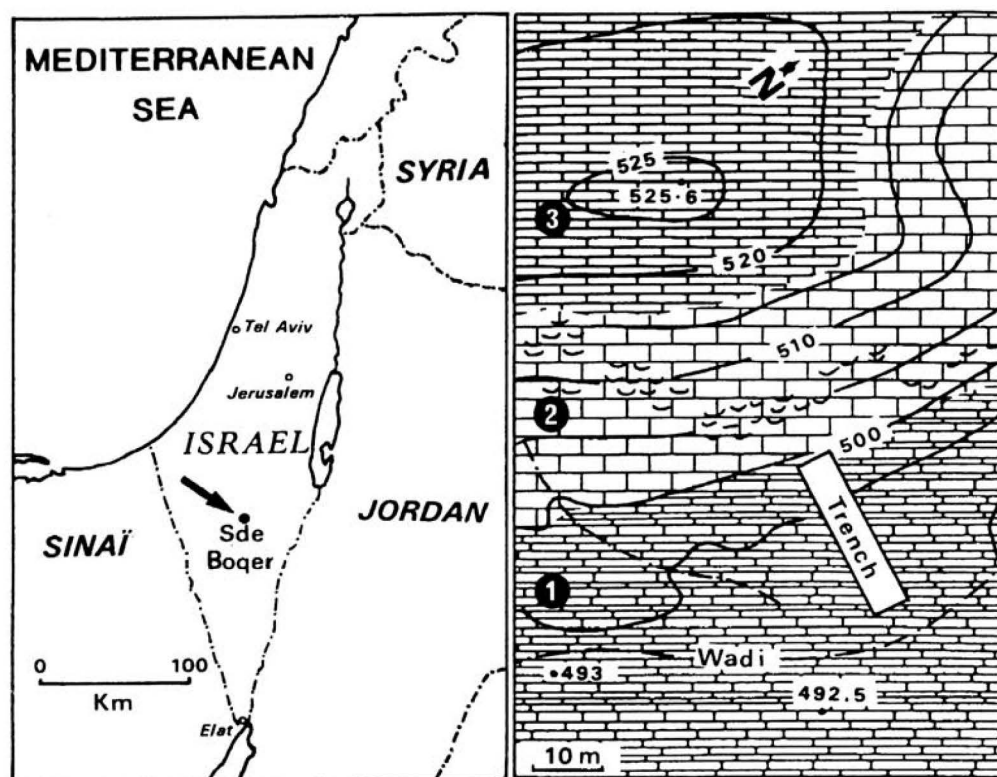


FIG. 1. Left, location of Sde Boqer in Israel (arrow). Right, site of the Sde Boqer calcrete complex: 1, Drorim formation; 2, Shivta formation; 3, Netzer formation. Shivta formation forms steps and small cliffs.

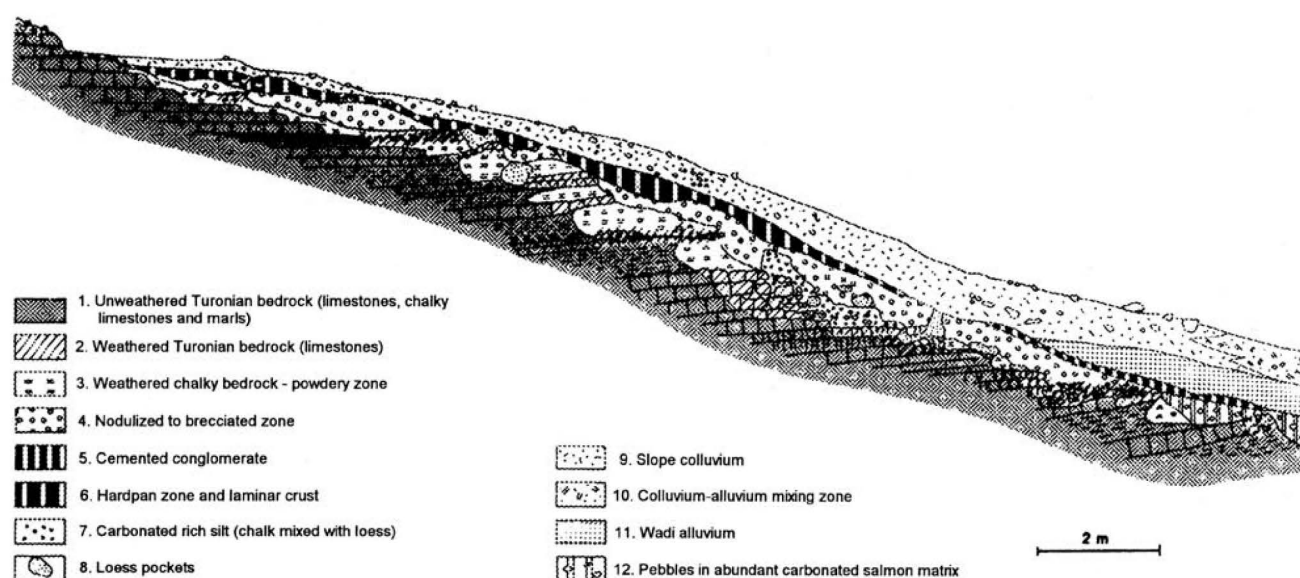


FIG. 2. Sketch of the cut of the Sde Boqer calcrete complex.

with thicker strata of harder crystalline limestone. The Shivta formation (2 in Fig. 1) overlies the Drorim formation and crops out at mid-slope, upslope of the calcrete complex. This is a massive crystalline marine limestone forming small cliffs and steps in the topography. Loamy soil material is found at the base of these steps, in rock crevices and along bedding planes. These soils are shallow brown lithosols (lithic torriorthents) with an A/C profile (Wieder *et al.*, 1985). Most of the Shivta outcrop is devoid of soil cover and exposed to weathering. The third formation is Netzer (3 in Fig. 1), cropping out at the top of the slope. It also comprises crystalline marine limestone like Shivta but is more porous and with numerous beds of chert and flint nodules. These siliceous inclusions are black, exposed to the surface due to differential erosion of limestones and can be covered by desert varnish. They also show numerous traces of dissolution and weathering.

The 22 m long trench (Fig. 1) was excavated in 1987 by bulldozer, exposing all calcrete formations from the unweathered Turonian bedrock to the surface soil (Fig. 2). The calcrete complex starts at the contact between the Shivta and Drorim formations. It is 15 m long and does not extend to alluvial valley deposits.

As in Shephela (Yaalon & Singer, 1974; Dan, 1977) or in Galilee (Verrecchia, 1990), the calcrete cut shows four main facies which usually make up Middle East calcretes (known as nari) as the following: the bedrock; the lower nari; the upper

nari; and the laminar horizon. The upper soft soil is not considered to be part of the caliche. The bedrock consists of the Drorim formation (1 in Fig. 2). The lower nari is formed by powdery zones or weathered limestone strata according to the nature of the parent rock, chalky to marly, respectively (3 in Fig. 2), or crystalline (2 in Fig. 2). The harder strata of limestone, less weathered, can be followed inside the lower nari attesting to an *in situ* weathering of the bedrock. The relative homogeneity of the lower nari can be perturbed by loess pockets, frequently following the strata joints (8 in Fig. 2). The upper nari comprises two different levels as observed in Galilee (Verrecchia, 1992), (1) a nodulized to brecciated zone (4 in Fig. 2) with loess pockets; and (2) a hardpan zone covered irregularly by a laminar crust 1–5 cm thick (6 in Fig. 2). Horizontal cracks are present, emphasizing successive and irregular strata inside the hardpan zone, cross-cutting one another, subparallel to the slope. The soils on the colluvial material are loessal serozems (typic haplargids). The parent material is mainly of aeolian origin (Yaalon & Dan, 1974) and reworked along the slope by biogenic activity and runoff (Yair & Shachak, 1987). The present authors propose a large Pleistocene age for the calcrete.

METHODS

Ninety four samples were analysed along the catena. The total carbonate content was measured

using a Bernard calcimeter. X-ray diffraction (XRD) was performed on bulk samples in the form of un-oriented powder, and on a clay fraction (usually $<2\ \mu\text{m}$; for samples very poor in clay, the $<5\ \mu\text{m}$ fraction was used) in the form of oriented paste. After sample crushing, the clay fraction was obtained after carbonate dissolution with dilute HCl (0.1 N), followed by successive washings with deionized water. The suspension of clays was facilitated by the addition of sodium tripolyphosphate and the $<2\ \mu\text{m}$ fraction was sampled by sedimentation (Stokes' law). Saturated in Mg, the clay paste was air-dried and analysed with a Philips diffractometer (Co- $K\alpha$ radiation) first in its natural state, second after contact with ethylene glycol vapour for one night. Heating of paste sections at 500°C for 2 h was carried out to detect the presence of any chloritic minerals. The relative quantities of the minerals present were determined using correction factors to take into account the diffraction peak shapes (Holtzapffel, 1985). The expanding nature of smectites was quantified using the Biscaye index (Biscaye, 1965). In order to determine the tri- or di-octahedral nature of the clays, the b parameter was determined by XRD on un-oriented powder from the 060 reflection.

Concentrations of the main elements (Si, Al, Mg, K, Na, Ca) were measured with an atomic absorption spectrometer (AAS Perkin Elmer). The porosity of the samples was measured using a mercury micropore sizer (Micromeritics) on even slightly indurated sediments. Bulk samples were coated with gold for scanning electron microscopy studies (SEM JEOL 840 A and 8400) and microprobe analysis was performed on carbon-coated thin-sections and minerals (Link Analytical LZ 5 and Voyager microprobes). Isolated crystals, for structural formula calculation, were obtained after centrifugation of the dissolution residue and dilution in distilled water. After separation of the clay fraction from the whole sample, small drops of the dispersed suspensions were deposited on a grid and carbon coated for transmission electron microscopy (TEM JEM 100 C).

In order to visualize the distribution of the different minerals and elements along the calcrete complex, graphs were performed on a Sun-Spark Workstation with ARC-Info software running the TIN generator for map contouring application. Ninety four samples gave the points grid for the interpolation calculation (triangulation function). Cluster and principal component analyses were

used to classify 88 samples of the calcrete using clay mineralogy and a few elements as discriminate variables.

RESULTS

Nature and distribution of the clay minerals in the calcrete complex

Using XRD analysis we distinguished smectites, kaolinite, palygorskite, illite, chlorite, $10\ \text{\AA}$ (illite) - $14\ \text{\AA}$ (smectite), $14\ \text{\AA}$ (chlorite) - $14\ \text{\AA}$ (smectite) mixed-layers and sepiolite. The first five clay minerals constitute more than 98% of the clays present in the calcrete. Sepiolite was only detected in one sample from the bedrock. Quantitatively, smectites are the most abundant in the $<2\ \mu\text{m}$ fraction (a range from $r = 0$ to 90%, with a mean of $m = 55.8\%$ for the calcrete complex and a standard deviation of $\sigma = 24.5$) followed by palygorskite ($r = 0$ to 55%, $m = 21.7\%$, $\sigma = 17$), kaolinite ($r = 0$ to 20%, $m = 6.5\%$, $\sigma = 4.3$), illite ($r = 0$ to 10%, $m = 2.6\%$, $\sigma = 0.2$) and chlorite ($r = 0$ to 10%, $m = 2.4\%$, $\sigma = 0.2$). The mixed-layer clay minerals are only present in a few samples, frequently associated with loess pockets or containing a loess fraction. The ratio never exceeds 5%.

The crystalline bedrock is either almost devoid of clay minerals (i.e. $>99\%$ CaCO_3 and $<1\%$ quartz) or contains $<2\%$ clays of which smectite represents more than 85–90% (Fig. 3). The marly to chalky limestone strata contain up to 4% clays, smectite being the most common clay mineral (85–90%, Fig. 3). No traces of palygorskite were detected in the bedrock. The calcrete shows a clay content varying from 2 to 3.5%, excluding the loess pockets and associated carbonate mixing zones much richer in clay (from 5–7%) and silt fractions. The lower and upper nari contain notable amounts of palygorskite and smectite, up to 50% and 75% of the clay fraction, respectively. The surficial Holocene soil contains 6.7–9.5% of clay. Smectites have the highest ratio (from 55% to 70% of the clay fraction) followed by kaolinite and palygorskite (15% to 25%) and chlorite and illite (0 to 10%). Dolomite is also present in the surficial soil (5–8% of the total sediment) as detrital fragments of aeolian origin.

The distribution of the main clay minerals shows an organized pattern (Fig. 3): (1) absence of palygorskite in the bedrock; (2) abundance of clay in loess pockets; (3) similarities in chlorite and

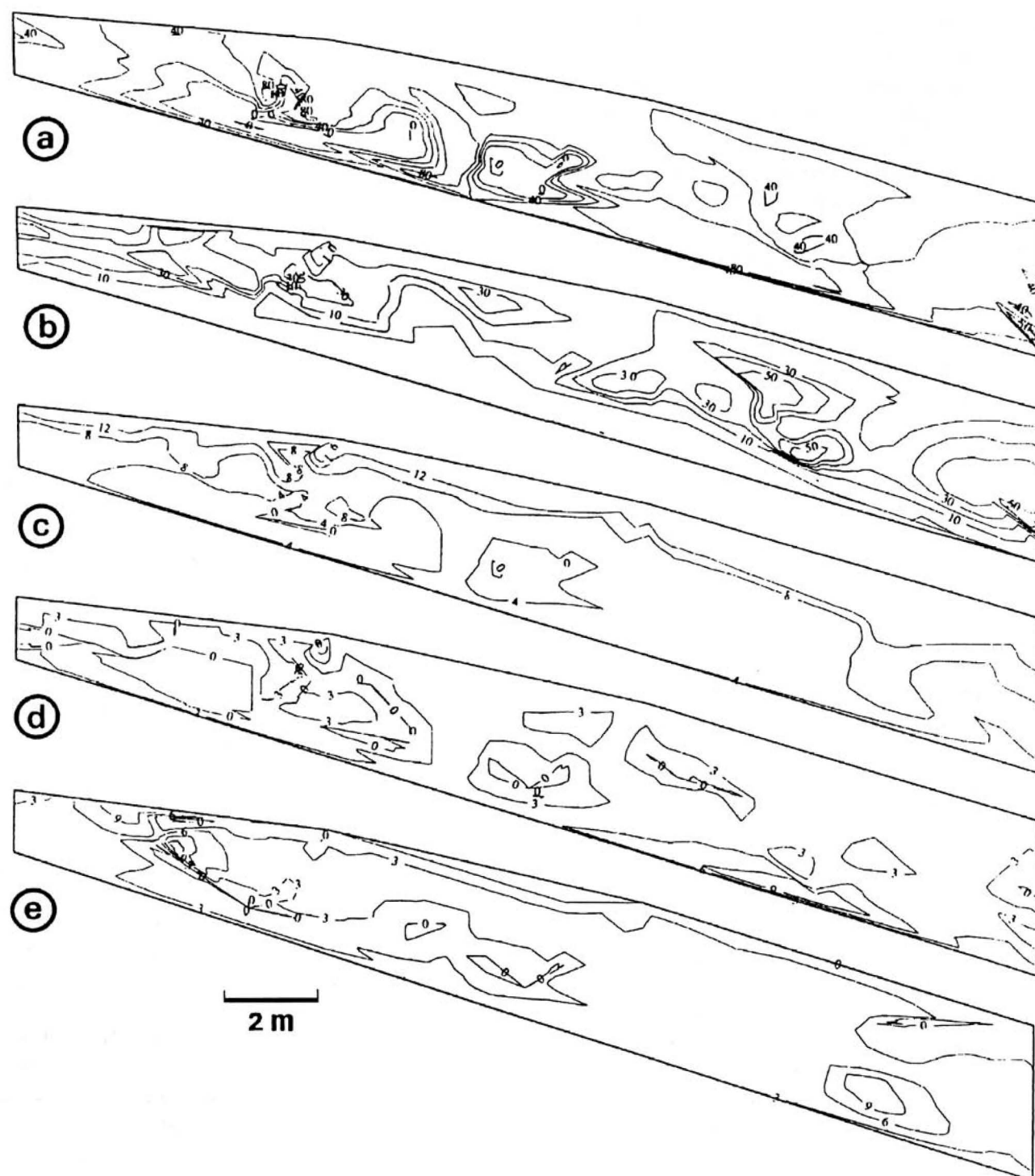


FIG. 3. Distribution of the main clay minerals in the calcrete complex. The values are given in percentage of the clay fraction. (a) smectite, (b) palygorskite, (c) kaolinite, (d) illite, (e) chlorite.

kaolinite distribution; (4) peculiarity of illite distribution, even if similar trends with chlorite-kaolinite distribution are visible; and (5) complex relationships between palygorskite and smectite distributions.

More information on similarities between the samples regarding their clay content and miner-

alogy can be obtained using cluster analysis (Fig. 4). Clay minerals were used as discriminating variables. At the lower level of classification, three branches appear: (1) the crystalline bedrock (without clays); (2) parts of the upper soft soil devoid of palygorskite and the unweathered and

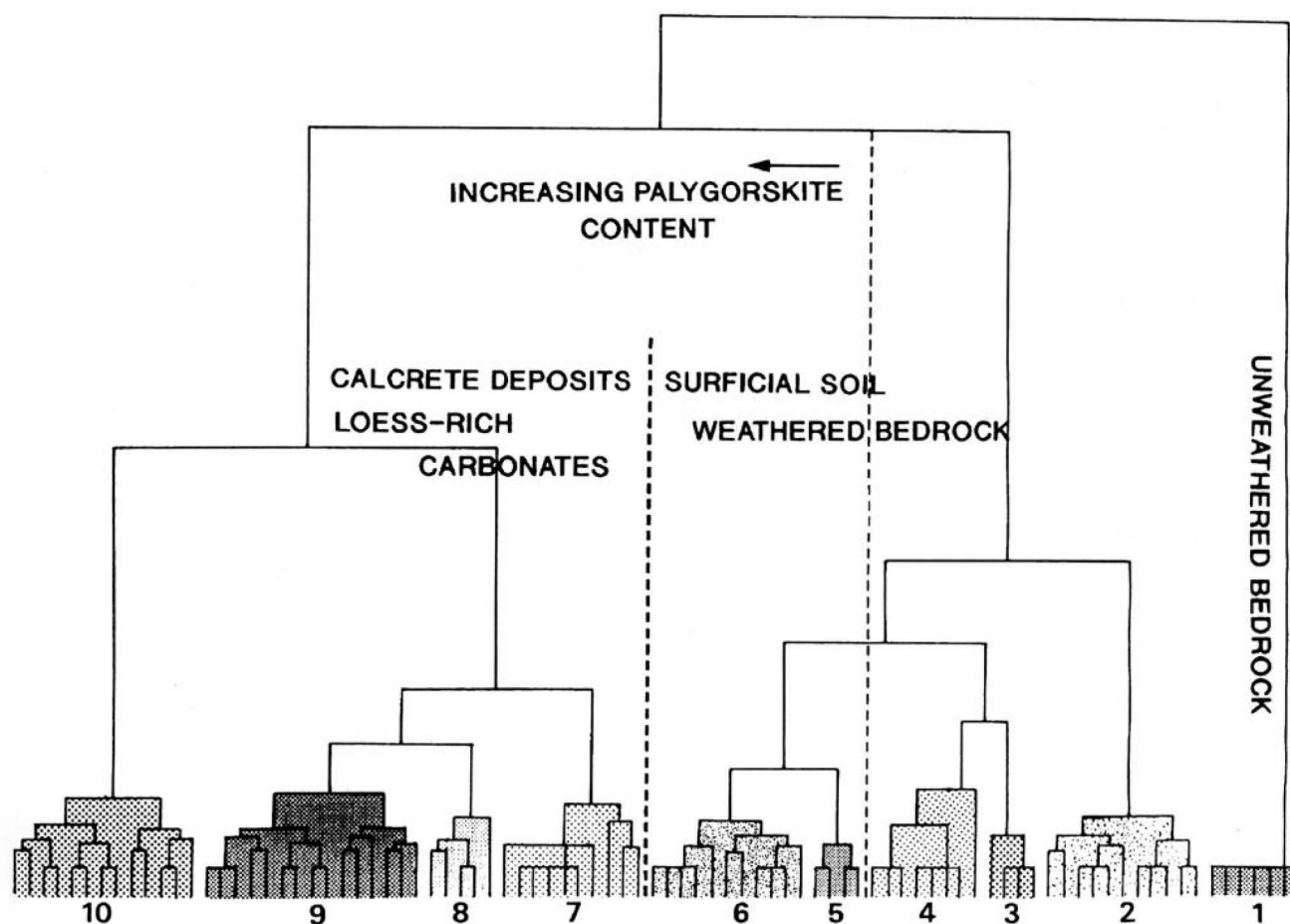


FIG. 4. Cluster analysis of samples from the Sde Boqer calcrete complex. Samples are clearly divided into three main categories grouping ten sets. Palygorskite increases from 0% (1–4) to 50% of the clay fraction (10).

weathered bedrock (with clays); and (3) the calcrete *sensu stricto*, loess pockets and conglomerates. Inside these groups, the classification reflects the increasing content of palygorskite from right (1–4, no palygorskite) to left (5–10, until 50% of palygorskite is present in the clay fraction). The distribution of clay minerals in general, and of palygorskite in particular, is directly influenced by the position of the sample in the calcrete complex, leading to the conclusion that local conditions determine the genesis of the clays.

The relationships between the clay minerals are not obvious. The only trend to be reported is that generally the amount of palygorskite increases when smectite levels decrease in the calcrete. But this trend is not strong enough to relate neoformation of palygorskite to smectite degradation, a process supported by El-Sherbini & Issa (1989), Patil & Surana (1992), Rodas *et al.* (1994), Sancho *et al.* (1992) and others (see Table 1). The

calculation of the mineral ratio for the bulk sample (proportion of each clay mineral actually contained in the rock) shows no relationship between palygorskite and smectite. Nevertheless, the possibility of a genetic link between palygorskite and smectite should not be ruled out (see Table 1 and above).

Relationship between smectite and palygorskite — morphology of clay minerals

The Biscaye index of smectites in the catena varies from 0.11 to 0.86. Lower values should indicate interstratification between expanding (smectite) and non-expanding (illite, collapsed smectite) layers, whereas higher values refer to fully expanded smectites. High Biscaye indices (>0.7) are concentrated in the bedrock and the lower nari (weathered bedrock). The upper soft soil and a few loess pockets always give the lowest index

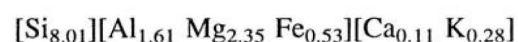
TABLE 2. Summary of published citations on palygorskite crystal sizes and characteristics.

Authors	General habit	Distinctive marks	Dimensions
Aba-Husayn & Sayeh (1977)	Bundles of a few fibres	Very fine and pointed	L = 1 μm
Botha & Hughes (1992)	Tubes	—	L < 1 μm
	Bundles of tubes	—	L = 2 μm
	Short tubes	—	L < 0.25 μm
Coudé-Gaussen <i>et al.</i> (1984)	Rods	Small and fine	L = 0.2–1 μm
	Bundles	Large	L = 1–2 μm
Grim (1968)	Elongated lath-shaped unit	Interwoven mats	w = 50–100 \AA
	Bundles		L = many μm
Hodge <i>et al.</i> (1984)	Rods in small rafts	Rods, laths	w = 100 \AA L = 1000–1500 \AA
Jones & Galán (1988)	Fibrous habit	—	w = 100–300 \AA L = 100 \AA – 4 μm
Lee <i>et al.</i> (1983)	Bundles of fibres	—	L = 2–5 μm
Muir (1951)	Lath-shaped particles in aggregates	Ends clean-cut, rounded or tapering	w = 0.05–0.25 μm L = 1–2 μm
Osmond & Stephen (1957)	Laths	Single lath or bundles	w = 0.8 μm L = 5–30 $\times 10^{-3}$ μm
Rogers <i>et al.</i> (1956)	Fibres	—	w = 0.05 μm L = 1 μm
Singer (1981)	Laths	Primary unit	w = 100–350 \AA
	Fibres as aggregates of laths	Interwoven mass Branched out	w = 0.12–0.5 μm L = 2–3 μm
Stephen (1954)	Elongated lath-shaped	Single lath Bundles of laths Regular ends	w = 0.03 μm

values (<0.38). In the calcrete complex (upper nari, conglomerate, hardpan caliche and laminar crust), the index values are between 0.4 and 0.6. This very well organized distribution of Biscaye index should be related to the evolution of smectite in the catena. In the bedrock and lower nari, smectite is directly inherited from the marine substrate and undergoes weak weathering. The structure of smectite is very perturbed in the soft soil where the medium is more aggressive, with wetting and drying periods, wide thermic amplitudes and more water and K-rich solutions available (rain and runoff) which contribute to the collapse of some smectite layers. Weathering of smectite in surface horizons was also observed by Shadfan & Dixon (1984) in Jordan Valley soils. Smectite is the major clay constituent of dust in the Negev desert (Azmon & Offer, 1989; Ganor 1991), and deposition of desert dust also contributes to fine-grained smectite enrichment, which is very reactive and easily degraded. In the upper nari, it seems that the calcrete constitutes a degrading medium for smectites.

To which products does altered smectite lead? Watts (1980, p. 674) noted that “the crystallinity of the palygorskite was generally high whilst that of montmorillonite decreased with increasing amounts of palygorskite”. The question is whether weathering of smectite allows neoformation of palygorskite, as supposed by many authors (see Table 1). To verify this hypothesis, a palygorskite vs. smectite ratio was correlated to the Biscaye index. Unfortunately, the correlation index r^2 is very low (0.27). Therefore, there is no obvious relationship between a low Biscaye index of smectite corresponding to clay alteration and palygorskite neoformation in the Sde Boqer calcrete.

The mean structural formula of palygorskite associated with loess pockets and upper nari, calculated assuming 21 oxygens in the dehydrated and dehydroxylated half unit layer, is:



This formula is comparable with those given in the literature (Bradley, 1940; Caillère & Hénin,

1961; Newman & Brown, 1987; Jones & Galan, 1988; Velde, 1992). In the Sde Boqer palygorskite, the average sum of octahedral cations is 4.49, which is within the range (with a mean of 3.97) given by Newman & Brown (1987) and Velde (1992), from 3.59 to 4.61 and from 2.38 to 6.77, respectively. In addition, Sde Boqer palygorskite is rich in Mg (2.35) but stays within the range given by Newman & Brown (1987) and Velde (1989), i.e. from 1.29 to 3.84 (with a mean of 2.04) and from 1.29 to 2.81, respectively.

In the literature, the morphology of palygorskite is often described as fibres associated in bundles (Table 2). In Sde Boqer, laths constitute the primary textural units (Fig. 5a,b,c), their width varying between 0.02 μm and 0.05 μm and their length between 0.2 μm and 4 μm with an average length of 2–3 μm . The laths agglomerate into fibres (Fig. 5d) constituting small rafts and bundles of various sizes (Fig. 5e,f). The ends of the crystals are clean-cut and pointed (Fig. 5a), straight (Fig. 5b) or slightly rounded (Fig. 5c). As observed by Singer (1981, p. 417), the fibres are frequently “branched out or intertwined” (Fig. 5g,h). Mesh formed by palygorskite around quartz grains may suggest an authigenic origin of this clay mineral because this delicate coating can not be the result of a destructive transport process. Differences can be noted between the fibres in relation to their positions in the profile. Moreover, as can be seen on Fig. 5, use of the electron microscope gave no evidence for the transformation of smectite into palygorskite, as noted by Singer (1981, p. 419). Although Rodas *et al.* (1994, p. 280) observed palygorskite fibres growing at the edge of smectite crystals, growth features were not observed in Sde Boqer samples. In addition, the calculation of the *b* parameter for smectites confirmed their dioctahedral nature, their average 060 reflection being at 1.503 Å, whereas quartz, present in this <2 μm fraction, has a reflection at 1.541 Å, which is very weak and can not be confused with the smectite peak. The replacement of trioctahedral smectites is, therefore, irrelevant in explaining palygorskite genesis in Sde Boqer.

Geochemistry of the calcrete complex and its relationship to clays

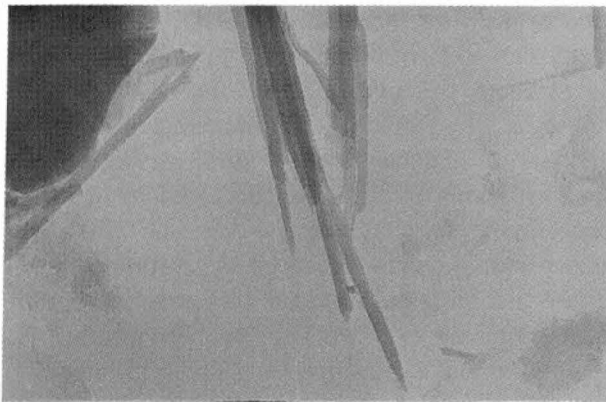
The clay percentage has been compared with various amounts of the chemical elements in the catena samples. First of all, the clay content

decreases with an increase of CaCO_3 . The Al_2O_3 content increases with increase of clay or SiO_2 . The non-carbonate fraction is, therefore, very rich in aluminosilicate minerals. Clay minerals also seem to be more abundant when sulphate increases. Sulphate (mainly gypsum) is concentrated in loess pockets and loess-rich carbonate deposits, which are also richer in clays due to initial loess composition; gypsum precipitation is related to the particular conditions of moisture in these pockets, leading to concentrations of supersaturated salty solutions.

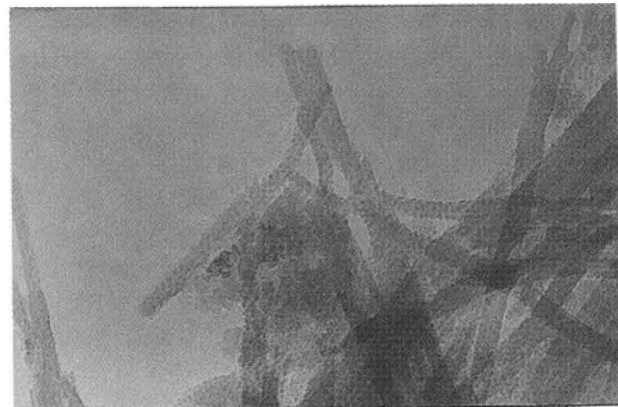
Regarding palygorskite, the behaviour of Mg is critical. There is a correlation between increasing clay fraction and MgO content. The Mg content seems to be directly related to clay content (mainly represented by palygorskite) rather than to carbonate rocks (except for samples with traces of dolomite).

A statistical treatment of the data by principal component analysis shows the relationships between chemical elements (Al, Si, Ca, Mg, S), clay minerals (smectite, kaolinite, palygorskite, illite, chlorite) and environments of the catena (Fig. 6). The samples (individuals) were clustered in six main groups in relation to their positions in the catena. The palygorskite pole is close to the Mg and SO_4 pole constituting an evaporitic pole mainly including samples of the lower part of the catena and a few of the loess-rich carbonate horizons. A detrital pole is constituted by other loess-rich pockets and surficial soils, under the influence of kaolinite, Si and Al elements. Opposite to the evaporitic pole are the samples influenced by very high Ca content. They constitute the marine pole where smectite prevails and include the bedrock and the lower nari. The small amounts of illite and chlorite do not allow particular conclusions.

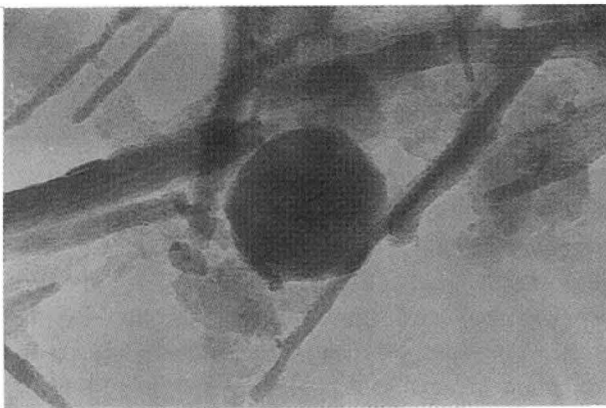
The comparison of sample clay content and its composition in terms of chemical elements leads to the following conclusions: (1) palygorskite, Mg and SO_4 constitute an evaporitic pole, but some palygorskite also exists in samples outside of this pole; (2) increasing kaolinite is clearly related to a detrital contribution (mainly aeolian); (3) smectite is strongly associated with the bedrock and is therefore mainly inherited when found in the lower nari; (4) each part of the calcrete complex shows distinct chemical and clay data. However, the statistical treatment of data does not allow any conclusion regarding the replacement of smectite by palygorskite as supposed by many authors (see Table 1).



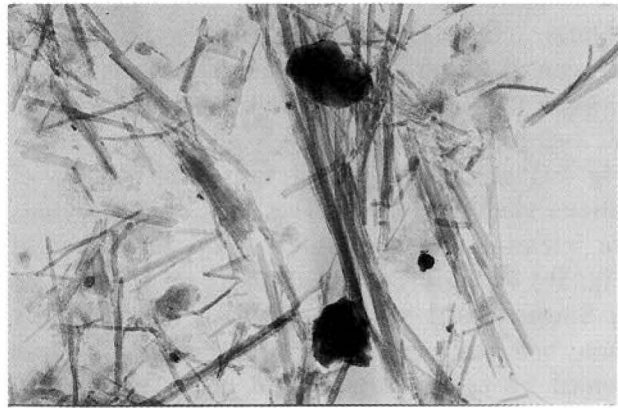
a 0.02 μm



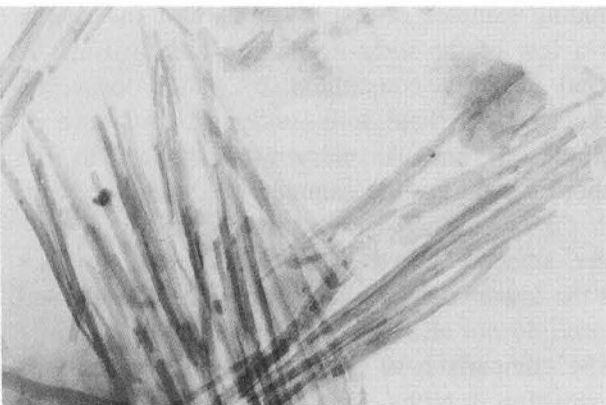
b 0.02 μm



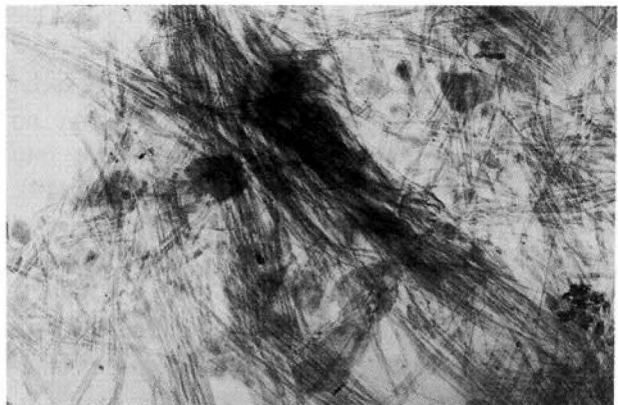
c 0.02 μm



d 1 μm



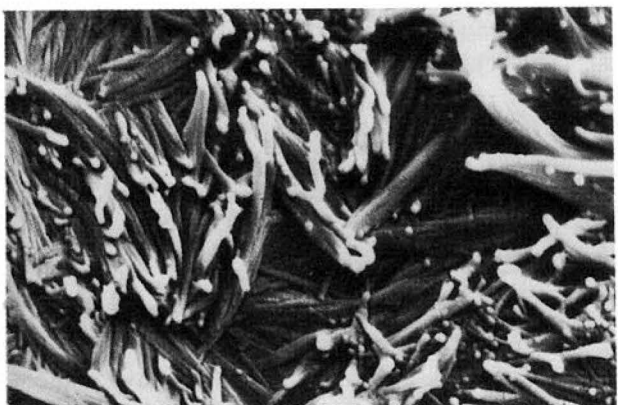
e 0.04 μm



f 1.5 μm



g 100 μm



h 1 μm

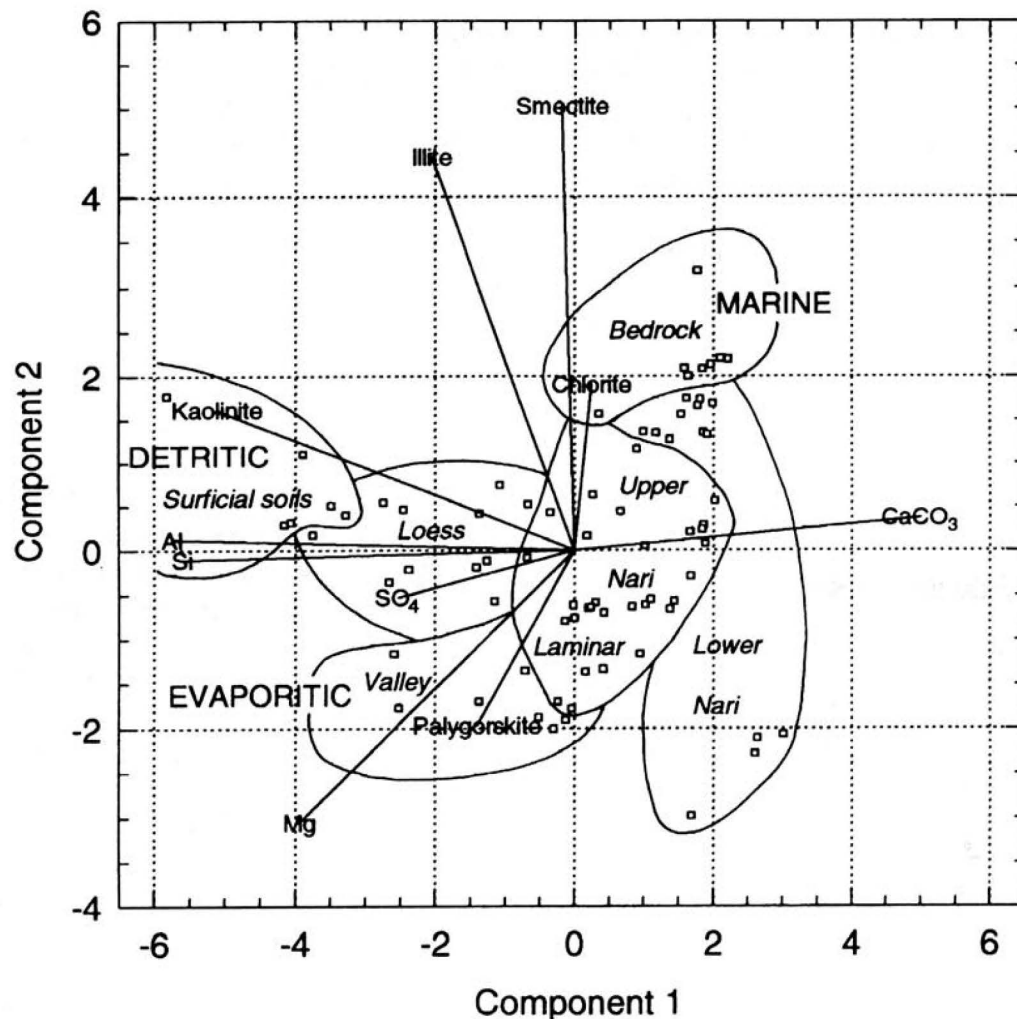


FIG. 6. Principal component analysis of clays and Si, Al, SO_4 and CaCO_3 contents in the Sde Boquer calcrete complex. This statistical analysis clearly shows the clustering of samples regarding their position in the catena, their mineralogical and chemical compositions and their possible origin.

Porosity distribution

Porosity along the catena varies from 4–49%. The crystalline limestone bedrock is the least

porous with a mean porosity of $7.28 \pm 2.43\%$ (standard deviation) and the least rich in clays. The marly bedrock is more porous with a mean of $16.55 \pm 3.00\%$. These porosity characteristics lead to

FIG. 5. Electron micrographs of palygorskite. (a) Transmission electron microscope (TEM) micrograph of palygorskite in the upper nari. The ends are tapered. In the lower right corner there are smectite crystals. (b) TEM micrograph of palygorskite found in loess pockets. The ends are straight and the crystals wider than in (a). (c) Same origin as (b): TEM view showing rounded ends of palygorskite crystals, flakes of smectite and a crystal of kaolinite. (d) TEM view. Bundles of short palygorskite crystals in loess pockets. The fibrous minerals are associated with smectite flakes and kaolinite (in dark). (e) Same origin as (d): TEM view showing the fibres formed by primary laths units and forming bundles. The ends of the crystals are straight. (f) TEM view. Long bundles of fine and pointed fibres of palygorskite in the upper nari (laminar crust). Compare with (e). (g) Scanning electron micrograph of a quartz grain surface covered by a mesh of palygorskite in the upper nari (hardpan). The structure of the coating is constituted by interwoven fibres, long, fine and tapered. (h) SEM view. Close-up of (g) showing the fine structure of the mesh.

different rates of weathering. Within the calcrete itself, the weathered bedrock and the platy caliche have a high porosity (mean of $43.78 \pm 4.74\%$). Loess pockets are slightly less porous (mean of $39.36 \pm 2.83\%$). Voids consist of vugs and complex packing voids that facilitate water retention (grain films). The laminar crust has a very low porosity ($13.1 \pm 3.25\%$), as shown by Verrecchia (1994). Comparison of porosity and clay content shows an increase of clay content with increasing porosity. Porosity plays a major role in water retention and moisture trapping. Sites having a high porosity are also richest in palygorskite.

DISCUSSION

Origin of clays other than palygorskite in the Sde Boqer calcrete complex

An important variable in the detrital pole of the principal component analysis, kaolinite can be clearly attributed to exogenous sources. Its greater abundance in loess-rich sediments and mostly surficial soils (up to 20% of the clay fraction) links its presence to aeolian contributions. Desert dust contains kaolinite (6–55% of the dust clay fraction from Ganor, 1991), about 3% of total dust from Danin & Ganor (1991) and contributes to an increase in the kaolinite ratio in the upper soft soil.

Chlorite is present in the loess pockets and more rarely in the bedrock, and is more or less uniformly distributed in the calcrete but is almost absent in the surficial soil. Present-day dust does not include chlorite (Danin & Ganor, 1991; Azmon & Offer, 1989; Ganor, 1991), which explains its absence in the surficial soil. But its occurrence is clearly related to the presence of loess, and chlorite can be a marker of ancient loess influence. In conclusion, this mineral is inherited either from ancient aeolian sediments or from the bedrock, and does not form in the calcrete medium.

Illite, which is only a minor component, is found in the bedrock as well as in the calcrete complex with some maxima in the surficial soils. In the weathered basement (lower nari), its inherited origin from the bedrock is obvious. But in the loess pockets, mixed carbonate-loess sediments and surficial soils, its origin can be very different. As noted by Singer (1988, p. 254), "illite concentration is highest in the surface horizons of some calciorthis from the Negev. (...) illite is actually

forming in these soils under the present arid conditions". Regarding the data (primary source of K and K-bearing minerals), illite pedogenesis in Sde Boqer is possible. The pedogenesis of illite is also favoured by wetting and drying cycles (Singer, 1988) that affect surface horizons of Sde Boqer soils and loess pockets in the calcrete, where moisture is maintained longer than in the other parts of the calcrete complex.

Smectites are ubiquitous and the main clay mineral in the catena. Smectite is the major clay mineral of calcareous soils in Israel (Ravikovitch *et al.*, 1960). They are also dominant in the $<2 \mu\text{m}$ fraction of present-day desert dust. They seem to be mainly inherited from the bedrock in the lower nari, where they represent up to 90% of the clay fraction. In the upper calcrete, they can be derived from the bedrock sediments and partly enriched by dust contribution in surficial soil and loess pockets. The variety of their Biscaye indices can be related to their weathering and relative instability in the calcrete medium (Paquet, 1983). Moreover, almost all of the smectites are dioctahedral minerals, which are more difficult to alter than trioctahedral structures. In addition, there is no evidence of transformation of smectite into palygorskite in Sde Boqer.

Origins of palygorskite in the Sde Boqer calcrete complex

Two main origins for palygorskite in arid soils and calcretes have been proposed in the literature (see Singer, 1979, 1989): inheritance or pedogenic authigenesis (*in situ* formation). The inheritance origin assumes two possible processes: palygorskite is already present in the geological bedrock and is, therefore, inherited from the parent rock during soil or calcrete formation, or palygorskite is detrital in origin, brought from sources in the soil profile by sedimentary processes (alluvial or aeolian). Many examples of palygorskite derived from parent rocks, mainly Tertiary limestones, were observed in the Middle East (Table 1).

On the other hand, if the bedrock does not contain any palygorskite, the mineral can be transported by alluvial or aeolian processes from other sources, principally Tertiary limestone basins: this detrital origin by means of wadi or wind was widely reported from Saudi Arabia by Shadfan & Mashhady (1985), Viani *et al.* (1983) and Lee *et al.* (1983) and from Tunisia by Coudé-Gaussen *et al.*

(1984). In Sde Boqer, the bedrock does not contain any palygorskite and, therefore, direct inheritance from the parent rock is unlikely. The sources of sedimentary bedrock containing palygorskite are far from the site, and very rare in the Negev (Bentor *et al.*, 1963), precluding any direct alluvial or aeolian contribution to palygorskite accumulation. In addition, the dust from the Sde Boqer area does not even contain traces of palygorskite (Offer *et al.*, 1993), nor does an average dust storm in Israel (Danin & Ganor, 1991). However, Ganor (1991) noted that present-day dust storms, originating in Saudi Arabia, Jordan and Dead Sea Deserts, can transport noticeable amounts of palygorskite. This process can solely explain part of the chain-mineral present in the surficial soil, but not its occurrence in all of the calcrete complex, the clay leaching process being very weak or non-existent. In conclusion, an inherited or detrital origin for palygorskite is very unlikely in Sde Boqer, an *in situ* formation being much more probable.

Palygorskite authigenesis can be explained by two processes (Table 1): (1) alteration of pre-existing phyllosilicate minerals such as mica, kaolinite or smectite and then transformation into palygorskite; or (2) precipitation from soil solutions. An association with evaporative authigenic gypsum, salts or salty or brackish solutions has been widely reported in the literature (Elgabaly, 1962, p. 389; Eswaran & Barzanji, 1974, p. 159; Yaalon & Wieder, 1976, p. 74; Hassouba & Shaw, 1980, p. 82; Smith & Whalley, 1982, p. 308; Shadfan & Dixon, 1984, p. 194; Sancho *et al.*, 1992, p. 305; Aqrawi, 1993, p. 158).

In the case of alteration of smectite into palygorskite, it is rather difficult to explain the kinetics, in terms of energy required, of a transformation of a stable layer mineral into a chain clay (Weaver & Beck, 1977; Watts, 1980; Singer, 1989). In addition, Singer (1989, p. 864) noted that "the frequent association of these two clay minerals is a result of the proximity in their stability field, but does not necessarily imply a solid phase 'transformation' of one into another".

General conditions of palygorskite stability are discussed in Singer & Norrish (1974), Weaver & Beck (1977) and Velde (1985). A high pH, between 9 and 11 (Hay & Wiggins (1980) proposed between 7 and 8.5 in USA calcretes, and Eswaran & Barzanji (1974) about 7.9 in Iraqi gypsiferous soils) and high Mg and Si and low Al activity ratio constitute the best environment for

palygorskite precipitation, whether from soil solution or from groundwater (Hodges *et al.*, 1984). The source of Si can be provided by alteration of phyllosilicates, volcanic ash or silicate grains (see Table 1). The source of Mg can have the same origin or a transformation of high Mg calcite (HMC) into low Mg calcite (LMC) (Yaalon & Wieder, 1976; Hassouba & Shaw, 1980; Watts, 1980). Contrary to Millot *et al.* (1977) or Paquet (1983) who considered palygorskite to form during an early 'argillization' stage before calcretization, the development of palygorskite neof ormation takes place after or during carbonate deposition and cementation in Sde Boqer. No obvious epigenesis of clays by calcite was observed in the calcrete complex. This was also noted in the Kalahari calcretes by Watts (1980) and in the Levante (Spain) caliche by Montenat (1977). Finally, the microsites where palygorskite seems to precipitate preferentially are "inorganic crystalline substrates such as silt-sized calcite or gypsum crystals and coatings of quartz or feldspar" as reported by Singer (1984). Pore-space also seems to play a major role as sharp textural transitions (Yaalon & Wieder, 1976; Singer, 1989).

In Sde Boqer, the highest values (>40%) of palygorskite in the clay fraction are concentrated in three microenvironments: (1) the upper part of the toposequence, (2) loess pockets in the upper part of the catena; and (3) the lower part of the toposequence. This distribution corroborates an *in situ* origin of palygorskite from soil solutions: (1) After runoff on the Shivta formation, water from the slope concentrates and infiltrates in the upper part of the catena, this part being the most humid of the toposequence (Yair & Shachak, 1987). This water, already containing soluble silica (from Netzer formation) and Mg, can be enriched in these elements in calcrete microenvironments (dissolution of quartz and detrital dolomite). When the conditions are attained, palygorskite can be precipitated from the soil solutions, mainly in the micropores of laminar crust, which contain numerous quartz grains and detrital Mg-carbonates. (2) In loess pockets, the conditions are slightly different: the water retention is higher than in the hard carbonate horizons of the calcrete complex, allowing a concentration of the solutions with time and precipitation of palygorskite at textural transitions as noted by Yaalon & Wieder (1976). (3) In the lower part of the toposequence, the presence of gypsum demonstrates the high salinity of the

solutions and the evaporative conditions that favour deposition of palygorskite, as discussed above.

In two of these three particular microenvironments, palygorskite is well formed, consisting of authigenic long meshes of fibres with sharp extremities and agglomerated as fine coatings on skeleton grains (quartz, feldspar or gypsum) as observed with the electron microscopes. In the other part of the nari calcrete, microporosity seems to play a major role in palygorskite precipitation; but here again, palygorskite occurrence is related to precipitation from soil solutions. The source of Al and Si is provided by the solutions coming from the slope (the watershed) and the calcrete medium itself: numerous quartz and feldspars show dissolution features. In loess pockets, the remaining humidity and water films on skeletal grains facilitate the quartz and feldspar dissolution, enriching the solution for palygorskite precipitation. As seen above, Mg can be provided by detrital dolomite but Mg is also available in runoff water up to levels of 7.5 mg/l (Yaïr *et al.*, 1991; measurements done during winter 1981/1982) and in dust (Ganor *et al.*, 1991). In addition, Mg can be provided from the weathered parent rock itself, the lower nari being depleted in Mg. In conclusion, in Sde Boqer, palygorskite is mainly precipitated from soil solution and no evidence was found to support any transformation of smectite into palygorskite.

CONCLUSION

The geochemical and mineralogical study of the Sde Boqer calcrete complex emphasized the diverse origins of clay minerals, one part being detrital or inherited, the other being neoformed. Smectite, kaolinite, mixed-layer minerals, chlorite and some illite are inherited directly from the bedrock or from external sources by means of aeolian desert dust and loess. On the other hand, part of illite and palygorskite are authigenic in origin, formed *in situ*. According to the literature, palygorskite can have multiple origins: in Sde Boqer, an *in situ* and authigenic origin seems to be the most probable. In the calcrete medium, pH, availability of Si, Al, Mg ions, the concentrations of solutions and the microporosity provide the appropriate conditions for palygorskite precipitation. In loess pockets and porous sediments, the concentration of moisture and textural transitions seem to favour the neoformation of fibrous clay minerals. Finally, in the bottom part of the toposequence, the evaporitic conditions also

give an appropriate medium for palygorskite formation. Along the catena, various conditions occur that lead to palygorskite precipitation from soil solutions. As noted by Watts (1980, p. 674) about palygorskites "their almost ubiquitous presence suggests that they play an integral role in calcrete formation". In Sde Boqer, palygorskite is the final step of the silica cycle in the calcrete: there is no secondary silica precipitation, e.g. calcedonite, but many quartz and feldspar crystals are partially dissolved and runoff water contains dissolved silica (Yaïr *et al.*, 1991). Silica must accumulate somewhere. In the calcrete medium, the alkaline conditions facilitate silica mobility, which can combine into palygorskite mainly directly at the contact of silica grains where the solutions circulate preferentially and where water films stay for the longest period of time during the evaporation phase. This is why palygorskite occurs principally as coatings in the calcrete. In loess pockets, the conditions are different and lead to precipitation in the micropores and textural transitions, where the solutions are concentrated during evaporation. The different morphologies of the palygorskite fibres can be explained using this range of precipitation conditions. Finally, the presence of palygorskite, mainly around quartz grains, in micropores or associated with secondary products such as gypsum, support the idea that palygorskite precipitates after the calcrete formation and constitutes a late diagenetic product occurring in an appropriate environment such as the alkaline medium of limecrusts.

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REFERENCES

- ABA-HUSAYN M.M. & SAYEGH A.H. (1977) Mineralogy of the Al-Hasa desert soils (Saudi Arabia). *Clays Clay Miner.* **25**, 138–147.
- ABTAHI A. (1977) Effect of a saline and alkaline groundwater on soil genesis in semi-arid southern Iran. *Soil Sci. Soc. Am. J.*, **41**, 583–588.
- AL RAWI G.J. & SYS C. (1967) A comparative study between Euphrates and Tigris sediments in the Mesopotamian Flood Plain. *Pedologie*, **Gand 17**, 187–211.
- AQRAWI A.A.M. (1993) Palygorskite in the recent fluvio-lacustrine and deltaic sediments of southern Mesopotamia. *Clay Miner.* **28**, 153–159.
- AZMON E. & OFFER Z.Y. (1989) Pollution of Quaternary cover on aquifers of Eocene chalk in Ramat Hovav industrial area in Israel. *Water, Air and Soil Pollution* **44**, 203–214.
- BACHMANN G.O. & MACHETTE M.N. (1977) Calcic soils and calcretes in the southwestern United States. *U.S. Geological Survey, Open-file Report 77-794*, 163 pp.
- BADRAOUI M., BLOOM P.R. & BOUABIB R. (1992) Palygorskite-smectite association in a Xerochrept of the High Chaouia Region of Morocco. *Soil Sci. Soc. Am. J.*, **56**, 1640–1646.
- BARSHAD I., HALEVY E., GOLD H.A. & HAGIN J. (1956) Clay minerals in some limestones soils from Israel. *Soil Sci.* **81**, 423–437.
- BEATTIE J.A. (1970) Peculiar features of soil development in parna deposits in the Eastern Riverina, N.S.W. *Aust. J. Soil Res.* **8**, 145–156.
- BEQ-GIRAUDON J.-F. & FREYTET P. (1976) L'Oligocène du fossé de Saint-Maixent (Deux-Sèvres): observations paléontologiques et pétrographiques sur les calcaires 'lacustres' à attapulгите. *C. R. Acad. Sci. Paris*, **282**, 1943–1946.
- BENTOR Y.K., BODENHEIMER W. & HELLER L. (1963) A reconnaissance survey of the relationship between clay mineralogy and geological environment in the Negev (Southern Israel). *J. Sed. Pet.* **33**, 874–903.
- BISCAYE P.E. (1965) Mineralogy and sedimentation of recent deep sea clay in Atlantic Ocean and adjacent seas and oceans. *Geol. Soc. Amer. Bull.* **76**, 803–832.
- BOTHA G.A. & HUGHES J.C. (1992) Pedogenic palygorskite and dolomite in a late Neogene sedimentary succession, northwestern Transvaal, South Africa. *Geoderma* **53**, 139–154.
- BRADLEY W.F. (1940) The structural scheme of attapulгите. *Am. Miner.* **25**, 405–410.
- CAILLERE A. & HENIN S. (1961) Palygorskite. Pp. 343–353 in: *The X-Ray Identification and Crystal Structures of Clay Minerals* (G. Brown, editor). Mineralogical Society, London.
- COUDÉ-GAUSSIN G., M.-N. LE COUSTOMER & ROGNON P. (1984) Paléosols d'âge Pléistocène supérieur dans les loess des Matmata (Sud Tunisien). *Sci. Géol. Bull.* **37**, 359–386.
- DAN J. (1977) The distribution of nari and other limecrusts in Israel. *Israel J. Earth Sci.* **26**, 68–83.
- DANIN A. & GANOR E. (1991) Trapping of airborne dust by mosses in the Negev Desert, Israel. *Earth Surf. Proc. Landforms* **16**, 153–162.
- EL-SHERBINI M.I. & ISSA G.I. (1989) Composition and origin of some calcrete deposits in South Western Desert of Egypt. *J. Afr. Earth Sci.* **9**, 461–466.
- ELGABALY M.M. (1962) The presence of attapulгите in some soils of the western desert of Egypt. *Soil Sci.* **93**, 387–390.
- ELLOY R. & THOMAS G. (1981) Dynamique de la genèse des croûtes calcaires (calcretes) développées sur séries rouges pléistocènes en Algérie N.Occ. Contexte géomorphologique et climatique. Pétrographie et géochimie. *Bull. Centre Rech. Explo.-Prod. Elf Aquitaine*, **5**, 53–112.
- ELPRINCE A.M., MASHHADY A.S. & ABA-HUSAYN M.M. (1979) The occurrence of pedogenic palygorskite (attapulгите) in Saudi Arabia. *Soil Sci.* **128**, 214–218.
- ESWARAN J. & BARZANJI A.F. (1974) Evidence for the neof ormation of attapulгите in some soils of Iraq. *Trans. 10th Int. Congr. Soil Sci. Moscow*, **7**, 154–161.
- FRYE J.C., GLASS H.D., LEONARD A.B. & COLEMAN D.D. (1974) Caliche and clay mineral zonation of Ogallala Formation, central-eastern New Mexico. *New Mexico Bureau of Mines and Mineral Resources, Circular 144*, 16 pp.
- GANOR E. (1991) The composition of clay minerals transported to Israel as indicators of Saharan dust emission. *Atmos. Env.* **25A**, 2657–2664.
- GANOR E., FONER H.A., BRENNER S., NEEMAN E. & LAVI N. (1991) The chemical composition of aerosols settling in Israel following dust storms. *Atmos. Env.* **25A**, 2665–2670.
- GARDNER L.R. (1972) Origin of the Mormon Mesa Caliche, Clark County, Nevada. *Geol. Soc. Amer. Bull.* **83**, 143–156.
- GAUTHIER-LAFAYE F., TAIEB R., PAQUET H., CHAHI A., PRUDENCIO I. & SEQUEIRA BRAGA M.-A. (1993) Composition isotopique de l'oxygène de palygorskites associées à des calcretes: conditions de formation. *C. R. Acad. Sci. Paris*, **316**, 1239–1245.
- GILE L.H., HAWLEY J.W. & GROSSMAN R.B. (1981) Soils and geomorphology in the Basin and Range area of Southern New-Mexico, Guidebook to the Desert Project. *New-Mexico Bur. Mines Mineral Res., Memoir 39*, 222 pp.
- GRIM R.E. (1968) *Clay Mineralogy*. McGraw-Hill, New York.
- HASSOUBA H. & SHAW H.F. (1980) The occurrence of palygorskite in Quaternary sediments of the coastal plain of North-West Egypt. *Clay Miner.* **15**, 77–83.

- HAY R.L. & WIGGINS B. (1980) Pellets, ooids, sepiolite and silica in three calcretes of South western United States. *Sedimentology*, **27**, 559–576.
- HEYSTEK H. & SCHMIDT E. (1953) The mineralogy of the attapulgitic-montmorillonite deposit in the Springbok Flats, Transvaal. *Trans. Geol. S. Afr.* **56**, 99–115.
- HODGE T., TURCHENEK L.W. & OADES J.M. (1984) Occurrence of palygorskite in ground-water rendzinas (petrocalcic Calciaquolls) in Southeast South Australia. Pp. 199–210 in: *Palygorskite-Sepiolite: Occurrences, Genesis and Uses* (A. Singer & E. Galán, editors). Developments in Sedimentology, Elsevier, **37**.
- HOLTZAPFFEL T. (1985) Les minéraux argileux, préparation, analyse diffractométrique et détermination. *Soc. Géol. du Nord, Spec. Publ.* **12**, 136 pp.
- HUTTON J.T. & DIXON J.C. (1981) The chemistry and mineralogy of some South Australia calcretes and associated soft carbonates and their dolomitization. *J. Geol. Soc. Aust.* **28**, 71–79.
- ISPHORDING W.C. (1973) Discussion of the occurrence and origin of sedimentary palygorskite-sepiolite deposits. *Clays Clay Miner.* **21**, 391–401.
- JONES B.F. & GALAN E. (1988) Palygorskite - Sepiolite. Pp. 631–674 in: *Hydrous Phyllosilicates (exclusive of micas)* (S.W. Bailey, editor). Mineral. Soc. Amer., Reviews in Mineralogy, **19**.
- LAMOUREUX M., PAQUET H. & MILLOT G. (1973) Evolution des minéraux argileux dans les sols du Liban. *Pédologie* **23**, 53–71.
- LANG J. & PIAS J. (1971) Morphogénèse dunaire et pédogénèse dans le bassin intramontagneux de Bamian (Afghanistan central). *Rev. Géogr. Phys. et Géol. Dyn.* **13**, 359–367.
- LEE S.Y., DIXON J.B. & ABA-HUSAYN M.M. (1983) Mineralogy of Saudi Arabian soils: Eastern region. *Soil Sci. Soc. Am. J.* **47**, 321–326.
- MACKENZIE R.C., WILSON M.J. & MASHHADY A.S. (1984) Origin of the palygorskite in some soils of the Arabian Peninsula. Pp. 177–186 in: *Palygorskite-Sepiolite: Occurrences, Genesis and Uses* (A. Singer & E. Galán, editors). Developments in Sedimentology, Elsevier, **37**.
- MARTIN DE VILADES J.L., JIMENEZ BALLESTRA R. & GUERRA A. (1987) Pedogenic significance of palygorskite in paleosols developed on terraces of the river Tajo (Spain). Pp. 535–548 in: *Geochemistry and Mineral Formation in the Earth Surface* (R. Rodriguez Clemente & Y. Tardy, editors). C.S.I.C., Madrid.
- MASHHADY A.S., REDA M., WILSON M.J. & MACKENZIE R.C. (1980) Clay and silt mineralogy of some soils from Qasim, Saudi Arabia. *J. Soil Sci.* **31**, 101–115.
- MCGRAWTH D.B. & HAWLEY J.W. (1987) Geomorphic evolution and soil-geomorphic relationships in the Socorro area, Central New Mexico. Pp. 55–67 in: *Guidebook to the Socorro Area, New Mexico* (V.T. McLemore & M.R. Bowie, editors). New Mexico Bureau of Mines & Mineral Resources.
- MCLEAN S.A., ALLEN B.L. & CRAIG J.R. (1972) The occurrence of sepiolite and attapulgitic on the southern High Plains. *Clays Clay Miner.* **20**, 143–149.
- MILLOT G., PAQUET H. & RUELLAN A. (1969) Néof ormation d'attapulgitic dans les sols à carapaces calcaires de la Basse Moulouya (Maroc oriental). *Comptes Rendus Acad. Sci. Paris*, **268**, 2771–2775.
- MILLOT G., RADIER H. & BONIFAS M. (1957) La sédimentation argileuse à attapulgitic et montmorillonite. *Bull. Soc. Géol. France* **6**, 425–433.
- MILLOT G., NAHON D., PAQUET H., RUELLAN A. & TARDY Y. (1977) L'épigénie calcaire des roches silicatées dans les encroûtements carbonatés en pays sub-aride, Anti-Atlas, Maroc. *Sci. Géol. Bull.* **30**, 129–152.
- MONGER H.C. & DAUGHERTY L.A. (1991) Neof ormation of palygorskite in a southern New Mexico aridisol. *Soil Sci. Soc. Am. J.* **55**, 1646–1650.
- MONTENAT C. (1977) Les bassins néogènes du Levant d'Alicante et de Murcie (Cordillères Bétiques orientales, Espagne) - Straigraphie, paléogéographie et evolution dynamique. *Documents Labo. Géol. Faculté des Sci., Lyon*, **69**, 345 pp.
- MUIR A. (1951) Notes on soils of Syria. *J. Soil Sci.* **2**, 163–182.
- NAHON D., PAQUET H., RUELLAN A. & MILLOT G. (1975) Encroûtements calcaires dans les alétrations des marnes éocènes de la falaise de Thiès (Sénégal): organisation morphologique et minéralogie. *Sci. Géol. Bull.* **28**, 29–46.
- NEWMAN A.C.D. & BROWN G. (1987) The chemical constitution of clays. Pp. 1–128 in: *Chemistry of Clays and Clay Minerals* (A.C.D. Newman, editor), Mineral. Soc. London. Monograph 6.
- OFFER Z.Y., ZANGVIL A. & AZMON E. (1993) Characterization of airborne dust in the Sede Boker area. *Israel J. Earth Sci.* **41**, 239–245.
- OSMOND D.A. & STEPHEN I. (1957) The micropedology of some red soils from Cyprus. *J. Soil Sci.* **8**, 19–26.
- PAQUET H. (1983) Stability, instability and significance of attapulgitic in the calcretes of Mediterranean and tropical areas with marked dry seasons. *Sciences Géologiques, Université Louis Pasteur de Strasbourg*, **72**, 131–140.
- PATIL D.N. & SURANA A.P. (1992) Origin of the calcrete deposits of Saswad-Nira area, Western Maharashtra, India. *J. Geol. Soc. India*, **39**, 105–117.
- PI-PUJOL M. D. & BUURMAN P. (1987) Authigenic palygorskite and smectite in early Paleogene paleosols of the SE Ebro basin (Catalonia, NE Spain). *Geol. Mijnbouw*, **65**, 287–296.
- RAVIKOVITCH S., PINES F. & BEN-YAIR M. (1960) Composition of colloids in soils of Israel. *J. Soil Sci.* **11**, 82–91.
- REEVES C.C. JR. (1976) *Calciche*. Estacado Books,

- Lubbock, Texas.
- REGAYA K. (1984) Les accumulations calcaires dans les limons de Matmata de la région de Gabès en Tunisie. *Sci. Géol. Bull.* **37**, 387–398.
- REGAYA K. (1992) Les croûtes calcaires de Tunisie orientale aux environs de Sousse. Signification climatique et historique. *Sci. Géol. Bull.* **45**, 99–107.
- RODAS M., LUQUE F.-J., MAS R. & GARZON M.G. (1994) Calcretes, palycretes and silcretes in the paleogene detrital sediments of the Duero and Tajo Basins, Central Spain. *Clay Miner.* **29**, 273–285.
- ROGERS L.E.R., MARTIN A.E. & NORRISH K. (1954) The occurrence of palygorskite, near Ipswich, Queensland. *Mineral. Mag.* **30**, 534–540.
- ROGERS L.E.R., QUIRK J.P. & NORRISH K. (1956) Occurrence of an aluminium-sepiolite in a soil having unusual water relationships. *J. Soil Sci.* **7**, 177–185
- SANCHO C., MELENDEZ A., SIGNES M. & BASTIDA J. (1992) Chemical and mineralogical characteristics of Pleistocene caliche deposits from the central Ebro Basin, NE Spain. *Clay Miner.* **27**, 293–308.
- SHADFAN H. & DIXON J.B. (1984) Occurrence of palygorskite in the soils and rocks of the Jordan Valley. Pp. 187–198 in: *Palygorskite-Sepiolite: Occurrences, Genesis and Uses* (A. Singer & E. Galán, editors). Developments in Sedimentology, Elsevier, **37**.
- SHADFAN H. & MASHHADY A.S. (1985) Distribution of palygorskite in sediments and soils of Eastern Saudi Arabia. *Soil Sci. Soc. Am. J.* **49**, 243–250.
- SHADFAN H., DIXON J.B. & KIPPENBERGER L.A. (1985a) Palygorskite distribution in Tertiary limestone and associated soils of Northern Jordan. *Soil Sci.* **140**, 206–212.
- SHADFAN H., HUSSEN A.A. & ALAILY F. (1985b) Occurrence of palygorskite in Tertiary sediments of western Egypt. *Clay Miner.* **20**, 405–413.
- SINGER A. (1971) Clay minerals in the soils of the southern Golan Heights. *Isr. J. Earth Sci.* **20**, 105–112
- SINGER A. (1979) Palygorskite in sediments: detrital, diagenetic or neofomed — a critical review. *Geol. Rundsch.* **68**, 996–1008.
- SINGER A. (1981) The texture of palygorskite from the Rift Valley, Southern Israel. *Clay Miner.* **16**, 415–419.
- SINGER A. (1984) Pedogenic palygorskite in the arid environment. Pp. 169–176 in: *Palygorskite-Sepiolite: Occurrences, Genesis and Uses* (A. Singer & E. Galán, editors). Developments in Sedimentology, Elsevier, **37**.
- SINGER A. (1988) Illite in aridic soils, desert dust and desert loess. *Sedim. Geol.* **59**, 251–259.
- SINGER A. (1989) Palygorskite and sepiolite group minerals. Pp. 829–872 in: *Minerals in Soil Environments* (J.B. Dixon & S.B. Weed, editors). Soil Sci. Soc. Amer. Book Series, Madison, 1.
- SINGER A. & NORRISH K. (1974) Pedogenic palygorskite occurrences in Australia. *Am. Miner.* **59**, 508–517.
- SMITH B.J. & WHALLEY W.B. (1982) Observations on the composition and mineralogy of an Algerian duricrust complex. *Geoderma* **28**, 285–311.
- STEPHEN I. (1954) An occurrence of palygorskite in the Shetland Isles. *Mineral. Mag.* **30**, 471–480.
- STRAKHOV N.M. (1970) *Principles of Lithogenesis*. Plenum Publ. Corp. New York, Oliver & Boyd, Edinburg.
- VANDEN HEUVEL R.C. (1966) The occurrence of sepiolite and attapulgite in the calcareous zone of a soil near Las Cruces, New Mexico. *Clays Clay Miner.* **13**, 193–207.
- VELDE B. (1985) *Clay minerals — A Physico-chemical Explanation of their Occurrence*. Developments in Sedimentology, Elsevier **40**.
- VELDE B. (1992) *Introduction to Clay Minerals*. Chapman & Hall, London.
- VERRECCHIA E.P. (1990) New micromorphological interpretation of nari-calcrete (Israel). Pp. 677–682 in: *Soil Micromorphology: a Basic and Applied Science* (L.A. Douglas, editor). Elsevier, Amsterdam.
- VERRECCHIA E.P. (1992) Le rôle de la sédimentation, de l'activité biologique et de la diagénèse dans l'édification des nari-calcretes de Nazareth (Galilée, Israël). *Mém. Sci. de la Terre* 92-17, Univ. P. et M. Curie, Paris.
- VERRECCHIA E.P. (1994) L'origine biologique et superficielle des croûtes zonaires. *Bull. Soc. Géol. de France*, **165**, 583–592.
- VIANI B.E., AL-MASHHADY A.S. & DIXON J.B. (1983) Mineralogy of Saudi Arabian soils: Central alluvial basins. *Soil Sci. Soc. Am. J.* **47**, 149–157.
- WATTS N.L. (1980) Quaternary pedogenic calcretes from the Kalahari (Southern Africa): mineralogy, genesis and diagenesis. *Sedimentology* **27**, 661–686.
- WIEDER M., YAIR A. & ARZI A. (1985) Catenary soil relationships on arid hillslopes. *Catena Suppl.* **6**, 41–57.
- WEAVER C.E. & BECK K.C. (1977) Miocene of the S.E. United States: a model for chemical sedimentation in a peri-marine environment. Developments in Sedimentology, Elsevier **22**, 1–234.
- YAALON D.H. (1955) Clays and some non-carbonate minerals in limestones and associated soils of Israel. *Bull. Res. Counc. Isr.* 5B-2 Sect. Bio.-Geo., 161–173.
- YAALON D.H. & SINGER S. (1974) Vertical variation in strength and porosity of calcrete (nari) on chalk, Shefela, Israel and interpretation of its origin. *J. Sed. Pet.* **44**, 1016–1023.
- YAALON D.H. & DAN J. (1974) Accumulation and distribution of loess-derived deposits in the semi-desert and desert fringe areas of Israel. *Z. f.*

- Geomorph. Suppl.* **20**, 91–105.
- YAALON D.H. & WIEDER M. (1976) Pedogenic palygorskite in some arid brown (calciorthid) soils of Israel. *Clay Miner.* **11**, 73–80.
- YAİR A. & SHACHAK M. (1987) Studies in watershed ecology of an arid area. Pp. 145–193 in: *Progress in Desert Research* (L. Berkofsky & M.G. Wurtele, editors), Rowman & Littlefield Publ.
- YAİR A., KARNIELI A. & ISSAR A. (1991) The chemical composition of precipitation and runoff water on an arid limestone hillside, northern Negev, Israel. *J. Hydrol.* **129**, 371–388.