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Petroduric and 'petrosepiolitic' horizons in soils of Namaqualand, South Africa

Horizontes petrodúricos y "petrosepiolíticos" en suelos de Namaqualand, Suráfrica
Horizontes petrodúricos e "petrosepiolíticos" em solos de Namaqualand, África do Sul

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ABSTRACT

Indurated, light-coloured 'sepiocrete' horizons have been found in Namaqualand Calcisols and Durisols. These horizons resembled calcrete but were non- to only mildly calcareous, resisted slaking in acid and alkali, and often broke with a conchoidal fracture. The presence of elevated quantities of sepiolite in the bulk-soil was confirmed by XRD analysis. The degree of induration in some these horizons suggested cementation by silica, and so in this paper the slaking properties, bulk chemistry, mineralogy and micromorphology of these horizons are compared with the typical silica-cemented, reddish-brown petroduric/duripan (*dorbank*) encountered in the region. 'Sepiocrete' horizons are chemically, mineralogically and morphologically distinct from the petrocalcic and petroduric horizons with which they are commonly associated. Micromorphology of the petroduric horizons revealed prominent illuviation in the form of oriented clay parallel to grains and crescent coatings on voids, a red matrix due to iron oxides, and translucent, isotropic amorphous silica coatings on grains and voids. In the 'sepiocrete' horizons, sepiolite appeared as a matrix of interlocking, sub-parallel fibres while the amorphous material was localised. The amorphous material was silica-rich with prominent aluminium and lesser magnesium; light brown under plane polarised light; not completely isotropic and had a lower birefringence than the sepiolite. The calcite was usually micritic, but also appeared as loose granules and as elongate crystals in a sepiolite matrix. The presence of the laminar Si-Al -rich areas on the sections suggested at the least localised duric properties and so mutual reinforcement of sepiolite and silica is possible. However, the 'sepiocrete' horizons did not meet the slaking requirements of the petroduric (*dorbank*) horizons and are distinct in appearance to the typical petroduric horizons in the region. They contained more MgO than the region's typical petroduric, and too little SiO_2 to be silcrete. While the '-crete' terminology provides a useful expression of the cemented nature of the horizon, in order to fit existing soil classification and description schemes the terms 'sepiolitic' and 'petrosepiolitic' (in the same sense as 'calcic' and 'petrocalcic') are proposed and defined. The term 'sepiolitic' would be useful in the adjectival form in petrocalcic or petroduric horizons where sepiolite is significant but not the primary cement. The genesis of the 'petrosepiolitic' horizons is likely to be essentially similar to that of petrocalcic and petroduric horizons, except for chemical differences in the matrix solutions from which secondary minerals were precipitated, dictated by the pH and evaporative evolution of the soil solution.

RESUMEN

En Calcisols y Durisols de Namaqualand se encuentran horizontes endurecidos y de colores claros denominados "sepiocretas". Estos horizontes son similares a calcretas pero no son calizos –o solo ligeramente–, resisten el colapso en ácidos y álcalis y tienen a menudo una fractura concoidal. Mediante análisis de difracción de RX se confirmó la presencia de elevadas cantidades de sepiolita. Debido a que la dureza de algunos de estos horizontes sugiere que están cementados por sílice, el objetivo de esta investigación es comparar su composición química, mineralógica y micromorfológica, así como su colapso, con las de los horizontes petrodúricos/duripanes ("dorbank") pardo-rojizos cementados por sílice que se encuentran en la región. Los horizontes "sepiocreta" se distinguen de los horizontes

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petrocálcicos y petrodúricos con los que están comúnmente asociados desde los puntos de vista químico, mineralógico y morfológico. Los horizontes petrodúricos muestran una intensa iluviación en forma de arcilla orientada paralelamente a los granos y de revestimientos crecientes en huecos; una matriz rojiza debida a óxidos de hierro; y revestimientos isotrópicos amorfos translúcidos de sílice en granos y huecos. En los horizontes de "sepiocreta" la sepiolita se encuentra como una matriz de fibras entrelazadas subhorizontales, yuxtapuesta a un material amorfo compuesto principalmente de sílice, con considerables cantidades de aluminio y menos magnesio. Éste último es pardo claro en luz polarizada paralela, no completamente isotrópico y con una menor birrefringencia que la sepiolita. La calcita es normalmente micrítica, aunque aparece también como gránulos sueltos y cristales elongados en una matriz de sepiolita. La presencia de áreas con estructura laminar ricas en Si y Al sugiere que existen propiedades dúricas localizadas, por lo que no se puede descartar un refuerzo mutuo entre la sepiolita y la sílice. A pesar de ello, los horizontes de "sepiocreta" no cumplen los requisitos de colapso de los horizontes petrodúricos ("dorbank") en la región, de los que difieren en aspecto. Contienen más MgO que los horizontes petrodúricos asociados, y no contienen suficiente SiO_2 *para ser clasificados como silcreta. Si bien la terminología "-creta" es útil para designar la naturaleza cementada de un horizonte, se proponen específicamente los términos "sepiolítico" y "petrosepiolítico" (análogos a "cálcico" y "petrocálcico") para adaptarse a los sistemas de descripción y clasificación de suelos actuales. El término "sepiolítico" podría utilizarse como adjetivo en horizontes petrocálcicos o petrodúricos en que la sepiolita no es el principal agente cementante. Probablemente la génesis de los horizontes petrosepiolíticos es similar a la de los horizontes petrocálcicos y petrodúricos, excepto por las diferencias en la composición química de las soluciones matriz a partir de las que han precipitado los minerales secundarios, regidos por el pH y por la evolución de la solución del suelo a medida que se evapora.*

RESUMO

Nos Calcisols e Durisols de Namaqualand encontram-se horizontes endurecidos e de cor clara denominados de "sepiocretas". Estes horizontes são semelhantes às calcretas, porém, não são calcários (só ligeiramente), resistem ao colapso em ácidos e álcalis e freqüentemente têm fratura concoidal. Mediante análises de difração de RX confirmou-se a presença de quantidades elevadas de sepiolita. Devido a que a dureza de alguns destes horizontes sugere que estão cimentados por sílica, o objetivo desta pesquisa é comparar a sua composição química, mineralógica e micromorfológica, assim como o seu colapso, com as de horizontes petrodúricos/duripans ("dorbank") castanho-vermelhos cimentados por sílica que se acham na região. Os horizontes de "sepiocreta" distinguem-se dos horizontes petrocálcicos e petrodúricos com os que estão comumente associados do ponto de vista químico, mineralógico e micromorfológico. Os horizontes petrodúricos mostram intensa iluviação na forma de argila orientada paralelamente aos grãos e revestimentos crescentes em vazios; matriz vermelha devida aos óxidos de ferro; e revestimentos isotrópicos amorfos translúcidos de sílica nos grãos e vazios. Nos horizontes de "sepiocreta" a sepiolita se encontra como matriz de fibras interconectadas subhorizontais sobre material amorfo composto principalmente de sílica, com quantidades consideráveis de alumínio e menos magnésio. Este material é castanho claro em luz polarizada paralela, não completamente isotrópico e com menor birrefringência que a sepiolita. A calcita é normalmente micrítica, embora aparece também como grânulos soltos e cristais alongados em matriz de sepiolita. A presença de áreas com estrutura laminar ricas em Si e Al sugere a existência de propriedades dúricas localizadas, pelo que não pode-se descartar um esforço mutuo entre a sepiolita e a sílica. Apesar disso, os horizontes de "sepiocreta" não cumprem os requisitos de colapso dos horizontes petrodúricos ("dorbank") na região, dos quais diferem também em aspecto. Contêm mais MgO que os horizontes petrodúricos associados e não contêm suficiente SiO_2 *para ser classificados como silcreta. Embora a terminologia "-creta" seja útil para designar a natureza cimentada de um horizonte, propõem-se especificamente os termos "sepiolítico" e "petrosepiolítico" (análogos a "cálcico" e "petrocálcico") para adaptação aos sistemas de descrição e classificação de solos atuais. O termo "sepiolítico" poder-se-ia utilizar como adjetivo em horizontes petrocálcicos ou petrodúricos em que a sepiolita não seja o principal agente de cimentação. Provavelmente a gênese dos horizontes petrosepiolíticos seja similar à dos horizontes petrocálcicos e petrodúricos, exceto pelas diferenças em composição química das soluções matriz a partir das quais precipitaram os minerais secundários, regidos pelo pH e pela evolução da solução do solo na medida em que se evapora.*

KEY WORDS
Calcrete, duripan, palycrete, palygorskite, sepiolite, silcrete

PALABRAS CLAVE
Calcreta, duripán, palicreta, paligorskita, sepiolita, silcreta

PALAVRAS-CHAVE
Calcreta, duripan, palicreta, paligorskita, sepiolita, silcreta

1. Introduction

Sepiolite - like its close relative palygorskite- has the potential for indurating soil horizons. Massive sepiolite has sometimes been called ‘meerschaum’, especially in the gem trade when it occurs in compact masses or nodules (Sariiz and Isik 1995) suitable for carving objects such as pipes. Palygorskite-cemented material (‘palycrete’) has been documented from the Duero and Tajo Basins in Spain and in southern Portugal (Meyer and Pena dos Reis 1985; Mas et al. 1988; Rodas et al. 1994; Stahr et al. 2000). Sepiolite, for example, has been used to strengthen mortar (Kavas et al. 2004) and the tensile strength of artificial mixtures of sand-palygorskite-calcite disproportionately influenced by the palygorskite component (Mosaddeghi et al. 2006).

Namaqualand is an arid region along the south-western coast of Africa (**Figure 1**), recognised for its high species diversity and endemism (Desmet 2007). Its low agricultural and habitation density meant that information on the soils has been sparse in comparison to other areas in South Africa (Francis et al. 2007). Singer et al. (1995) studied the mineralogy of Namaqualand soils and found pedogenic palygorskite in the clay fraction of soils inland of the escarpment, and pedogenic sepiolite prominent in the clay fraction of soils from coastal areas, a distribution attributed to the marine-influenced increase in magnesium levels. Similar conclusions were drawn by Francis (2008, p. 95-106, 137-139).

During fieldwork in the sepiolite-dominated coastal plain we noted the presence of indurated, pale-coloured horizons that resembled calcrete but were non- to only mildly calcareous and broke with a conchoidal fracture (**Figure 2**). The degree of induration in some of these horizons suggested silica-cementation on first inspection but - in contrast to the typical silica-cemented horizons found in southern Africa- they resisted slaking in both acid and alkali, reacted positively to methyl orange in the field (Mifsud et al. 1979), and showed a very strong sepiolite peak in XRD analyses of bulk soil samples. These horizons were termed ‘sepiocrete’ by Francis et al. (2007).

Materials similar to sepio-/palycrete have been encountered before in southern Africa, but have neither been classified nor studied systematically. Palygorskite-rich hardpans that macroscopically resembled calcretes but were generally non-calcareous and did not slake in 30% NaOH were documented from Botswana by Netterberg (1969), who suggested however that the cementing medium was chalcedonic and opaline silica. Other locations in South Africa with similar material - resembling calcrete but containing little or no carbonate- are the Elandsfontein fossil site in the Western Cape near the Langebaan Lagoon (Netterbeg 2003, pers. comm.), near Ebenhaeser on the road to Papendorp, the Worcester area of the Western Cape, and Oudtshoorn in the Eastern Cape.

This paper aimed to describe the micromorphology, clay mineralogy and slaking characteristics of Namaqualand ‘sepiocretes’, to determine their cementing agent(s), and to derive a name for them which could be conveniently used in horizon descriptions and classification, since sepiolite and palygorskite-rich horizons are not accommodated in the World Reference Base, Soil Taxonomy, and South African systems. While the term ‘sepiocrete’ introduced by Francis et al. (2007) provided a useful expression of the cemented nature of the horizon, to fit existing soil classification schemes and to encompass situations where the sepiolite content of the horizon may be significant but not cementing, the terms ‘sepiolitic’ and ‘petrosepiolitic’ (in the same sense as ‘calcic’ and ‘petrocalcic’) are proposed. The degree of induration in some ‘petrosepiolitic’ horizons suggested silica-cementation on first inspection, and so this paper focuses on the occurrence of amorphous silica and sepiolite in these profiles, and compares them to the more typical silica-cemented, reddish-brown petroduric/duripan (*dorbank*) horizons encountered in the region.

2. Materials and Methods

Location of study area

Sampling was done in 2002 on the coastal plain in the Buffels Marine Complex (BMC) of De Beers Consolidated Mines Ltd-Namaqualand Mines in the Kleinzee-Port Nolloth area (profile SK11, **Figure 1**), and in 2004 on the Knersvlakte (profile KNERS, **Figure 1**), a subset from Francis (2008).

The area receives about 150 mm annual rainfall, increasing southwards, with regularity during the winter months (May-August) and supplemented by coastal fogs (Desmet 2007). Rainfall is higher than average about once every 10 years, causing ephemeral rivers to flow. The vegetation is the short scrub of the Succulent Karoo biome (Desmet 2007). The soils of the region were summarized by Watkeys (1999) and Francis et al. (2007).

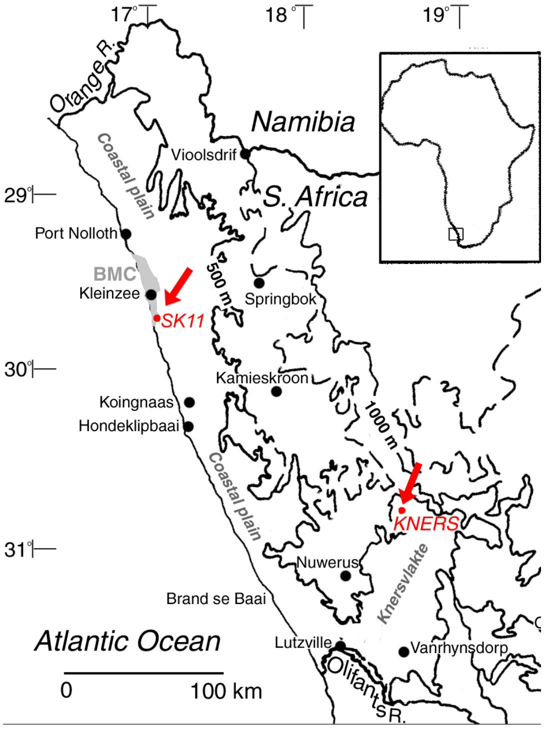


Figure 1. Location of profile SK11 within the Buffels Marine Complex (BMC) mining area near the northern border of South Africa, and the KNERS sampling site on the Knersvlakte plain.

Profile SK11 is located in an area dominated by Calcisols developed in late Tertiary marine sediments (Pether et al. 2000) adjacent to and in the sidewall of a mine excavation near 29° 42’ 06” S, 17° 42’ 13” E, on a flat plain 3 km from the sea, 60 m a.m.s.l. The Knersvlakte profile (KNERS) is located in a flat plain dominated by Durisols. The Knersvlakte is a broad low-lying plain covered by a distinctive quartz gravel pavement. It was created by the proto-Orange River around 20 million years ago (Desmet 2007) consisting of fluviatile sediments and gypsum at depth that is mined in some places. The profile is located in a borrow pit 53 km east of the Kliprand turnoff on N7, at 30° 48’ 47.3” S, 18° 43’ 25.3” E, 554 m a.m.s.l. It was associated with an old inactive heuweltjie (broad termite mound; Picker et al. 2007). The ‘petrosepiolitic’ horizons in the KNERS profile were covered by layered petroduric coatings 1-10 cm thick in some places (**Figure 2b**, **Table 1**). This was consistent with observations that in the drier northern area of Namaqualand, the petrocalcic horizon at the centre of a *heuweltjie* is sometimes partly replaced by a petroduric horizon (Ellis 2002). The sequence of horizons and soil forming processes within *heuweltjies*, with which sepiolite and palygorskite were strongly associated, was further described in Francis (2008, p. 145-197).

Methods

Four profiles were used in this study. Approximately 5 kg samples were taken of each horizon. Qualitative field tests were done in triplicate on each horizon for carbonate (HCl), Mn oxide (H_2O_2) and sepiolite (purple-pink colour of methyl orange, Mifsud et al. 1979) in the field. pH was measured in a 20 g to 50 mL soil-water mixture. Laboratory slaking tests were based on IUSS Working Group WRB (2006) definitions of petroduric, petrocalcic and fragic horizons. A fragment a few cm in diameter was submerged in water, 5M HCl or 6M NaOH and gently heated on a waterbath for four days. Samples which did not slake were subjected to alternating 5M HCl and 6M NaOH treatments.

Figure 2. Typical ‘petrosepiolitic’ material showing sepiolite veins (arrowed) and white sepiolite cutans (C). (**a**) ‘Petrosepiolitic’ KNERS/4, Knersvlakte. Hammer handle 15 cm long. (**b**) Reddish-brown petroduric coating (KNERS/1) on white ‘petrosepiolitic’ (KNERS/2), Knersvlakte. Scale 1 cm. (**c**) ‘Petrosepiolitic’ SK11/1, BMC mining area. Scale 2 cm.

Six thin sections for optical microscopy were prepared with polyester resin. Micromorphological descriptions followed Stoops (2003). Fine-grained calcite was identified by effervescence in 1M HCl under the optical microscope. Uncoated fragments and thin sections were observed before and after etching in 1M HCl using a Philips Xl30 environmental scanning electron microscope (ESEM) in low vacuum and with an energy dispersive X-ray analysis system (EDX). High vacuum SEM was done on Au-coated fragments using a Leo 1430VP SEM-EDX system. For chemical and mineralogical analysis, samples were air-dried, crushed in a pestle and mortar or milled for 5 minutes using a stainless steel ball mill and passed through a 2 mm sieve. Major element composition of bulk samples was determined by x-ray fluorescence (XRF). For x-ray diffraction (XRD) analysis, the <2 µm fraction was separated by gravity sedimentation after dispersion at pH 10 with Na_2CO_3. The 1-0.08 and <0.08 µm fractions were separated by centrifugation. The clay suspension was acidified to pH 5-7 with HCl and flocculated with $MgCl_2$. The suspension was then Mg-, Ca- or K-saturated, concentrated by centrifugation, and sedimented (or smeared to avoid cracking) onto a glass slide. XRD analyses were done with a stepsize of 0.05 degrees and steptime of 40 seconds, using a Bruker D8 Advance Powder diffractometer with graphite monochromator, and Cu Kα radiation generated at 40 kV and 40 mA. Ethylene glycol was sprayed lightly onto the surface of Mg-saturated slides.

3. Results

Slaking

The ‘petrosepiolitic’ horizons were generally non- to locally calcareous (**Table 1**) suggesting that calcite was not the primary cement. ‘Petrosepiolitic’ sample SK11/E showed partial slaking occurred after a 4-day submersion in water, similar to the petrocalcic sample SK11/9 below the ‘petrosepiolitic’ horizons (**Table 1**). In the ‘petrosepiolitic’ samples, neither HCl nor NaOH treatment resulted in slaking but partial slaking was observed when alkali and acid treatments were alternated. This is in contrast to petroduric samples from the same region, which slaked in NaOH even if they were calcareous (Francis 2008, p.54-58; **Table 1**). That the petroduric horizons did not slake in HCl also indicated that despite the typical red-brown colour of the petroduric horizons, iron oxides are not the cementing agent. The dithionite-citrate-bicarbonate extractable Fe (Mehra and Jackson 1960) content of a similar petroduric horizon in the region was only 0.4% (Francis 2008, p. 8), consistent with the range found by Chartres (1985, p. 329) for red-brown hardpans in Australia.

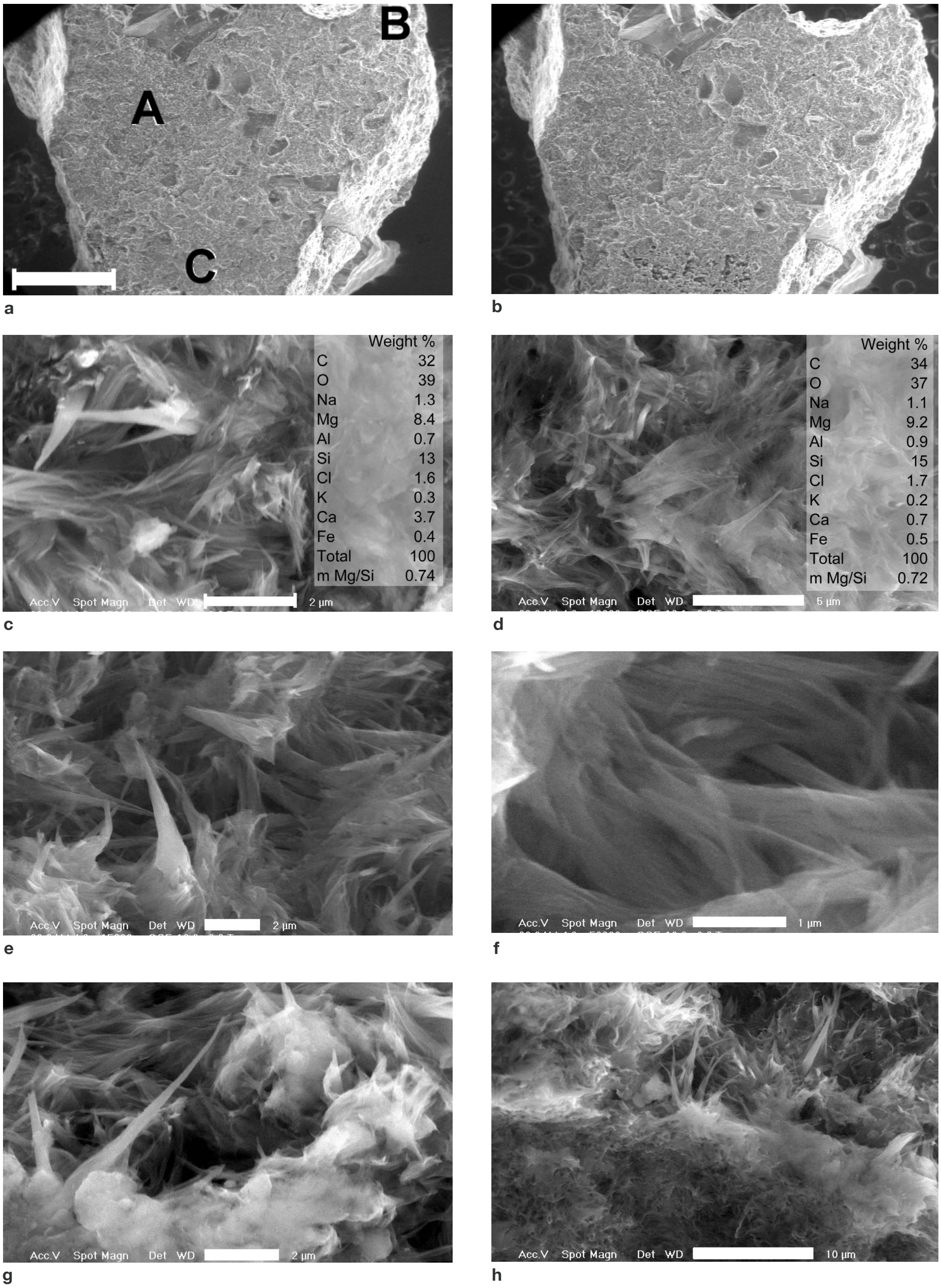
A ‘petrosepiolitic’ fragment (KNERS/4) was etched in 1M HCl for 30 seconds, by which time effervescence had ceased. Effervescence was only observed in the lower part of the fragment where pitting developed (area C in **Figure 3a**) and the sample remained very firm (**Figure 3b**), demonstrating that calcite was not the primary cement in these samples. Before etching, the calcite was present in the form of finely dispersed, <2 µm particles, consistent with the low Ca content shown by the EDAX analysis (**Figure 3c**). After etching, most of the calcite was removed (**Figure 3d**). The high Mg/Si ratio of the fibres both prior to and following etching (**Figures 3c** and **d**) is consistent with a molar Mg/Si of 0.67 for sepiolite (Stoessell 1988). The interlocking, subparallel morphology of the sepiolite fibers (**Figures 3e**, **f**) may have contributed to the induration of the horizon.

Mineralogy of clay fraction

The ‘petrosepiolitic’ samples in the Knersvlakte profile (**Figure 4**) showed strong sepiolite peaks in all size fractions. Palygorskite is a small shoulder on the mica peak, similar to that found by Singer et al. (1995). Amorphous silica, characterized by the X-ray powder diffraction pattern of opal A as a broad band at 20 to 30 degrees 2α (Smith 1998), was apparent in XRD traces of both the petroduric and petrosepiolitic of the Knersvlakte profile.

Table 1: Profile descriptions for the sepiocrete profiles SK11 and KNERS. Classifications according to Soil Classification Working Group (1991) and IUSS Working Group WRB (2006). Blank fields: not detected except for texture and consistence: not applicable. -: not tested. Slaking tests: relative scale from 0 (no slaking) to 5 (full slaking) after 4 days. Abbreviations: abun.-abundant; alt.-alternating; ang.-angular; bio.-biological; c.-coarse; f.-fine; med.-medium; mod.-moderate; occ.-occasional; O.M.-organic matter; qtz -quartz; sec.-seconds; sl.-slight; v.-very

	Depth /m	FAO (2006)	Horizon	pH 1:2.5	Munsell		Field Texture	>2mm Fragments	Structure	Consistence			Effervescence HCl	Methyl Orange reaction	Slake (0=no, 5=full)				Water absorption (sec.)	Transition	Other Features
					Dry	Moist				Dry	Moist	Wet			HCl	NaOH	H_2O	Alt. HCl/ NaOH			
'Sepiocrete' profile SK11: Pinedene Form (Orthic A - Yellow-brown apedal B - Signs of Wetness; Soil Classification Working Group, 1991). Adjacent to mine.																					
/A	0 -	A	Orthic A *(ochric).*	9.1	7.5YR 5/5	7.5YR 3/4	Med.- f. sand.		Single grain apedal.	Loose.	Loose.	Non- plastic, non- sticky.	None.						4	Abrupt, smooth.	Bio. crust, O.M., occ. droppings; many roots.
/B	0.2 -	Bw	Yellow-brown apedal B *(cambic).*	9.2	7.5YR 6/6	7.5YR 4/6	Med.- f. sand.	Few.	Weak, f. blocky.	Loose.	Loose.	Non- plastic, non- sticky.	None.						2	Clear, smooth.	Few roots.
/C	0.6 -	E	Gleyed sand *(albic).*	9.1	7.5YR 6/4	7.5YR 5/4	Med. sand.		Apedal single grain.	Loose.	Loose.	Non- plastic, non- sticky.	None.						1	Abrupt, smooth.	
/D	0.65 -	Bt	Neocutanic *(argic).*	8.7	7.5YR 5/6	7.5YR 4/6	Loamy sand.		Weak, c., ang. blocky.	Sl. hard.	Loose.	Sl. plastic, sticky.	None.						3	Abrupt, smooth.	Few roots; few clay cutans.
/E	0.7 -	Bm	'Petrosepiolitic'.	8.4									None.	Purple -pink.	2-3	2-3	2-3	-	>20		
SK11: New profile 30 m away, upper material removed by mining. Mining excavation. Horizon SK11/E continues from SK11/1.																					
/1	0.01 -	Bm	'Petrosepiolitic'.	8.7	10YR 7/3	10YR 6/4			Laminar .	V. hard.	V. firm.		Strong.	Purple-pink.	0	0-1	-	2-3	>20	Gradual, wavy.	Diffuse Mn coating some peds.
/9	0.45 - 1.1	Bkm	Hardpan carbonate *(petrocalcic).*	8.8	10YR 8/3	7.5YR 7/6			Laminar.	V. hard.	Firm-v. firm.		Strong.	Sl. - none.	3	2-3	2	-	12	Clear, wavy.	Mn spots on some peds.
/4b	1.15 - 1.5	Bk	Neocarbonate *(calcic).*	8.7	10YR 7/4	10YR 6/4	Loamy sand.		Weak., c.,blocky.	Loose.	Loose.	Sl. plastic, sl. sticky.	Mod.						1	Clear, wavy.	
/7	1.5 - 2.2	Ck	Sediment.	8.4	5Y 7/4	10YR 6/3	Sandy loam.	Local.	Mod., c., blocky.	Firm.	Loose.	Sl. plastic, sl. sticky.	Local.						3	Not reached.	
'Sepiocrete' profile KNERS: Borrow pit, truncated Knersvlakte Form (Orthic A horizon absent, petroduric horizon exposed at surface, common on Knersvlakte). Associated with 'heuweltjie' (termite mound) .																					
Profile 1																					
/A	~0.1	Bm	'Petrosepiolitic'.	-	5YR 8/2	7.5YR 6.5/6		Abun.	Massive.	V. hard.	V. firm.		Mod.-sl.; locally none.	Purple-pink.	1	0	-	2-3	5		Covered by white sepiolite cutan.
/1	~0.15	Dorbank *(petroduric)* cutan few cm thick on Kners2.		-	5YR 7/6	5YR 5/6			Laminar coating.	V. hard.	Firm.		None.	None.	0	5	-	-	>20		This sample is the cutan to Kners 2.
/2	~0.15	Bm	'Petrosepiolitic'.	-	5YR 8/3	7.5YR 6/6		Mod.	Massive.	V. hard.	Firm- v. firm.		Slight.	Purple-pink.	2-3	0	-	-	5		Many cracks, sepiolite veins.
Profile 2: From opposite side of borrow pit.																					
/5	~0.15	Bqm	Dorbank *(Petroduric).*	8.8	5YR 6/6	5YR 5/6		Abun. qtz .	Platy to blocky.	Hard.	Firm.		None.	None.	0	5	-	-	15		Abun. cracks; occ. Mn; few roots.
/4	~1	Bm	'Petrosepiolitic'.	8.7	5YR 8/2	7.5YR 6.5/6		Abun. qtz .	Massive.	V. hard.	V. firm.		Mod.-sl.; locally none.	Purple-pink.	0	0-1	-	2	5		Covered by white sepiolite cutan; many sepiolite veins.



Panel c:

	Weight %
C	32
O	39
Na	1.3
Mg	8.4
Al	0.7
Si	13
Cl	1.6
K	0.3
Ca	3.7
Fe	0.4
Total	100
m Mg/Si	0.74

Panel d:

	Weight %
C	34
O	37
Na	1.1
Mg	9.2
Al	0.9
Si	15
Cl	1.7
K	0.2
Ca	0.7
Fe	0.5
Total	100
m Mg/Si	0.72

Figure 3. SEM: 1M HCl etching (2 hours) of ‘petrosepiolitic’ sample KNERS/2. EDX analyses semi-quantitative. Mg/Si ratios molar ratios. (**a**) Before etching. Scale 1 mm; (**b**) After etching: pitting in area C; (**c**) Before etching, area B: sepiolite fibres, calcite (1 µm equant grains). Scale 2 µm; (**d**) After etching, area B: Ca removed, calcite absent (1 µm equant pits). Scale 5 µm; (**e**) After etching, area B: interlocking sepiolite fibres. Scale 2 µm; (**f**) Magnification of (e). Scale 1 µm; (**g**) After etching, area A: fibrous sepiolite, smooth amorphous silica. Scale 2 µm; (**h**) After etching, area C: fibrous sepiolite, smooth amorphous silica. Scale 10 µm.

In contrast to the 'petrosepiolitic' samples, the petroduric samples from the same profile showed broad, low peaks for the silicate clay minerals. This characteristic was noted by both Flach et al. (1969) and Blank and Fosberg (1991) for petroduric horizons, who attributed it to inhibited orientation by disordered siliceous coatings.

The <2 µm fraction of partially slaked 'petrosepiolitic' samples (KNERS/4) were milled and analysed. The HCl treatment caused a significant broadening and reduction in intensity of the sepiolite peak in comparison to the NaOH treatment (**Figure 4**), suggesting the sepiolite was partially destroyed by the acid attack (González et al. 1984; Dékány et al. 1999). The amorphous silica rise was also slightly reduced.

In profile SK11 (**Figure 5**), the 'petrosepiolitc' sample SK11/E that slaked partially after prolonged soaking in water (**Table 1**) contained monomineralic sepiolite in the clay fraction. The other horizons in the profile (petrocalcic and cambic) contained smectite, kaolinite and mica in addition to sepiolite. Palygorskite appeared to be a minor constituent, with the 0.664 nm peak best defined in the <1 µm fraction. Amorphous silica did not appear in the clay fraction, in contrast to the Knersvlakte profile (**Figure 4**).

Micromorphology

• *Petroduric samples in the Knersvlakte profile*

The micromorphology of the petroduric horizons resembled that of other similar horizons in Southern Africa (Ellis 1988; Francis 2008). The petroduric samples had vughy microstructure, where voids and channels variably occupied 5-20% across a ped, and a coarse/fine (c/f) related-distribution (limit 5 µm) that was chito-gefuric to close porphyric, with a coarse/fine ratio of 8:1. The micromass was dominated by the reddish orange colour imparted by the Fe (hydr)oxides, with strongly oriented clay more prominent than amorphous silica in many places (**Figure 6**) giving a dominantly granostriated b-fabric. The amorphous silica was generally clear, yellowish or in some cases was the colour of the Fe, and isotropic. Illuviation of clay has been a dominant soil forming process, with strong orientation of clay parallel to grains and crescent coatings on the lower part of voids (**Figures 6a-b**). The silica was generally concentrated on the void side of the clay coatings (**Figures 6a-b**), similar to that described by Litchfield and Mabbutt (1962) for 'red-brown hardpans' in Western Australia. This suggested that clay illuviation had occurred before silica precipitation. Laminated and layer-coated nodules and aggregates were present in KNERS/5 (**Figure 6c-d**), which appeared remarkably similar to the compound 'glaebular aggregates' from silcretes in the Riversdale-Albertina area (Summerfield 1983a, p. 903).

• *'Petrosepiolitic' samples in the Knersvlakte profile*

These had a weakly separated granular to massive microstructure, with granules 0.6-0.05 mm diameter, and vughs approximately 2-5% of ped (**Figures 7** and **8**). The coarse/fine (c/f) related-distribution (limit 5 µm) was open porphyric, with a c/f ratio of 1:8. The micromass was speckled grey-yellow, consisting of interstitial sepiolite (**Figure 7**) and finely dispersed grey calcite giving a crystallitic b-fabric. Calcite pendants and cappings were present in the KNERS profile. It was sometimes difficult to distinguish sepiolite from silica with certainty under the optical microscope, given the low birefringence of sepiolite (Mees 2010). The darker limpid material arrowed in **Figure 8** had a lower birefringence than the areas labelled as sepiolite in the same figure, which suggested that it could be amorphous silica. Elemental mapping of a similar feature (**Figure 9**) showed that the amorphous laminar area (L) was poorer in Mg than the clearly Mg-Si rich fibrous areas. The laminar areas were composed dominantly of Si, with secondary Al and less Mg.

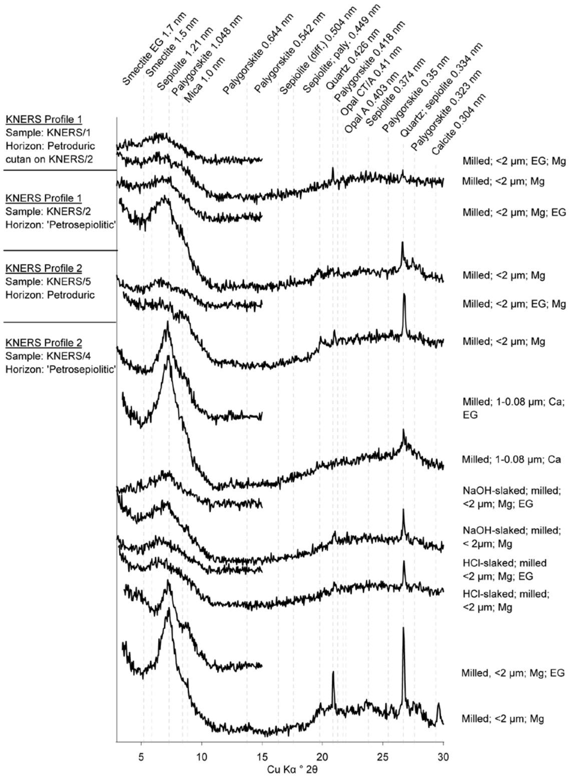


Figure 4. XRD patterns of Mg- or Ca- saturated clay fractions from the Knersvlakte profile KNERS. Diff: diffuse; EG: ethylene glycol.

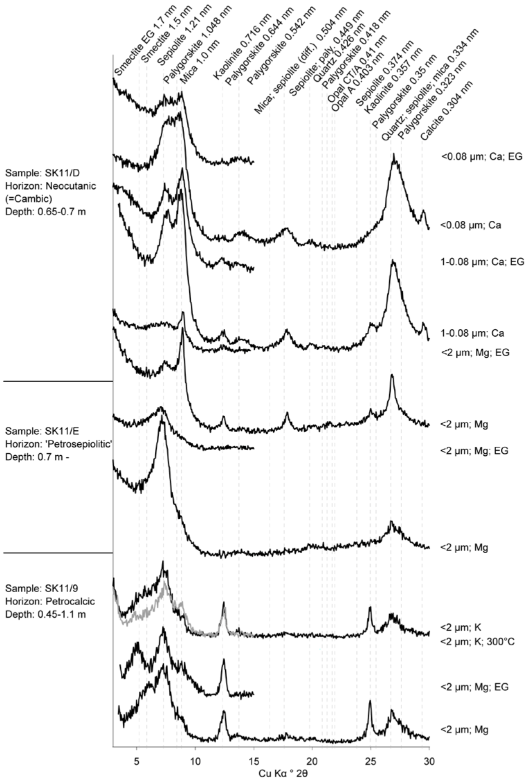


Figure 5. XRD patterns of Mg-, K- or Ca- saturated clay fractions from profile SK11. Diff: diffuse; EG: ethylene glycol.

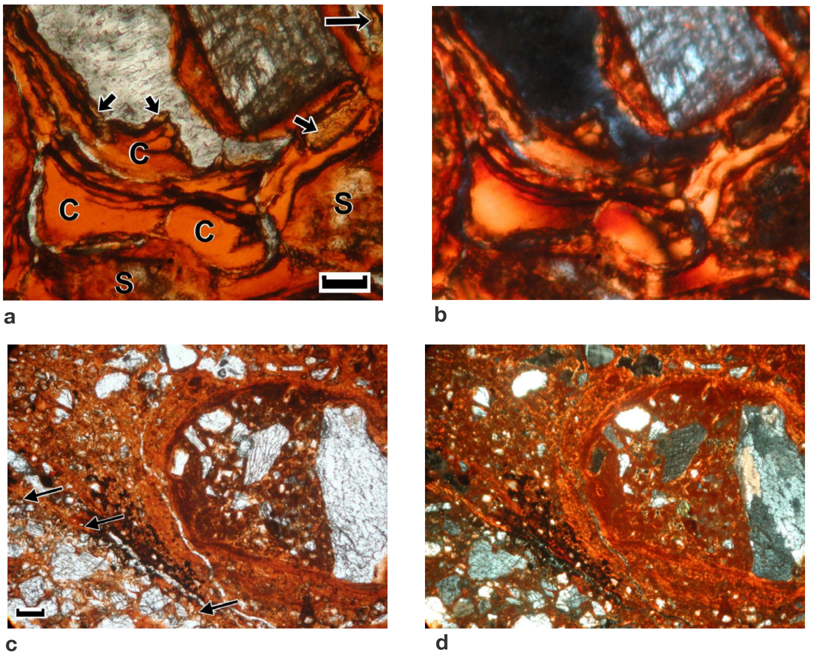


Figure 6. Typical micromorphological views of petroduric (dorbank) horizons from the Knersvlakte. Way-up is top of page. (**a**) Silica (S), limpid crescent clay coating (C), and amorphous silica (arrowed) on the void-side of clay coatings. KNERS/1, PPL. Scale 0.1 mm; (**b**) Same view as (**a**), XPL; (**c**) Portion of complex aggregate (border with matrix arrowed). KNERS/5, PPL. Scale 0.2 mm; (**d**) Same view as (**c**), XPL.

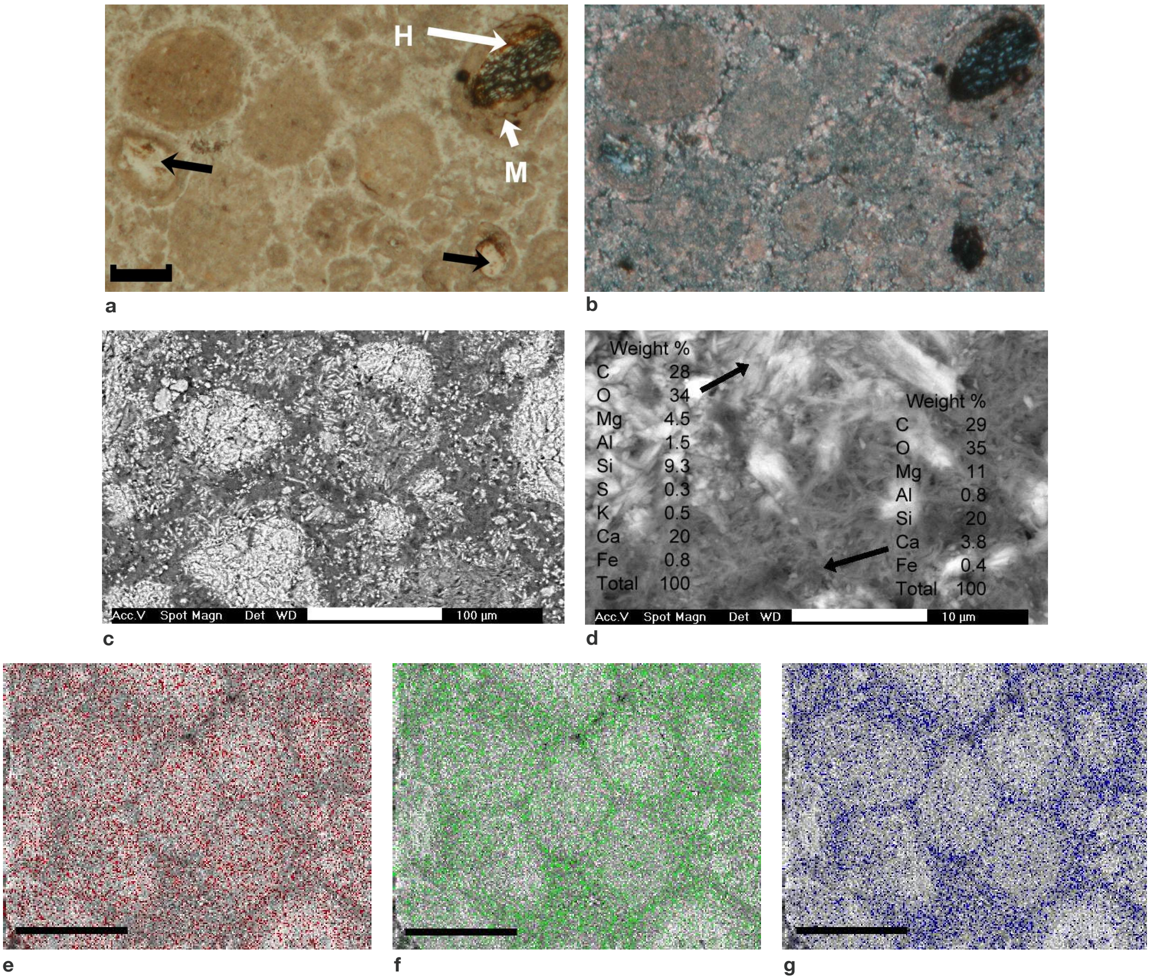


Figure 7. Images of 'petrosepiolitic' thin sections. Way-up is top of page. (**a**) KNERS/4, PPL. Granular microstructure; hematite (H)-micrite (M) compound coating on detrital grain and limpid sepiolite nodules (Mees 2010), black arrows. Scale 0.2 mm; (**b**) Same view as (**a**), XPL. Prolate calcite crystals project into voids; (**c**) SEM: calcium-rich granules (white) in fibrous sepiolite matrix (grey). Scale 100 µm, KNERS/2; (**d**) Magnification of (**c**). Scale 10 µm; (**e**) Sample KNERS/2. SEM-EDAX image showing calcium distribution, scale 200 µm; (**f**) Sample KNERS/2. SEM-EDAX image showing magnesium distribution, scale 200 µm; (**g**) Sample KNERS/2. SEM-EDAX image showing silica distribution, scale 200 µm.

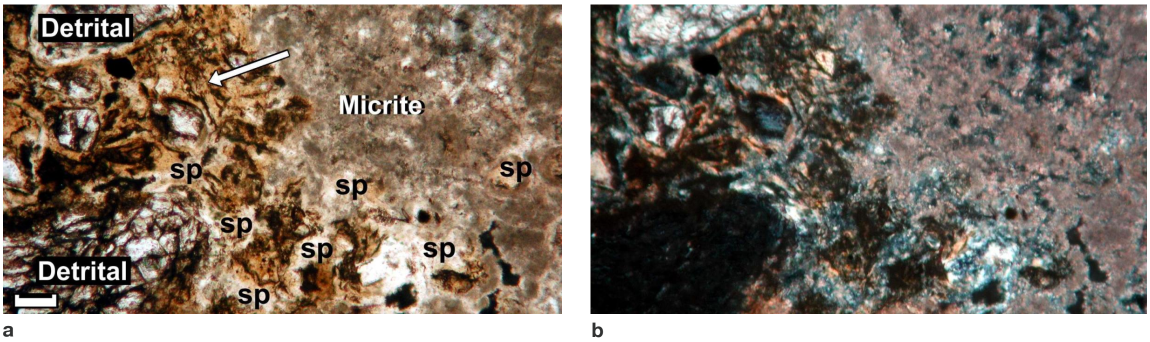


Figure 8. Images of sepiolite matrix in 'petrosepiolitic' thin sections sample KNERS/4. Micrite zone effervesced with 10% HCl. Sp: sepiolite. White arrowed area equivalent to lamellar area 'L' in Figure 9. Way-up is top of page. (**a**) Scale 0.1 mm, PPL; (**b**) Same view as (**a**), XPL.

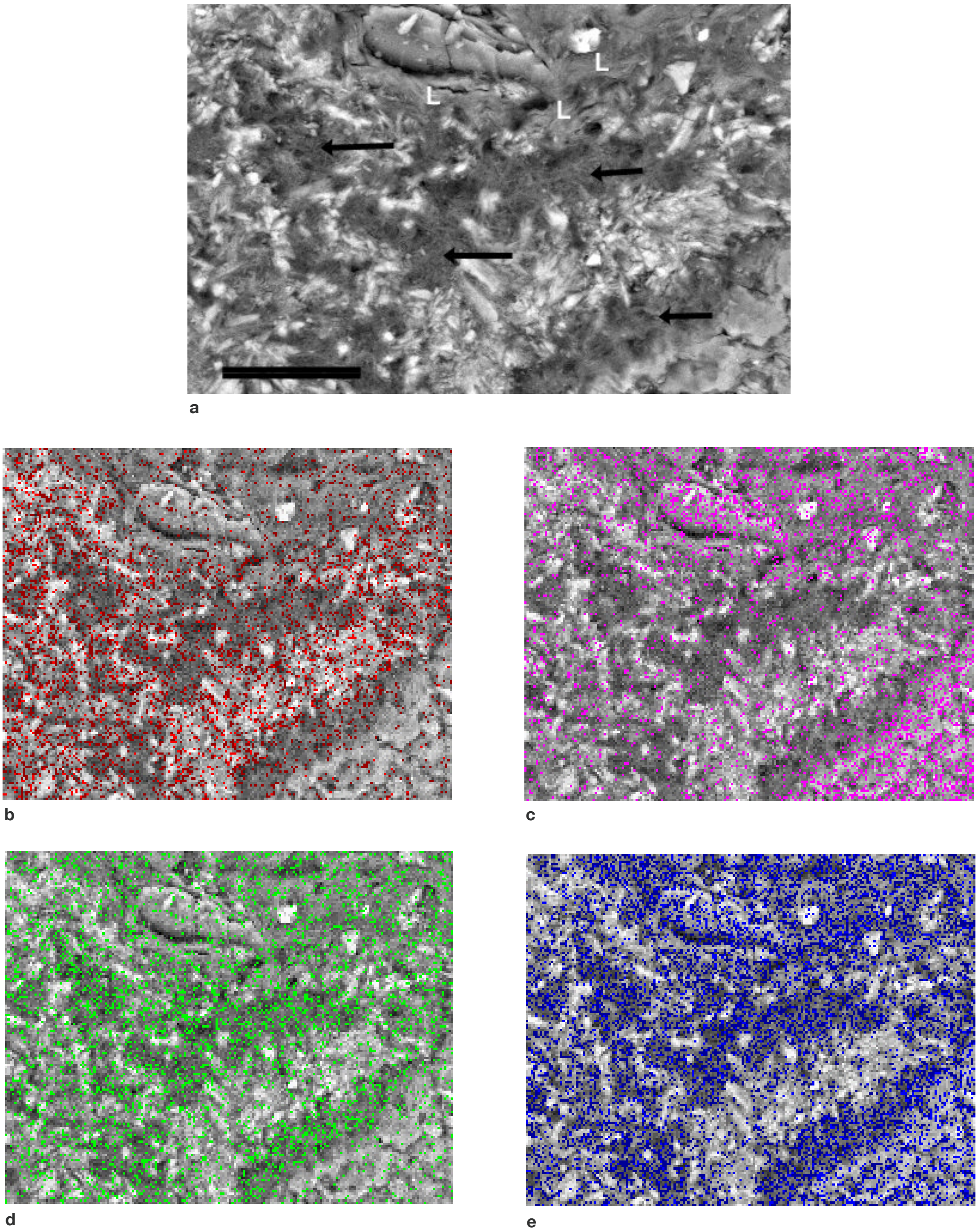


Figure 9. SEM-EDX images of matrix composition of ‘petrosepiolitic’ sample KNERS/2. (**a**)‘L’: lamellae. Fiber zones arrowed. Composition shown in Figures b-e. Scale 20 µm; (**b**) Ca distribution; (**c**) Al distribution; (**d**) Mg distribution; (**e**) Si distribution.

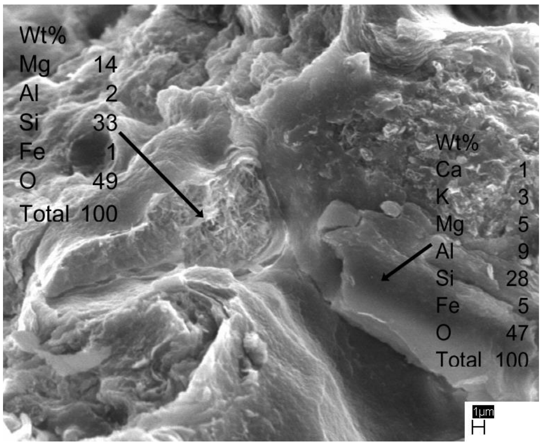


Figure 10. SEM image of sepiolite-filled void and amorphous Al-Si rich coating in ‘petrosepiolitic’ sample KNERS/4. EDAX analyses semi-quantitative, beam diameter 1 µm. Scale 1 µm. Au-coated.

Pedofeatures similar but lighter in colour to the laminar Si-Al-Mg -rich areas in **Figures 7**, **9** have been described from Sardinia, Italy, in >2.7 Ma buried paleosols (Usai and Dalrymple 2003), comprising different phases of silica and ≈ 25% Al_2O_3, 5% MgO, 2 to 4.6% Fe_2O_3 and 2% CaO, attributed to chemisorbed impurities or to analytical imprecision. Singh et al. (1992) noted cementation in Australian silcretes composed of very fine-grained kaolinite (<5 µm) and amorphous silica almost homogeneously mixed at a sub-micron scale, leading to gel-like optical properties and almost uniform Al-silicate composition. The gel-like texture in the ‘petrosepiolitic’ sample KNERS/4 is evident in **Figure 10**, where it surrounds a void containing well crystalised sepiolite needles.

Several examples of etched quartz grains are present in close proximity to sepiolite in both the ‘petrosepiolitic’ profiles SK11/1 and KNERS/4 (**Figure 11**), suggesting the localised dissolution and redistribution of silica within the profile. Silica is visible closely associated with sepiolite in **Figures 3g, h**. The association of sepiolite with silica has been noted before, with the source of silica often proposed to be the dissolution of existing silicates (Reheis et al. 1992; Vaniman et al. 1994; Brock and Buck 2005). Blank and Fosberg (1991) observed sepiolite crystals radiating outward from laminae of opaline silica in duripans in Idaho, and suggested that some sepiolite formed via the addition of Mg to opal. Hay and Wiggins (1980) observed opal replacing sepiolite (and calcite) in calcrete of the southwestern United States. Bustillo and Alonso-Zarza (2007) noted the pseudomorphic replacement of sepiolite by opal in deposits in the Madrid Basin, Spain, which preserved the fibrous microstructure and striated birefringence of the sepiolite. Bustillo and Bustillo (2000) suggested that silicification could occur as a function of the sepiolite precipitation as initial precipitation of sepiolite depleted the solution in Mg.

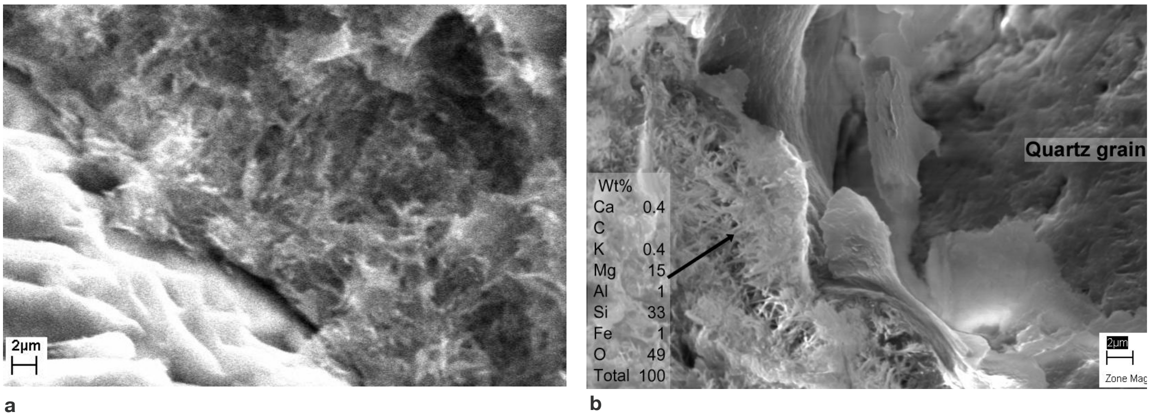


Figure 11. SEM images of pitted quartz grains and fibrous sepiolite in surrounding matrix. Samples Au-coated. (**a**) Sample SK11/1. Scale 2 µm; (**b**) Sample KNERS/4. EDAX analyses semi-quantitative, beam diameter 1 µm. Scale 2 µm.

The open porphyric c/f related-distribution across much of the 'petrosepiolitic' horizons suggested that the sepiolite matrix is more similar to that of ionically bonded calcite and gypsum, which cement by the growth and interlocking of authigenic crystals, than it is to covalently bonded silica, iron or aluminium cements which produced close porphyric related-distribution patterns (Chadwick and Nettleton 1990), as were seen in the petroduric horizons in **Figure 6**.

Genesis

Although the 'petrosepiolitic' materials investigated were enriched with sepiolite in large quantities, they generally contained accessory carbonate and/or amorphous silica and occurred in an environment where petrocalcic (often with sepiolite as an accessory mineral) and petroduric horizons have been widely found (Francis et al. 2007). Consequently, the genesis of 'petrosepiolitic' horizons is likely to be similar to that of petrocalcic and petroduric horizons, except for chemical differences in the matrix solutions from which secondary minerals were precipitated.

Sepiolite and palygorskite occur in arid soils, particularly associated with calcretes (Vanden Heuvel 1964; Hay and Wiggins 1980; Watts 1980; Verrecchia and Le Coustumer 1996; Hirmas and Allen 2007). Large accumulations of sepiolite are more common in arid-region alkaline lake sediments such as in the Tertiary Madrid Basin (Armenteros et al. 1995), the Amboseli Basin (Kenya/Tanzania) near Kilimanjaro (Stoessell and Hay 1978) and Tunisian sequences (Jamoussi et al. 2003; Zaaboub et al. 2005). Authigenic Na-sepiolite (loughlinite) has been found in pans in the Northern Cape (Roelofse and Roelofse 2011). Stahr et al. (2000) suggested an intermittent playa lake environment for palycrete formation in southern Portugal. Rodas et al. (1994) attributed palycrete in central Spain to the chemical evolution of alkaline phreatic waters moving through a semi-arid alluvial fan sediments.

Singer and Norrish (1974), considering occurrences of palygorskite in Australian soils, suggested that a soil solution having a similar composition to that of lakes from arid regions where palygorskite typically occurs, would itself constitute a suitable medium for palygorskite formation. Bouza et al. (2007) concluded that the association of calcite, fluorite, sepiolite, and possibly opal-CT in Argentinian Aridisols indicated a successive precipitation of these minerals under alkaline conditions during evaporation. The soil mantle in Namaqualand is analogous to an evaporative basin in that it loses more water by evaporation than it does by hydraulic flow, evident in the accumulation of evaporite minerals at the surface. Lateral subsurface water movement is suggested by the presence of eluvial and bleached horizons (Francis et al. 2007, p.596-597) as in profile SK11 in **Table 1**. Buol et al. (1997) suggested eluvial horizons in arid region soils may reflect the rainfall of the extreme, rather than the average, years-consistent with the extreme rainfall every decade causing the regions's ephemeral rivers to flow.

Using increasing Cl^- activity as a proxy for evaporation on the Namaqualand coastal plain, Francis (2008, p. 123) attributed the large quantities of sepiolite to increasing Mg^{2+} activity relative to Ca^{2+} and a decrease in HCO_3^-, due to the Mg-dominated marine-influenced initial solutions according to the Hardie Eugster model (Eugster and Jones 1979). It is consistent with Wang et al.'s (1993) model of calcrete and associated sepiolite genesis.

The effect of pH on mineral solubility would also help explain the relationships between (petro) calcic, '(petro)sepiolitic' and (petro)duric soils and their intergrades. It has been shown to be important for the genesis of calcrete-silcrete intergrades in the Kalahari (Nash and Shaw 1998; Kampunzu et al. 2007). Francis (2008, p. 134-138) found that even the lowest Mg^{2+} and H_4SiO_4 activity encountered on the Namaqualand coastal plain was sufficient for sepiolite saturation, but only given an appropriate environmental pH. Since the sepiolite-containing horizons were commonly also calcareous, the pH of these soils is low enough to promote the precipitation of silica in solutions entering these horizons. The buffering effect of sepiolite at pH 8.6 (Martínez-Ramírez et al. 1996) could have augmented that of carbonates in promoting silica precipitation. In addition, water retention by sepiolite due to its high water-holding capacity could also have played a role in arresting silica migration.

F. Netterberg (pers. comm., 2003) suggested that some 'petrosepiolitic' material may have originated as decalcified calcrete. Evidence in support of this hypothesis are the presence of calcic pendants and cappings from the Kners profile indicating mobilisation of calcite; and in profile SK11 the calcic horizons occurred below the sepiolite-rich horizons (**Table 1**), which suggested preferential leaching of calcite to the lower part of the profile.

Classification

The presence of the laminar Si-Al -rich areas on the 'petrosepiolitic' horizons sections suggested at the least localised duric properties. However, the 'petrosepiolitic' horizons did not meet the slaking requirements for petroduric horizons in the WRB, USDA and the South African classification systems. Also, they contained more MgO than typical petroduric *dorbank* (**Table 2**), and too little SiO_2 to be classified a 'silcrete' after Summerfield (1983b) and Nash and Shaw (1998), which required more than 85% SiO_2. Additionally, the sepiocrete horizons did not contain the crystalline forms of silica associated with 'silcrete' (Summerfield 1983a; Gutiérrez-Castorena and Effland 2010). Rodas et al. (1994) defined palycrete as generally having more than 65% palygorskite. XRD analysis of palycrete bulk samples showed a palygorskite peak (Stahr et al. 2000), similar to the XRD analysis of bulk sepiocrete.

We therefore propose the following criteria for defining the sepiolite-bearing materials: 'Sepiolitic' horizons contain sepiolite in amounts great enough for it to be detected by XRD in the bulk soil. If the horizon is in addition cemented to such a degree that (a) it has an extremely hard consistence when dry, so that it cannot be penetrated by spade or auger; and (b) roots cannot enter except along vertical fractures have an average horizontal spacing of 10 cm or more and which occupy less than 20 percent (by volume) of the layer; and (c) less than 50% by volume will slake in acid (so cannot be clas-

Table 2: Selection of XRF analyses of petroduric and 'petrosepiolitic' horizons from the Namaqualand area

	Petroduric *(Dorbank)*		`Petrosepiolitic'			Sepiolite
	<2 µm ^{*a}	<2 µm ^{*b}	<2 µm ^{*c}	BULK ^{*d}	BULK ^{*e}	'Ideal' ^{*f}
Al_2O_3	12.2	10.6	3.74	6.87	2.22	-
CaO	4.67	2.85	2.55	13.1	13.3	-
Fe_2O_3	5.31	5.49	2.27	1.92	1.00	-
K_2O	2.20	2.32	2.02	2.32	0.71	-
MgO	4.73	4.45	21.9	9.8	14.0	24.89
MnO				0.07	0.05	-
Na_2O	2.52	1.17	0.59	1.63	1.38	-
P_2O_5	0.15	0.11	0.07	0.11	0.19	-
SiO_2	56.6	64.6	56.9	54.1	57.0	55.65
TiO_2	0.46	0.59	0.16	0.42	0.24	-
H_2O^-				2.02	2.40	-
LOI	11.8	8.61	10.7	4.06	4.37	19.46
Total	100.8	100.8	101.0	96.4	96.8	-
molar Mg/Si	0.12	0.10	0.57	0.27	0.37	0.67

^{*a} KNERS/5, milled, Mg-saturated. ^{*b} KV196T/2, crushed, Mg-saturated (Francis 2008).

^{*c} SK11/E, crushed, K-saturated. ^{*d} SK11/1. ^{*e} KNERS/4. ^{*f} Stoessel (1988) sified as petrocalcic), nor in alkali and only partially on alternating (and so cannot be classified as petroduric); then the term 'petrosepiolitic' would be appropriate. The terms could easily be extended to accommodate palygorskite-containing soils.

The addition of an orderly term for soils where these minerals are abundant would be useful to soil users in these regions, for example Philander and Rozendaal (2011) described the difficulties of extracting heavy minerals from 'sepiocrete' further south along the Namaqualand coastal plain, and Neaman and Singer (2004) outlined the effects of palygorskite, including 'palycrete' on soil properties. Ouhadi and Yong (2003) outlined the need to classify marly soils based on their sepiolite/palygorskite content due to the effect of large quantities of these on the geoenvironmental and geotechnical character of soils.

4. Conclusions

The genesis of these sepiolite-cemented horizons have enough in common with other evaporite hardpans (petroduric, petrocalcic and petrogypsic) to be considered as one further, mineralogically specific manifestation of pedogenic cements. They are, however, chemically, mineralogically and morphologically distinct from the petrocalcic and petroduric horizons with which they are commonly associated. While the '-crete' terminology provides a useful expression of the cemented nature of the horizon, to fit existing soil classification schemes, the terms 'sepiolitic' and 'petrosepiolitic' are proposed. The term 'sepiolitic' would be particularly useful in the adjectival form, where i) it could be used for intergrade horizons where the horizon is silica- and/or calcite-cemented but has a significant sepiolite content, and ii) it would be possible to more easily describe those horizons where the sepiolite content was sufficient to have an effect on soil properties but where the horizon fulfills higher ranking diagnostic criteria.

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