

Pedogenic Palygorskite Occurrences in Australia

ARIEH SINGER

*Department of Soils and Water, The Hebrew University of Jerusalem,
Rehovot, Israel*

KEITH NORRISH

*Division of Soils, CSIRO,
Glen Osmond, South Australia 5064*

Abstract

Palygorskite forms crusts or cutans on the surfaces of soil peds from two regions in Australia, Alice Springs (Northern Territory) and Eastern Riverina (New South Wales). Electron microscope examination of replicas prepared from cutans showed the palygorskite fibers to be arranged in parallel orientation within thick mats. Fibers were occasionally observed on top of coarse-grained skeleton grains. X-ray diffraction showed that, while the cutans contain almost exclusively palygorskite, the mineral is absent from within the soil peds. The chemical composition of crusts, determined by electron microprobe analysis, corresponds to that of Mg-rich palygorskite. Chemical examination of transects through crusts indicates that while the palygorskite content of the Northern Territory crusts is fairly constant, the mineralogically pure palygorskite in the periphery of the Riverina crust is becoming gradually intermixed with illite within the crust.

The equilibrium constant of a pure Australian palygorskite (Mt. Flinders) was determined by dissolution in distilled water under air and nitrogen. The standard free energy of formation ($a\Delta F_1^\circ$) is -1131.5 kcal/mole. The information from the solubility experiments was used to construct stability diagrams showing the stability of palygorskite as a function of pH, pMg, and pSi. The composition of 1:1 water extracts from soil horizons containing palygorskite coatings, plotted onto one of these diagrams, falls within the stability field for palygorskite. It is concluded that soil water with a suitable composition, and not only lake water, can satisfy the conditions required for the formation of palygorskite, and that the pedogenic formation of that mineral is therefore feasible.

Introduction

The very common association of palygorskite ($2\text{MgO}\cdot 3\text{SiO}_2\cdot 4\text{H}_2\text{O}$) with lacustrine sediments has for a long time supported the belief that the non-hydrothermal formation of this clay mineral is feasible only under the alkaline conditions typical of lakes from arid or semi-arid areas. Millot (1964) summarized this belief when he stated that this mineral does not exist in soils but is a neof ormation characteristic for sedimentation basins with an alkaline character.

The first part of this latter statement needed revision some time ago when reports of palygorskite occurrences in soils from several parts of the world became known. In the Near East, Muir (1951) reported the presence of palygorskite in brown calcareous desert soils from Syria, and Barshad *et al* (1956), Yaalon (1955), Ravikovitch, Pines, and Ben-Yair (1960), and Singer (1971) from calcareous soils in Israel. A decrease in the palygorskite content

of the clay during the transition from calcareous Pleistocene deposits into recent red calcareous clay soils in Cyprus was reported by Osmond and Stephen (1957). Elgabaly (1962) describes two soil profiles containing palygorskite in the western desert of Egypt. The occurrence of palygorskite in Terra Rossa soils from the south of France was noted by Michaud, Cerighelli, and Drouineau (1945). Pickering has shown that palygorskite is a common component of the desert loams of Australia (Stace *et al*, 1968).

In most of these soils, however, the palygorskite seemed to be inherited from sedimentary parent material of lacustrine or brackish water origin which contained palygorskite. Moreover, the mineral appeared to be unstable in most soils and to persist only where leaching was restricted, primarily in arid areas. In areas with higher rainfall it seemed to disintegrate rapidly and to disappear from the solum even where it was present in the soil parent material (Gremillion, 1965; Yaalon *et al*, 1966).

More recent reports on palygorskite occurrences in soils have raised the question of the pedogenic formation of this mineral. Van den Heuvel (1966) was the first to suggest this possibility for soils formed on a relict basin fill near Las Cruces, New Mexico. In desert soils of Iraq, Al-Rawi and Sys (1967) pointed also to that possibility. Millot, Paquet, and Ruellan (1969) and Paquet *et al* (1969) believe they have proved pedogenesis of palygorskite in soils from the arid and semi-arid plains of Morocco since they could not detect this clay mineral in any of the parent materials from these soils.

In Australia peculiar occurrences of palygorskite in soils have been reported (Beattie and Haldane, 1958; Beattie, 1970) which appear to support this hypothesis. Palygorskite occurs in the form of cutans or crusts coating soil aggregates. The mineral is absent within the aggregates, strongly suggesting authigenic formation. These occurrences prompted a closer study of the conditions for palygorskite formation.

The hypothesis to be examined in this study is whether a soil solution, having a similar chemical composition to that of some lakes in which the mineral forms, could not also constitute a suitable medium for its formation. Except for Lake Eyre (Taylor and Pickering, 1962), however, no data are available on the composition of water from palygorskite-containing lakes, and even if existing they would have been of little help since it is highly improbable that the water of these lakes would be in equilibrium with palygorskite only. The only promising approach, therefore, appeared to be the experimental determination of the stability fields for pure palygorskite and, based on them, the evaluation of the soil solutions.

The study therefore is divided into two parts: (a) a close examination of the occurrence of palygorskite in some Australian soils; and (b) the determination of the equilibrium constants for a pure Australian palygorskite and the evaluation of the soil chemistry on the basis of the stability fields for this palygorskite.

Description of Soils with Palygorskite Occurrences

The palygorskite coatings were observed in two major (and fairly different) soil groups:

(a) *Calcareous Red Earths, near Alice Springs, in the Northern Territory.*

The soils are situated on the southern and northern margins of the Burt plain, adjacent to the MacDonnell

Ranges, and have been described by Jackson (1962) and Litchfield (1969). The soils occur on alluvial grit and also on weathered pediments consisting of Precambrian schists and gneisses. The climate is arid with an average annual rainfall of 255 mm. The soils are red-brown to red, with sandy-loam surfaces changing gradually with depth to clay subsoils with a prismatic structure. Concretionary carbonate (calcrete) occurs at a depth of about 160–180 cm. Below that the soil grades into weathered rock or alluvial grit. Horizons above the calcrete are acid in reaction. Next to and below the calcrete, soil reaction is alkaline. Halite and gypsum are occasionally also present in the subsoil. Clay minerals identified include kaolinite, illite, and occasionally smectite and randomly interstratified varieties. Clay-sized hematite is the most common ore mineral. The white crusts of palygorskite occur below the calcrete layer, coating the soil aggregates and weathered grit fragments.

(b) *Red Earth and Red-Brown Earth Soils, in the Eastern Riverina, New South Wales.*

The soils, on gently undulating uplands and sloping plains north and south of the Murrumbidgee River, have been described by Beattie and Haldane (1958) and Beattie (1970). They have developed from layered deposits of clay occurring as a blanket over diverse substrates, mainly Ordovician metasediments including shale, slate, and quartzite into which large granite masses had been intruded. Butler (1956) proposed an aeolian origin for this material and gave it the name of "parna." The present local climate is warm temperate, with a mean annual rainfall of 530 mm. The soils are subplastic clays with secondary calcareous deposits. Beattie (1970) distinguished three consecutive layers, with the paleosols which developed from them. Surface exposures of the various paleosols are frequent. Barite (BaSO_4) and possibly witherite (BaCO_3) are sometimes found associated with the calcite. Magnesian calcite and dolomite sometimes supplement calcite. Clay minerals identified include kaolinite, illite, and smectite. The crusts occur on the peds of some of these paleosolic layers, particularly the middle one, and are often associated with mangans.

Description of the Coatings

The palygorskite crusts are visible as a white, shiny material covering fracture surfaces of soil peds, and sometimes also coating rock fragments. Their thickness rarely exceeds 0.3–0.4 mm. When less developed

they form fine transparent films (cutans)¹. In the Northern Territory samples, the crusts appear as small specks, while in the Eastern Riverina they may cover surfaces up to several square centimeters, and are associated with mangans. Though close to carbonate concentrations, particularly in the Eastern Riverina, they were never observed in the direct proximity of these concentrations.

Microscopic Examinations

Thin sections were prepared from soil peds with crusts. Under the petrological microscope the interior of the peds is seen to consist of skeleton grains, primarily quartz, embedded in a matrix consisting of clay and silt-sized material (Fig. 1). The coatings are clearly discernible on the periphery of the soil ped. They are distinguishable from the interior by their fairly homogeneous particle size and their optical characteristics which resemble those of smectite (Fig. 2). Preferred orientation appears to exist only to a limited degree. The transition to the mass of the ped appears sharp. The coatings are not continuous but seem to develop only on major fracture planes. On internal fissure planes they were not present.

Transmission electron micrographs of palygorskite coatings were obtained by dispersing material scraped off ped surfaces. The palygorskite fibers are clearly evident and dominate the field (Fig. 3). Very minor amounts of other minerals are also present.

Replicas of ped surfaces were prepared in order to examine the coatings in the undisturbed state. The replicas were prepared both from surfaces where the crusts were clearly visible, and also from surfaces where the coatings were only suspected. In the crusts the palygorskite fibers are arranged in the form of thick mats (Fig. 4). The mats are not continuous units but are subdivided into approximately parallel strips. Within each strip the fibers have again a more or less parallel orientation. The orientation of the fibers in adjacent strips is at a sharp angle. Some intertwining of differently oriented fibers occur where strips overlap. On surfaces with cutans only, the fibers are less numerous, less oriented, and many other minerals are interspersed amongst them. Occasionally palygorskite fibers were observed situated on top of coarse-sized skeleton grains (Fig. 5). Using this replica technique, palygorskite was observed on the surfaces of peds from some soils where there were no coatings visible to the eye. It is likely that the paly-

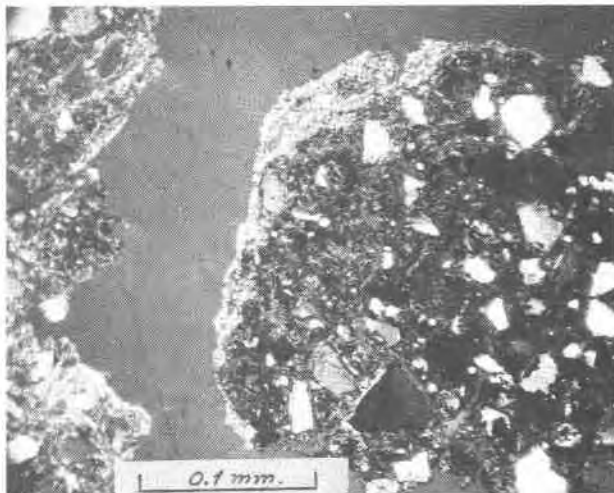


FIG. 1. Photomicrograph of a soil ped cross-section from a Red Calcareous Earth. The palygorskite crust is visible at upper center. Within the ped quartz skeleton grains are embedded in a clay matrix.

gorskite layer is only easily visible when it is relatively well developed and many soils may have a thin coating which would not be observed by normal mineralogical techniques.

X-Ray Diffraction Examination

Because of the difficulty in obtaining sufficient material for diffractometry, the X-ray diffraction examinations were carried out with a 57.5 mm diameter camera (modified by Norrish to record low-angle reflections) and Co radiation. Such exam-



FIG. 2. Detail from Figure 1. The crust is seen to consist of somewhat oriented clay particles, with optical characteristics resembling those of smectite. Transition from the crust to the mass of the ped appears sharp.

¹ Terminology after Brewer (1964).

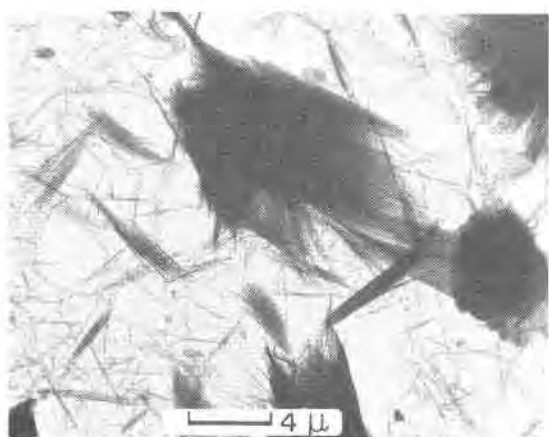


FIG. 3. Electron transmission photograph of material scraped off a crust from a Northern Territory soil.

the Calcareous Red Earth from the Northern Territory, kaolinite predominates, while in the Riverina paleosols illite is the most important mineral. Smectite was occasionally present in small quantities in the samples from both areas. Ubiquitous accessory minerals were calcite and quartz, and in the Northern Territory also hematite.

Chemical Composition of the Coatings

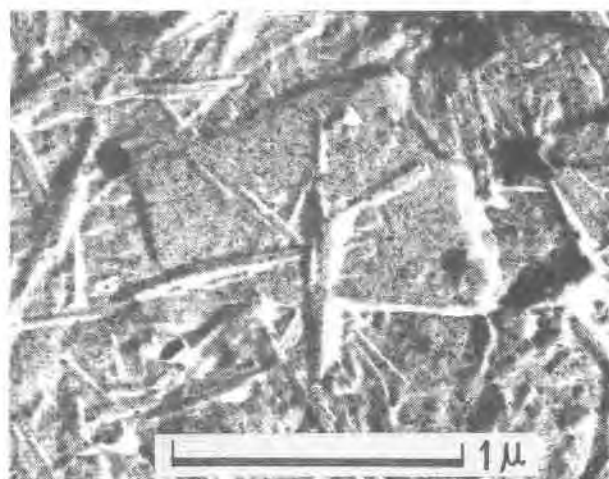
Electron probe determinations were made on thin cuts of peds containing coatings. In Table 1 the chemical compositions of random points from the crust seen in Figure 2 are given. The composition of

ination showed that the crusts consist of almost pure palygorskite. Very weak reflections indicate also the presence of traces of kaolinite, illite, and quartz, perhaps because of imperfect separations of the crust from the underlying material.

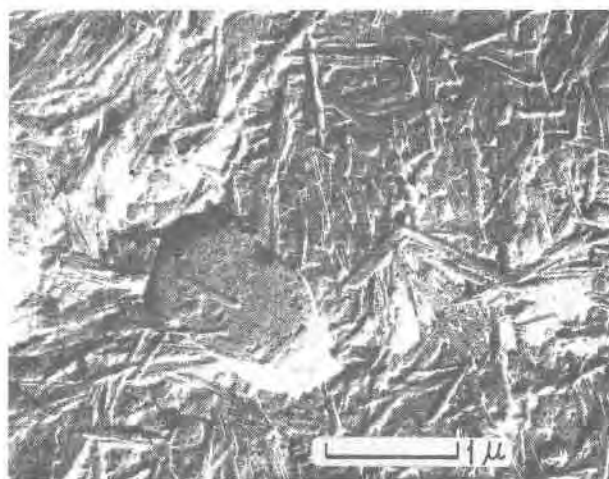
Clay from within the soil peds contained as major components illite, kaolinite, and quartz but no palygorskite. When illite was present, the identification of palygorskite was based on the presence of the 200 reflections at 6.4 Å. Detection was improved by heating the sample in the diffractometer to 140°C, which increased the line intensity by a factor of 1.8 (Pickering, private communication; Nathan, 1969). In



FIG. 4. Electron transmission photograph of a replica prepared from an undisturbed palygorskite crust. The palygorskite fibers are arranged in the form of thick mats, subdivided into approximately parallel strips. Within each strip the fibers have again a more or less parallel orientation.



(A)



(B)

FIG 5. A. Palygorskite fibers situated on top of coarse-sized skeleton grains in replicas of a ped. B. Grit surface from a soil in the Northern Territory.

a random point from the clay matrix from within the ped is also given for reference. The same table contains the chemical composition of a palygorskite crust from the Riverina paleosol. The results represent the chemical composition of points taken at intervals of 20 μ on a transect from the edge of the crust inward.

The content in Mg of all the points in the Northern Territory crust and of the outermost points in the Riverina crust corresponds to that in reported analysis of Mg-rich palygorskite. These points can therefore be taken to represent the monomineralic phase of the crust. Ca content is low, and this is contrary to most reported compositions of palygorskite deposits (Gremillion, 1965).

Taking the Mg contents as standards for the degree of purity of the mineral, the palygorskite content of the Riverina crust appears to decrease gradually in an inward direction until reaching values close to those of the clay matrix in the interior of the peds, at a distance of 140 μ from the outer edge. This decrease is accompanied by a parallel increase in the Fe, Ti, and K contents. These variations in the chemical composition indicate that the Riverina crust is not uniform, and that the mineralogically pure palygorskite in the outermost periphery is gradually becoming intermixed with illite and other minerals within the crust.

The palygorskite content of the Northern Territory crust seems to be more uniform. Some of the Fe in the crust may be part of the palygorskite lattice.

Chemistry of the Soil-Water Extracts

Table 2 contains the chemical characteristics of the 1:1 soil-water extracts (after equilibration for 24 hours) from soil layers having palygorskite coatings, and from some adjacent soil layers. All the soils are alkaline in their lower horizons, and some have also high salt concentrations. The Si content of the extracts (determined by the heteropoly blue method) is generally high, particularly in the Riverina paleosols where values are attained far out of the normal range for soils (Bradford, Bair, and Hunsaker, 1970). Mg contents (determined by atomic absorption) are relatively low in the salt-free soils, but rise to high values in the salt-containing soils or layers. Al (determined colorimetrically by the haematoxylin method of Dalal, 1972) is always below 0.2 ppm and Fe below 0.1 ppm except in the Riverina paleosols where higher values are attained. For comparison, data are given (Table 2) for the lower horizons of a group of fine-textured alkaline soils from the same areas, but which do not contain palygorskite.

Equilibrium Constant

Materials

The choice of the Australian palygorskite for the dissolution experiments was based on the degree of purity of the mineral. Most of the well known palygorskites contain admixtures of other clay minerals, mainly smectite, and are therefore unsuitable for

TABLE 1. Chemical Composition of Palygorskite Crusts Compared to That of Clay Matrices*

	Crust from cal. red earth, Northern Territory. Random points					Microprobe analysis of crust from paleosol, Riverina, N.S.W. (composition in % of oxide is given at intervals, measured in microns, from outer edge)								
	1	2	3	4	Clay matrix	Edge	20 μ	40 μ	60 μ	80 μ	100 μ	120 μ	140 μ	Clay matrix
Fe ₂ O ₃	3.08	2.22	.74	1.69	16.14	.41	.68	1.15	1.81	3.26	5.90	3.41	7.07	7.30
TiO ₂	.11	.10	.08	.14	.69	.09	.10	.14	.18	.30	.60	.57	1.86	.88
CaO	.08	.14	.07	.14	.57	.24	.15	.32	.18	.30	.30	.35	.39	.39
K ₂ O	.36	.39	.24	.46	1.75	.62	1.12	1.15	.92	1.45	2.18	2.82	2.50	2.32
SiO ₂	58.58	60.29	61.32	59.29	46.48	62.77	63.81	59.59	58.34	64.60	54.17	57.00	51.58	50.75
Al ₂ O ₃	11.19	11.86	12.77	13.20	18.20	12.33	12.31	12.53	12.38	13.39	19.38	8.46	23.66	23.95
MgO	9.94	10.26	10.54	9.25	2.29	9.62	9.76	8.88	8.00	5.60	4.28	.70	1.71	1.61
Na ₂ O	.16	.15	.09	.13	.18	.33	.43	.40	.36	.28	.53	.20	.55	.64
Total	83.53	85.44	85.87	84.31	86.71	86.42	88.39	84.19	82.21	89.21	87.35	73.51	89.33	87.87

* Electron microprobe analyses. Analytical methods and corrections according to Sweatman and Long (1969).

TABLE 2. Chemical Composition of Soil-Water Extracts (1:1) from Soils with Palygorskite Coatings and from Fine-Textured Alkaline Soils Containing No Palygorskite (in ppm).

Soil No.**	Classification	Depth	Conduct. mmho/cm	pH	SiO ₂	Mg	Al	Fe
Soils with palygorskite coatings								
NT 36	Calc. Red Earth	140-165 cm	n.d.	7.60	46.0	1.8	n.d.	n.d.
		165-180 cm*	n.d.	8.45	26.4	6.4	0.17	0.05
NT P13	Calc. Red Earth	60- 75 cm	0.47	6.80	39.0	10.5	0.14	<0.1
		113-133 cm*		8.35	39.6	6.8	0.08	<0.1
NT P15	Calc. Red Earth	60- 90 cm	n.d.	6.85	46.0	4.2	n.d.	n.d.
		115-145 cm*	n.d.	8.15	46.0	11.0	n.d.	n.d.
NT P16	Solonetz	40- 60 cm	n.d.	7.40	40.0	12.0	n.d.	n.d.
		140-160 cm*	n.d.	8.05	25.0	125.0	n.d.	n.d.
	Riverina Paleosol Brucedale layer	(1) at 8 m	0.40	8.70	62.0	2.6	0.20	0.44
	Riverina Paleosol Brucedale layer	(1) at 6 m*	0.13	8.40	48.0	5.0	0.10	2.00
	Riverina Paleosol Willys layer	(1) at 20 cm	1.99	6.30	94.0	60	0.19	<0.1
		(2) at ~10 m*	0.94	7.75	74.0	14	0.19	<0.1
NT 52	Red soils with acid surface	32- 56 cm	2.38	7.90	16.0	85	0.11	<0.1
		83-144 cm*	6.19	8.05	16.4	380	n.d.	n.d.
NT 59	Red and brown clay soils	32- 78 cm	4.13	7.95	17.6	70	0.16	<0.1
		140-160 cm*	10.06	7.85	24.0	275	n.d.	0.05
NT 44	Red and brown clay soils	88-110 cm*	6.44	7.75	53.0	275	n.d.	0.05
NT 1	Solonetz soils	78- 88 cm	8.94	8.00	20.0	470	n.d.	<0.01
		108-123 cm*	n.d.	7.95	12.8	180	n.d.	n.d.
	Sediment from Lake Eyre South	10- 15 cm	118.34	7.70	11.4	525	0.22	1.0
Soils with no palygorskite								
NT 12	Calcimorphic soils	17- 32 cm	0.17	8.25	17.2	2.45	0.07	<0.1
NT 26	Calcimorphic soils	10- 22 cm	29.3	7.65	9.6	575	0.40	0.1
NT 21	Alkaline soils on alluvial deposits	27- 44 cm	0.23	7.90	17.2	5.0	0.12	<0.1
NT 27	Calcimorphic soils	26- 46 cm	1.20	8.70	8.4	4.8	0.08	<0.1
NT 13	Miscellaneous	265-287 cm	0.13	7.85	28.4	2.5	0.24	0.8

* Soil layer which contains palygorskite coatings.

** C.S.I.R.O. Division of Soils number.

dissolution experiments. The palygorskite chosen contains appreciable quantities of calcite but is free from other minerals, as far as could be ascertained by X-ray diffraction and electron microscope. It is from Mt. Flinders, near Ipswich, Queensland, and has been described by Rogers, Martin, and Norrish (1954).

The palygorskite was treated first for four hours with dilute (0.1 N) HCl in order to remove the carbonates. Preliminary experiments had revealed that such treatment increased the Si solubility up to 120-140 ppm, which is that of amorphous silica. The treatment was therefore repeated on new samples,

this time using H-saturated ion exchange resin. The material was then Na saturated and dispersed, and the $<2\mu$ fraction separated. The separated clay was Ca saturated; its chemical analysis is given in Table 3. As these data show, the palygorskite does not contain any elements indicating the presence of impurities. The structural formula (ignited basis) calculated from these data is:



The experimental approach to the dissolution experiment was similar to that of Reesman and Keller (1965) with adaptations from Wildman, Whittig, and Jackson (1971). Five grams of the treated clay were placed into polyethylene containers containing 250 ml of double distilled water. The containers were then closed to the atmosphere. Nitrogen in one series, air in another, was gently bubbled through the suspension, until equilibrium was obtained. The experiment was carried out in a controlled temperature room at 25.0(5)°C.

Values of pH and concentrations of Mg, Si(OH)₄, Al, and Fe were determined after 4, 8, and 20 hours and 4, 11, 18, 25, and 32 days. The pH was determined with a glass electrode in conjunction with a saturated calomel reference electrode, Si by a modified version of the heteropoly blue method (Boltz and Mellon, 1947), Fe and Mg by atomic absorption, and Al by the haematoxylin method (Dalal, 1972).

TABLE 3. Chemical Composition of Mt. Flinders Palygorskite (Ignited Basis)*

	wt. percent
SiO ₂	70.47
Al ₂ O ₃	6.84
Fe ₂ O ₃	5.65
TiO ₂	0.69
MnO	0.07
CaO	0.22
MgO	15.90
P ₂ O ₅	0.04
K ₂ O	0.004
Total	99.90
moisture loss	8.99
ignition loss	13.18
Ex. cap.	6 meq/100 g

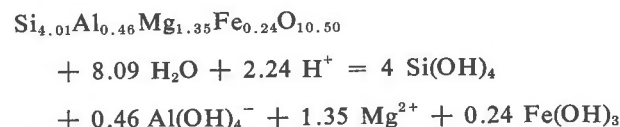
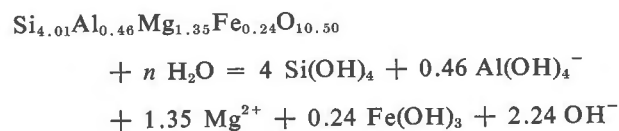
* Analyzed by X-ray fluorescent methods (Norrish and Hutton, 1969).

Results

Si concentration rose slowly during the first day and then levelled off. Mg continued to rise slowly and levelled off only after ten days. The concentrations of Fe and Al were nearly steady throughout the experiment. The pH values tended to fluctuate within a narrow range and became nearly constant after eleven days. These trends were common both to the air and nitrogen treatments.

Calculation of aK and $a\Delta F^\circ_f$

Solubility data for the Mt. Flinders palygorskite are given in Table 4. For the Mt. Flinders palygorskite, the dissolution of the mineral may be represented as a hydrolysis equation:



and the (apparent) equilibrium constant (aK) was obtained from this expression. The (apparent) equilibrium constant aK is related to the (apparent) standard free energy change of the reaction aF°_R by the expression:

$$a\Delta F^\circ_R = -RT \ln aK = -1.364 \log aK$$

also $a\Delta F^\circ_R = \sum a\Delta F^\circ_f \text{ products} - \sum a\Delta F^\circ_f \text{ reactants}$.

The values of the standard free energies of formation ($a\Delta F^\circ_f$) of the species appearing in the hydrolysis equation were taken from Reesman and Keller (1965). The species of aluminum ion in solution was assumed to be Al(OH)_4^- , because the pH of the reactions was above 6.70. Table 4 gives the equilibrium constants and the free energy of formation values for the palygorskite.

Discussion

Stability of Palygorskite

The information from the solubility experiments with the Mt. Flinders palygorskite was used to draw some conclusions regarding the stability relations of the mineral at earth-surface conditions. Using the approach of Garrels and Christ (1965), the stability of palygorskite is expressed in terms of H^+ and Mg^{2+}

TABLE 4. Solubility Data and (Apparent) Free Energy of Formation Value for Mt. Flinders Palygorskite*

Gas	Solubility Data					(Apparent) Free Energy of Formation		
	$\log[\text{Si}(\text{OH})_4]$	$\log[\text{Mg}^{2+}]$	$\log[\text{Al}(\text{OH})_4^-]$	$\log[\text{Fe}(\text{OH})_3]$	pH	$\log a_K$	$\frac{\Delta F^\circ}{R}$ kcal/mole	ΔF°_f pal. kcal/mole
air	-3.27	-3.61	-5.43	-6.15	8.05	-3.99	5.44	-1131.5
N ₂	-3.37	-3.91	-5.43	-6.15	8.55	-3.68	5.02	-1131.0

* After 32 days of equilibration with water under nitrogen or air.

activity at three different Si activity levels. The pH range of 6-9 is limited to that common in soils from arid areas. This choice also decreases the error introduced by assuming the Al and Fe activities to be constant. This error is small since the solubility of Fe(OH)₃ would hardly change at all in this pH range, while that of Al(OH)₄⁻ changes only slightly (Raupach, 1963).

From Fig. 6 it is seen that even at pSi = 2.6, the saturation solubility of amorphous silica (Garrels and Christ, 1965), palygorskite would not be stable below a pH of 5.9 and even then a pMg of 2 would be required to keep it stable. At a pSi of 3.6, which is close to the range encountered in normal soils, palygorskite would not be stable under a pH of 7.7 at high Mg concentrations and 9.0 at low Mg concentrations.

The data in Figure 6 was used to construct a three-dimensional stability diagram (Fig. 7) showing the stability of palygorskite as a function of three variables: pH, pMg, and pSi. From this diagram it is evident that palygorskite is stable in moderately acid soils only at very high Si and Mg concentration levels which are very uncommon in soils. Only at very high pH levels can (1) the palygorskite stability be maintained while decreasing the Mg concentration to below 10⁻⁷ mol/liter (at high Si concentrations) or (2) the Si concentration be decreased to below 10⁻⁴ mol/liter (at high Mg concentrations).

Evaluation of Soil: Water Extracts

Figure 8 shows a two-dimensional activity diagram incorporating the four variables of the system SiO₂-MgO-Al-H₂O. The position of the stability field

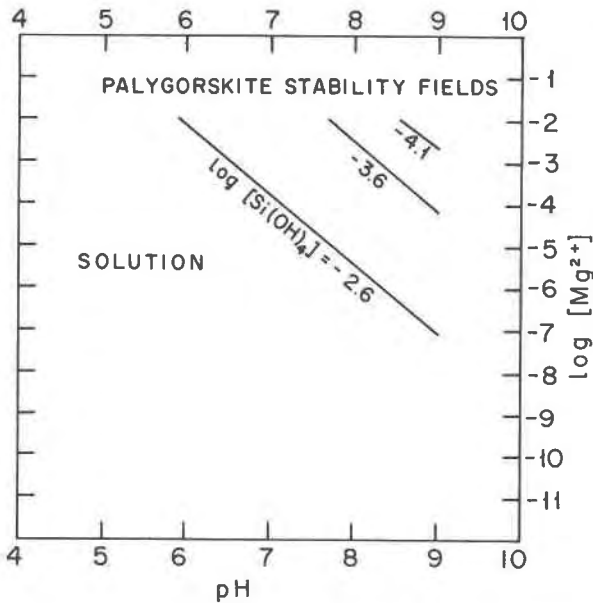


FIG. 6. Stability field of Mt. Flinders palygorskite expressed in terms of H⁺ and Mg²⁺ activity levels at three different Si activity levels. Al and Fe activities assumed to be constant in the pH range of 6-9.

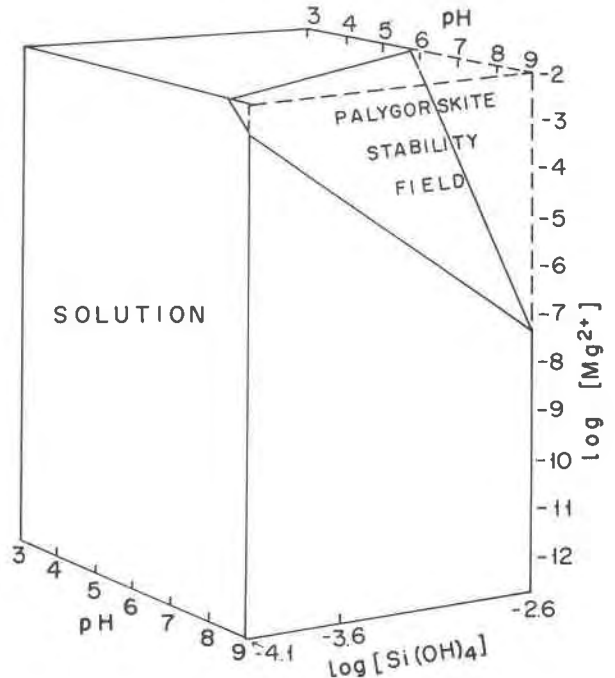


FIG. 7. Diagram showing the stability of Mt. Flinders palygorskite as a function of pH, pMg, and pSi.

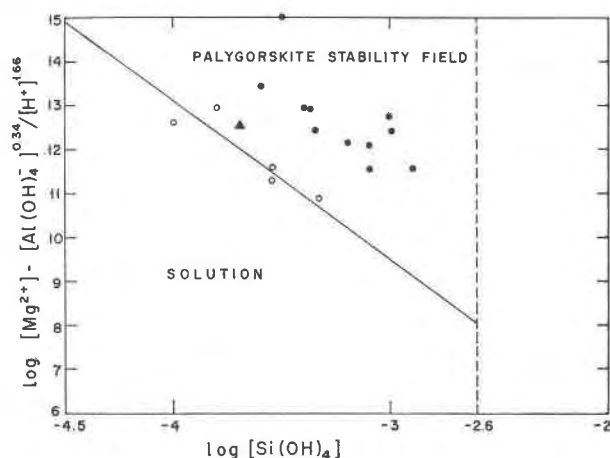


FIG. 8. Two-dimensional activity diagram for Mt. Flinders palygorskite, incorporating the four major variables of the system: $\text{SiO}_2\text{-MgO-Al-H}_2\text{O}$. The position of the stability field boundaries were calculated with the aid of the equilibrium constants attained experimentally. Full circles, composition of 1:1 soil-water extracts from soil horizons containing palygorskite coatings. Empty circles, composition of 1:1 soil-water extracts of the lower horizons of fine-textured, alkaline soils from the same areas, which do not contain coatings. Full triangle, extract from Lake Eyre South sediment.

boundary was calculated with the aid of the equilibrium constants for palygorskite obtained experimentally. In this diagram were also plotted the compositions of some 1:1 water extracts from soil horizons containing palygorskite coatings. All these extracts are seen to fall within the stability field for palygorskite. The composition of the extracts from soils which do not contain palygorskite are seen to flank the stability-field boundary line.

Conclusions

The position of the soil:water extracts in the stability diagram appears to support the field evidence for the pedogenic formation of palygorskite. Soil water with a suitable composition, and not only lake water, can apparently satisfy the conditions for the formation of this mineral. Dilute waters derived from rock weathering, draining into a depositional basin containing sedimentary soils in areas where annual evaporation exceeds precipitation, would be concentrated until values allowing for the precipitation of palygorskite could be created. Conceivably, impeded drainage and temporary water-logging in heavy-textured, low-lying soils would enhance these processes. Such conditions have been described for some of the Northern Territory soils in which palygorskite coatings have been identified (Litchfield,

1969). In the Riverina paleosols they could have been a feature of the past. Since the slow water-conductivity of the clay-soils is one of the reasons for the creating of the water-logging conditions, soil formation antedates palygorskite precipitation. Therefore, the palygorskite is found as coatings only and not within the soil peds.

Sedimentary deposits formed in saline or alkaline lacustrine environments rich in Si and Mg frequently contain sepiolite (Wollast, MacKenzie, and Bricker, 1968). Mg-Al equilibrium conditions probably determine whether sepiolite or palygorskite are formed in such environments. Stability diagrams calculated by Wildman *et al* (1971) indicate that solid Fe and Al hydroxides are always in contact with soil solutions in which mafic minerals are weathering. While sparingly soluble near a neutral pH, these hydroxides support small concentrations of Fe^{3+} and $\text{Al}(\text{OH})_2^+$ sufficient to effect partial alumination of silicate surfaces. The reason for the formation of chain minerals in preference to high-Mg sheet minerals is not clear.

Acknowledgments

The authors gratefully acknowledge the assistance of Mr. J. W. Cock in the electron microscopy and Mr. J. G. Pickering in the X-ray diffraction work. Invaluable was the field guidance in sampling the Northern Territory soils provided by Mr. M. Wright. Thanks are extended to Dr. J. Beattie from the University of Tasmania for his field guidance of the Riverina soils. The senior author is very indebted to the CSIRO, Australia, for granting him a visiting scientist tenure at their Soil Division, and to Dr. E. G. Hallsworth, Chief of the Soils Division, for his aid in obtaining this tenure.

References

- AL-RAWI, G. J., AND C. SYS (1967) A comparative study between Euphrates and Tigris sediments in the Mesopotamian Flood Plain. *Pedologie, Gand*, **17**, 187-211.
- BARSHAD, E., E. HALEVY, H. A. GOLD, AND J. HAGIN (1956) Clay minerals in some limestone soils of 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.
- , AND A. D. HALDANE (1958) The occurrence of palygorskite and barytes in certain parna soils of the Murrumbidgee region, New South Wales. *Aust. J. Sci.* **20**, 274-275.
- BOLTZ, D. F., AND M. G. MELLON (1947) Determination of phosphorus, germanium, silicon and arsenic by the heteropoly blue method. *Anal. Chem.* **19**, 873-877.
- BRADFORD, G. R., F. L. BAIR, AND V. HUNSAKER (1970) Trace and major element contents of soil saturation extracts. *Soil Sci.* **112**, 225-231.
- BREWER, R. (1964) *Fabric and Mineral Analysis of Soils*. John Wiley and Sons, Inc., New York.

- BUTLER, B. E. (1956) Parna—an aeolian clay. *Aust. J. Sci.* **18**, 145–151.
- DALAL, R. C. (1972) Colorimetric determination of aluminum in soil extracts using haematoxylin. *Plant and Soil*, **36**, 223–231.
- ELGABALY, M. M. (1962) The presence of attapulgite in some soils of the western desert of Egypt. *Soil Sci.* **93**, 387–390.
- GARRELS, R. M., AND C. L. CHRIST (1965) *Solutions, Minerals, and Equilibria*. Harper and Row, New York.
- GREMILLION, R. L. (1965) *The Origin of Attapulgite in the Miocene Strata of Florida and Georgia*. Ph.D. Thesis, Florida State University, Tallahassee, Florida.
- JACKSON, E. A. (1962) Soil studies in Central Australia: Alice Springs-Hermannsburg-Rodinga areas. *CSIRO Aust. Soil Publ. No.* **19**.
- LITCHFIELD, W. H. (1969) Soil surfaces and sedimentary history near the MacDonnell Ranges, N. T. *CSIRO Aust. Soil Publ. No.* **25**.
- MICHAUD, R., R. CERIGHELLI, AND G. DROUINEAU (1945) Sur les spectres de rayons X des argiles extraites de sols Méditerranéens. *C. R. Acad. Sci. Paris*, **222**, 94–95.
- MILLOT, G. (1964) *Geologie des Argiles*. Masson et Cie, Paris.
- , H. PAQUET, AND A. RUELLAN (1969) Neof ormation de l'attapulgite dans les sols a carpaces calcaires de la Basse Moulouya (Maroc oriental). *C. R. Acad. Sci. Paris*, **268**, 2771–2774.
- MUIR, A. (1951) Notes on Syrian soils. *J. Soil Sci.* **2**, 163–181.
- NATHAN, Y. (1969) *Studies on Palygorskite*. Ph.D. Thesis, Hebrew University, Jerusalem (in Hebrew).
- NORRISH, K., AND J. T. HUTTON (1969) An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta*, **33**, 431–453.
- OSMOND, D. A., AND I. STEPHEN (1957) The micropedology of some red soils from Cyprus. *J. Soil Sci.* **8**, 19–26.
- PAQUET, H., A. RUELLAN, Y. TARDY, AND G. MILLOT (1969) Géochimie d'un bassin versant au Maroc oriental. Evolution des argiles dans les sols des montagnes et des plaines de la Basse Moulouya. *C. R. Acad. Sci. Paris*, **269**, 1839–1842.
- RAUPACH, M. (1963) Solubility of single aluminum compounds expected in soils. *Aust. J. Soil Res.* **1**, 36–45.
- RAVIKOVITCH, S., F. PINES, AND M. BEN-YAIR (1960) Composition of the colloids in the soils of Israel. *J. Soil Sci.* **11**, 82–91.
- REESMAN, A. L., AND W. D. KELLER (1965) Calculation of apparent standard free energies of formation of six rock-forming silicate minerals from solubility data. *Am. Mineral.* **50**, 1729–1739.
- ROGERS, L. E., A. E. MARTIN, AND K. NORRISH (1954) The occurrence of palygorskite near Ipswich, Queensland. *Mineral. Mag.* **30**, 534–540.
- SINGER, A. (1971) Clay minerals in the soils of the Southern Ramat Hagolan. *Israel J. Earth Sci.* **20**, 105–112.
- STACE, H. C. T., G. D. HUBBLE, R. BREWER, K. H. NORTH-COTE, J. R. SLEEMAN, M. J. MULCAHY, AND E. G. HALLSWORTH (1968) *Handbook of Australian Soils*. Rellim. Technical Publications, South Australia.
- SWEATMAN, T. R., AND J. V. P. LONG (1969) Quantitative electron-probe microanalysis of rock forming minerals. *J. Petrol.* **10**, 332–379.
- TAYLOR, R. M., AND J. G. PICKERING (1962) Mineralogy of bore samples from Madigan's Gulf, Lake Eyre, South Australia. *CSIRO Aust. Div. Soils, Div. Rep., No.* **5/62** (mimeo).
- VAN DEN HEUVEL, R. C. (1966) The occurrence of sepiolite and attapulgite in the calcareous zone of a soil near Las Cruces, New Mexico. *Clays Clay Minerals, Proc. Conf. (1964)*, **13**, p. 193–207.
- WILDMAN, W. E., L. D. WHITTIG, AND M. L. JACKSON (1971) Serpentine stability in relation to formation of iron-rich montmorillonite in some California soils. *Am. Mineral.* **56**, 587–602.
- WOLLAST, R., F. T. MACKENZIE, AND O. P. BRICKER (1968) Experimental precipitation and genesis of sepiolite at earth-surface conditions. *Am. Mineral.* **53**, 1645–1662.
- YAALON, D. H. (1955) Note on the clay mineralogy of the major soil types in Israel. *Bull. Res. Council. Israel*, **58**, 168–173.
- , Y. NATHAN, H. KOYUMDJISKY, AND J. DAN (1966) Weathering and catenary differentiation of clay minerals in soils on various parent materials in Israel. *Proc. Int. Clay Conf. Jerusalem*, **1**, 187–198.

Manuscript received, October 29, 1973; accepted for publication, January 22, 1974.