Neoformation of palygorskite in Calcids of Central Iran

Authors: Amin, Peyman, and Akhavan Ghalibaf, Mohammad

Source: Canadian Journal of Soil Science, 102(2) : 253-262

Published By: Canadian Science Publishing

URL: https://doi.org/10.1139/CJSS-2021-0086

Canadian Science Publishing

ARTICLE

Neoformation of palygorskite in Calcids of Central Iran

Peyman Amin and Mohammad Akhavan Ghalibaf

Abstract: Palygorskite has been reported in alluvial sediments and in soil clays in Central Iran, but it is not known if it is inherited or formed in situ. Here, we sampled Calcids developed from Triassic and Cambrian dolomitic formations in the southwestern part of Yazd and performed soil and clay characterization by X-ray diffraction and fluorescence, optical and scanning electron microscopy and energy dispersive X-ray spectrometer analyses. Our results suggested palygorskite neoformation in the calcic soil horizons in Calcids. The soils with aridic soil moisture regime and high Mg concentration, during the formation of a calcic horizon by precipitation of secondary calcite, conditions were suitable for authigenic palygorskite crystals of long size (>10–20 μm) and their stability. In addition, the occurrence of short-size (about 2 μm) palygorskite fibers in the lower gypsic horizon probably resulted from its translocation from the upper horizons. Therefore, such results suggested palygorskite neoformation in the calcic soil horizons in these Calcids of Iran.

Key words: Aridisols, soil mineralogy, soil microscopy, soil genesis, secondary minerals.

Résumé : La présence de palygorskite a été signalée dans les alluvions et les sols argileux du centre de l'Iran, mais on ignore si le minéral s'est formé *in situ* ou y a été importé. Les auteurs ont échantillonné les calcides qui se sont développés au Trias et au Cambrien dans les formations dolomitiques du sud-ouest de Yazd pour caractériser le sol et l'argile par diffraction et fluorescence aux rayons X, microscopie optique et électronique à balayage, et spectrométrie dispersive en énergie. Les résultats obtenus indiquent la néoformation de palygorskite dans l'horizon calcique des calcides. Dans les sols arides très riches en magnésium, les conditions sont propices à la formation et à la stabilisation de longs (>10 – 20 μm) cristaux authigènes de palygorskite durant la genèse de l'horizon calcique, par précipitation de la calcite secondaire. La présence de courtes (environ 2 μm) fibres de palygorskite dans l'horizon inférieur de gypse est sans doute attribuable à une translocation à partir des horizons supérieurs. Ces résultats appuient donc la néoformation de palygorskite dans l'horizon calcique des calcides iraniens. [Traduit par la Rédaction].

Mots-clés : aridisols, minéralogie du sol, microscopie du sol, pédogenèse, minéraux secondaires.

Introduction

The occurrence of palygorskite in the soils of Central Asia (Minashina and Gradusov 1973; Travnikova 1980; Khabarov and Chizhikova 1984) is a lithological legacy from the evaporation basins of Tertiary times. Soil scientists in a number of countries have mentioned the prevalence of palygorskites in soils that have developed on deposits of Tertiary, mainly of Eocene period (Bigham et al. 1980; Golden et al. 1985). According to Gradusov (1992), neoformation of palygorskite in soils has been the focus of individual attention in Australia, Israel, and the Planosols of Argentina. Equilibrium conditions and concentration charts of palygorskite by Elprince et al. (1979) and Brinkman (1979) indicate that the stability of this mineral is possible under alkaline conditions and the high concentration of Si^{4+} and Mg^{2+} in the soil. The structure of palygorskite presents continuous planes of tetrahedral basal oxygen atoms spaced approximately 0.65 nm apart from one another (Singer 2002). The ribbons have an average width along the b-axis of two linked tetrahedral chains. Ribbons with apices pointing up are linked vertically to ribbons with apices pointing down by forming octahedral coordination groups around Mg and Al. 2:1 layers continuous along the a-axis and with limited lateral extent along the b-axis are thus formed (Bailey 1980). Monger and Daugherty (1991) reported that palygorskite was the dominant clay mineral in a petrocalcic horizon of the

Received 3 July 2021. Accepted 25 November 2021.

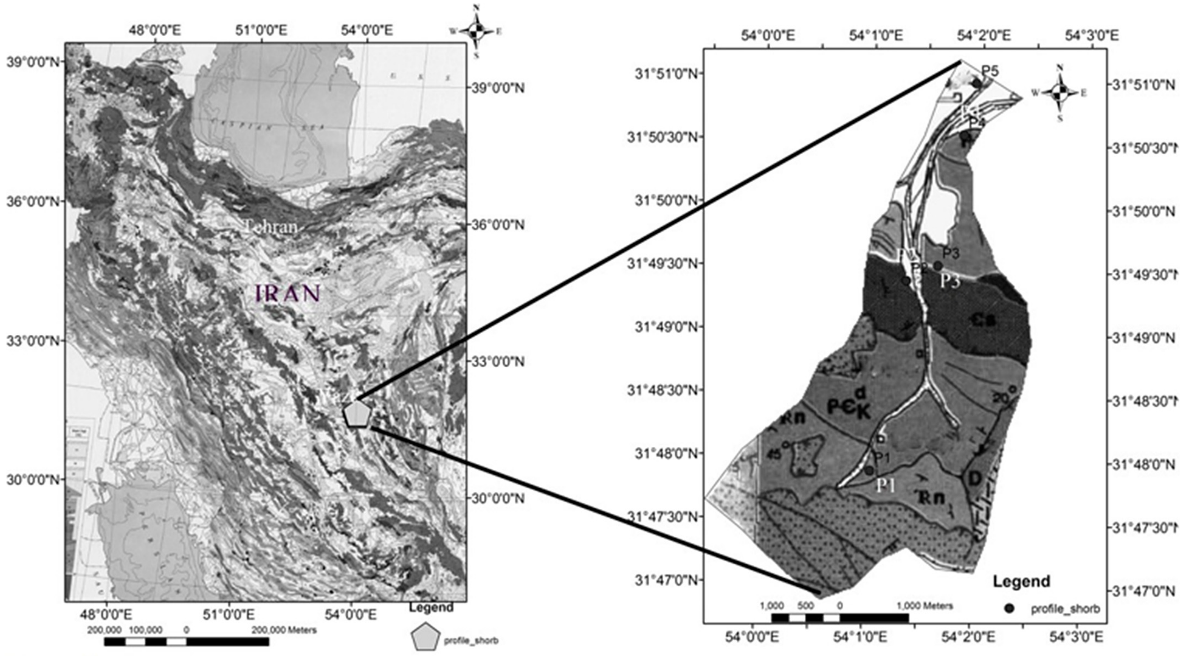
P. Amin. Desert Management Department, Natural Resources and Desert Studies Faculty of Yazd University, Yazd, Iran.

M. Akhavan Ghalibaf. Soil Science Department, Natural Resources and Desert Studies Faculty of Yazd University, Yazd, Iran.

Corresponding author: Mohammad Akhavan Ghalibaf (email: makhavan_ghalibaf@hotmail.com).

Can. J. Soil Sci. **102:** 253–262 (2022) dx.doi.org/10.1139/cjss-2021-0086

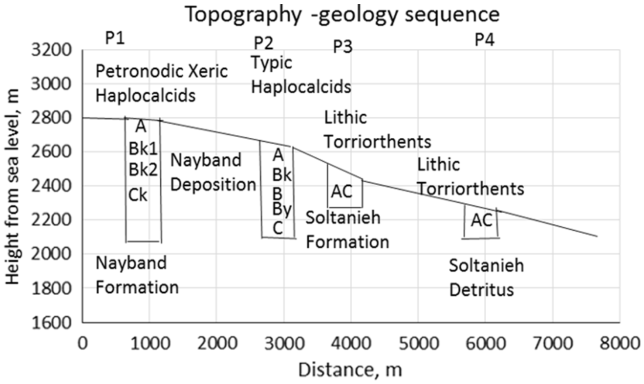
Fig. 1. The study area on the geological map of Iran. The map is from Haghipour and Aghanabati (1989) and has been modified using Arc Map version 10.



Legend:
●**P1**: Soil profile 1, **TRn**: Naibandan Formation on Triassic, **Cs**: Soltanieh Formation on Cambrian deposits.

Rotura soil series (a coarse-loamy, mixed, thermic, Typic Haplargid), a soil of middle Pleistocene age in southern New Mexico. The state of H_2O associated with the minerals has been investigated, as well as the characteristics of the adsorption sites. These aspects are very important for the development of industrial uses for palygorskite in its pure form, as well as for an appreciation of the role of this mineral in agro-chemistry and ecology. Kaplan et al. (2014) showed that the development of palygorskite mainly on relict calcite crystals indicates its formation during or shortly following calcite formation in calcretes.

Fig. 2. Position of the sampled profiles (P1, P2, P3 and P4) on the topographic–geological sequence.



Altaha (1997) proposed the possible formation of attapulgite formation in salt-affected soils in semiarid environments in the Southern Iran. The existence of palygorskite in floodplain soils, alluvial and eolian sediments of Yazd and other parts of Central Iran, as the Rudasht River alluvial terraces, has been reported by Akhavan Ghalibaf and Chizhikova (1998, 1999, 2000) and Akhavan Ghalibaf and Mohammadi (2011). However, the authigenic origin of this mineral remains open to argument. According to Hashemi et al. (2013), the highest amount of palygorskite was observed in soils with aridic moisture regimes, and its lowest amount was estimated in soils with xeric moisture regimes. Also, their results indicated that large amounts of well-bundled and elongated palygorskite in soils of piedmont plain are related to their authigenic formation. The formations of Nayband (Mesozoic) and Soltanieh (Paleozoic) are located in the vicinity with the same semiarid climatologic zone in Yazd. The soils on the Soltanieh formation of the lower Paleozoic with a higher quantity of dolomite have a limited pedogenesis; they are Entisols with shallow soil profiles. The Lower Mesozoic Nayband formation and its detritus are characterized by higher quantities of calcite and by deeper soil profiles classified as Petronodic Xeric Haplocalcids (Akhavan-Ghalibaf and Rahbar-Alam-Shirazi 2013). Rahbar-Alam-Shirazi and Akhavan-Ghalibaf (2014) suggested that limestone and dolomite sediments of Triassic and older ages could serve as the sources of palygorskite in the southwestern part of Yazd and supposed the inherited nature of this mineral in the local soils. This hypothesis was based on the abundance of

Table 1. Some physicochemical properties of the study soils.

Horizon	Depth, cm	EC, dS/m	O.M.	$CaCO_3$ (lime)	$CaSO_4 \times 2H_2O$	Ca^{2+}/Mg^{2+} in lime	Texture
			%				
Profile 1, on the Nayband formation							
A	0–15	0.22	0.66	21.75	0.20	nd	sl
Bk1	15–45	0.15	0.47	28.5	0.15	7.02	l
Bk2	45–95	0.43	0.25	35.75	0.10	nd	sl
Ck	95–150	0.18	0.13	38.75	0.13	nd	l
Profile 2, on the Nayband detritions							
A	0–25	0.18	0.16	28.50	0.11	nd	sl
Bk	25–80	0.19	0.09	31.00	0.10	6.99	sl
B	80–110	0.52	0.06	29.50	0.09	nd	ls
Cy	110–150	2.20	0.03	23.30	6.78	nd	ls
Profile 3, on the Soltanieh formation							
AC	0–15	0.23	0.79	38.75	0.14	1.00	sl
Profile 4, on the Soltanieh detritus							
AC	0–25	0.17	0.41	28.75	0.17	1.20	sl

Table 2. Contents of soluble captions and some chemical properties in 1:5 soil/water extract of the study soils.

Horizon	Depth, cm	pH (Soil/water suspension)		Cations in 1:5 soil/water extract, meq/l				Na+/ $(Ca^{2+}+Mg^{2+})$	Ca^{2+}/Mg^{2+}
		1:1	1:5	Mg^{2+}	Ca^{2+}	K^+	Na^+		
Profile 1, on the Nayband formation									
A	0–15	7.57	8.45	0.40	1.20	0.45	0.33	0.28	3.00
Bk1	15–45	8.14	8.62	0.80	2.00	0.26	0.08	0.09	2.50
Bk2	45–95	7.38	8.29	0.20	3.20	0.43	0.07	0.08	1.90
Ck	95–150	8.13	8.33	0.80	4.40	0.51	0.07	0.09	5.50
Profile 2, on the Nayband detritus									
A	0–25	8.40	8.69	0.80	1.20	0.46	0.06	0.23	1.50
Bk	25–80	8.30	8.68	1.20	1.20	0.82	0.03	0.34	1.00
B	80–110	8.06	8.48	2.00	4.40	1.48	0.46	0.23	2.20
Cy	110–150	7.78	7.87	27.20	5.20	0.51	0.08	0.02	0.19
Profile 3, on the Soltanieh formation									
AC	0–15	8.53	8.64	0.65	0.21	1.20	1.60	0.23	0.75
Profile 4, on the Soltanieh detritus									
AC	0–25	8.38	8.72	0.43	0.14	1.20	0.40	0.27	3.00

Table 3. Total contents of elements expressed as oxides in soil samples from profiles 2 and 3.

Horizon	Depth, cm	Total oxides, %						SiO_2/Al_2O_3	CaO/MgO
		SiO_2	Al_2O_3	CaO	MgO	CO_2	SO_3		
Profile 2, on the Nayband detritus									
A	0–25	48.2	13.3	20.8	3.5	5.2	0.1	3.6	5.94
Bk	25–80	46.2	12.2	23.2	3.5	10.3	0.1	3.8	6.71
B	80–110	47.7	12.2	21.8	3.2	10.2	0.2	3.9	6.63
Cy	110–150	46.6	11.6	23.5	3.2	9.6	1.0	4.0	7.34
Profile 3, on the Soltanieh formation									
AC	0–15	13.4	3.15	40.41	17.6	20.00	–	4.25	2.30

Fig. 3. Diffractograms of clay fraction (<1 μm) from the Bk horizon of profiles P1 (Left) and P2 (Right).

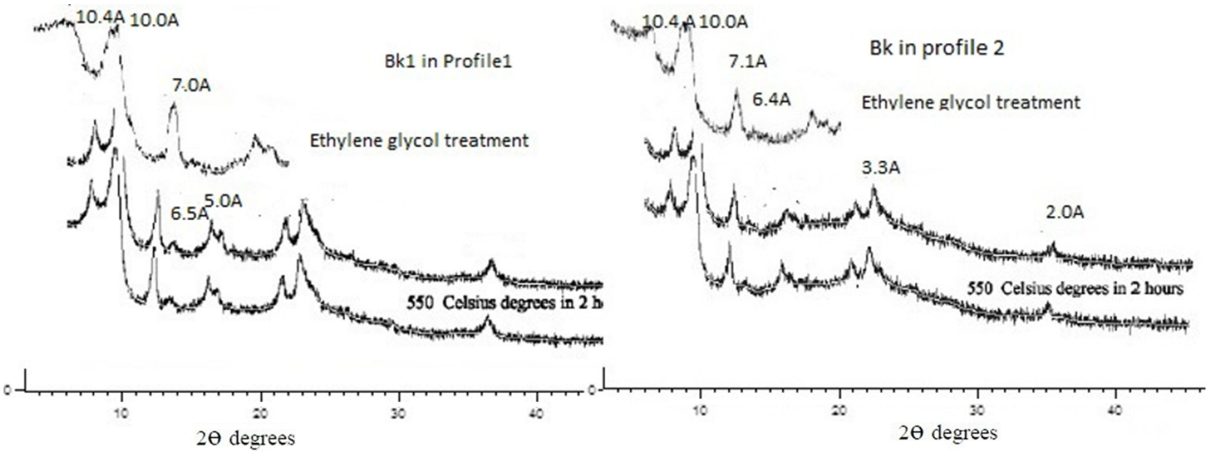
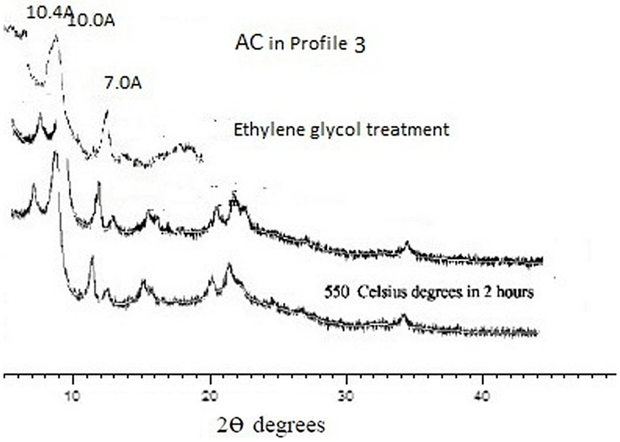


Fig. 4. Diffractograms of clay fraction (<1 μm) from the AC horizon of profile 3 on Soltanieh formation.



magnesium and silica that could ensure stability conditions for this mineral. No indications of the neoformation of palygorskite in these soils were found.

This study was based on the idea of the possibility of pedogenic origin of palygorskite in an arid environment area, because Iran is located in the desert belt of the world and most of its developed soils are Aridissols.

Materials and Methods

The sampled soil profiles were located in the southern part of Yazd, in Central Iran (Fig. 1). The profiles with a ratio of 1:4:5 including full profiles: half profiles: boreholes were drilled in a total of 50 positions on the transect randomly. The study soils have developed on limestone and dolomite formations of Nayband (Triassic period) and Soltanieh (Cambrian period) in the southwestern part of Yazd province as shown in the geological map sheets, 1:100 000 scale (Fig. 1). The study area located in an interval of 1600–2800 m (height from sea level), where soil temperature regime is mesic and soil moisture regime is aridic, but soil moisture regime borders on xeric in higher altitutes landforms. The location of the profiles within the topographic–geological sequence is shown in Fig. 2. The field study and soil sampling were based on a topographic–geological sequence, and observation and soil sampling were done (Fig. 2). The soil samples were collected up to the depth of 150 cm. Soil horizons description and classification were done according to Soil Survey Staff (2014).

Routine testing of soil chemical and physical properties was performed. To measure carbonates in soil, first reacted the soil sample (1 gr) with acid (25 ml HCl 1N) in a volumetric flask, and then in a certain volume of sample was measured Ca^{2+} and Mg^{2+} with complexometric titration method. Lime percentage and Ca^{2+}/Mg^{2+} in carbonates were calculated according to dissolved Ca^{2+} and Mg^{2+} in acid. Gypsum was calculated from the difference in the amounts of sulfate in 1:5 and 1:40 soil/water extracts (Khitrov and Ponizovskii 1990). Ion contents were analyzed in 1:5 soil/water extracts according to Page et al. (1982). Soil reaction was measured in 1:5 and 1:1 soil/water suspensions. Electrical conductivity (EC) was measured in 1:5 soil/water extract. Organic carbon was analyzed with Walkley–Black procedure (Walkley and Black 1934). For X-ray diffraction of clay, sample preparation was done according to Kittrick and Hope (1983) and Sosnovskaya et al. (1978). To remove the lime cementation agents, the soil samples (50 gr) were treated with 10 ml of HCl 1N for few minutes. The clay particles (<1 μm) were separated for X-ray diffractograms as oriented mounts running from 6° to 34° 2θ, at 40 KV with a Cu-K(alpha) target using a Philips (Holland) instrument. Clay mineralogy was identified according to Dixon and Weed (1989), and semi-quantitative measurements were done according to Biskaye (1964). X-ray fluorescence spectrometry (XRF) using S4 Explorer (Bruker) was performed for the bulk elemental analysis. Samples for XRF analyses were grindedand then pressed in the steel ring with boric acid as glue. A detailed analysis of rock fragments from the R horizon of profile 1 has been

Fig. 5. Thin sections from bedrock R horizon, in profile 1 with calcite, dolomite and quartz as dominant primary minerals (NII and N+, 40X). [Colour online.]

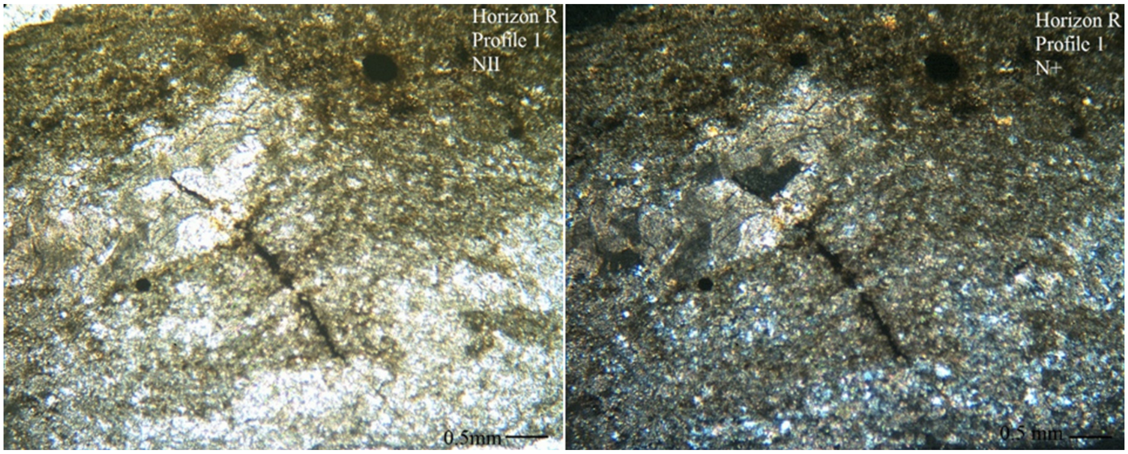


Fig. 6. SEM images with EDS spectrometers from horizons C and AC in profiles 1 and 3, respectively. [Colour online.]

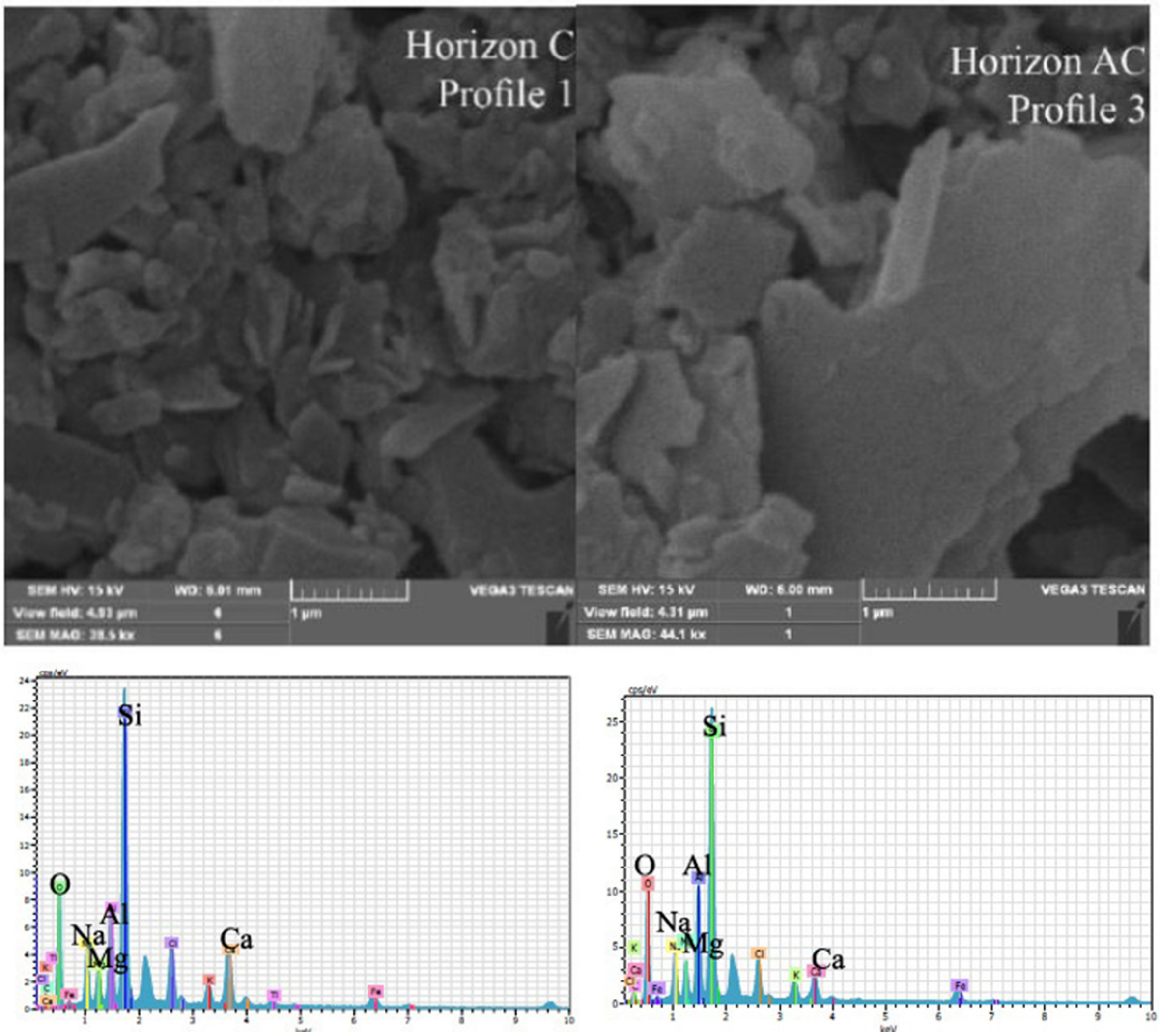
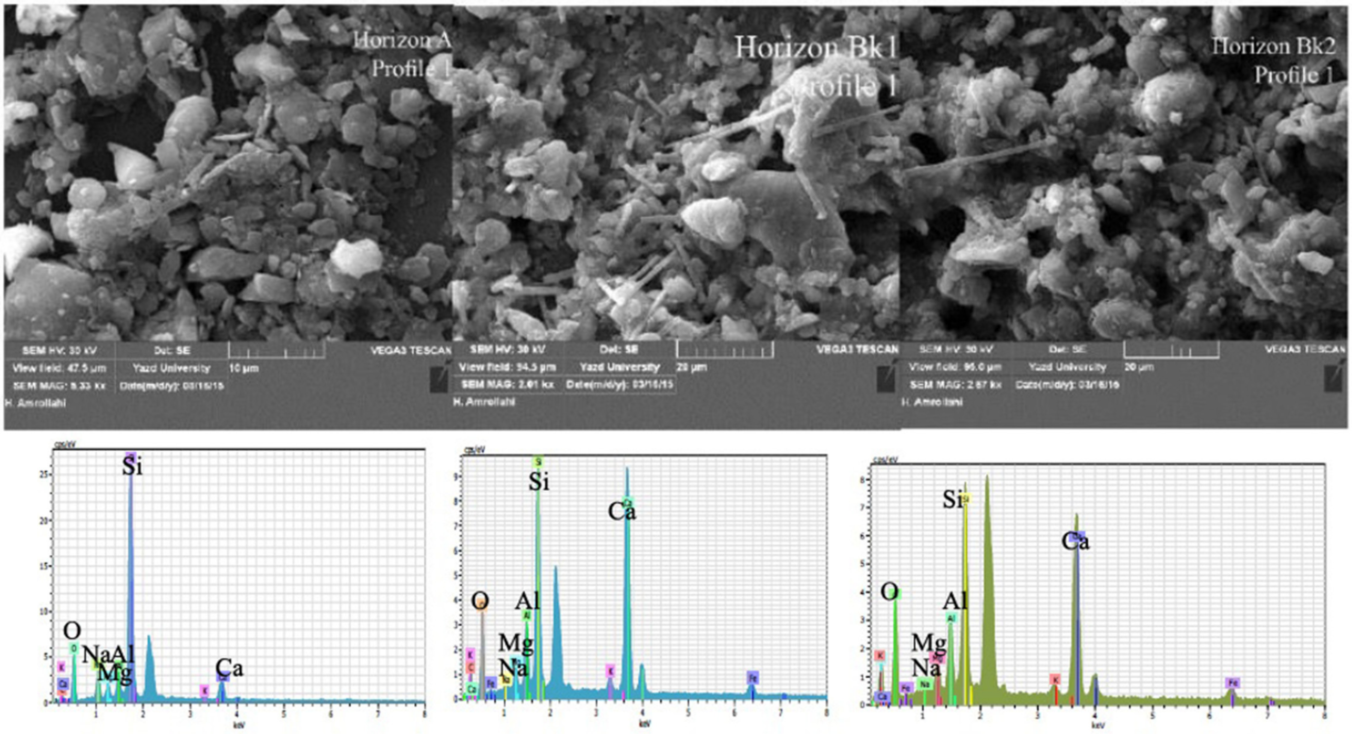


Fig. 7. The SEM images with EDS spectrometers of the upper A and middle-profile B_k1 and B_k2 horizons of profile 1 (from left to right, respectively). [Colour online.]



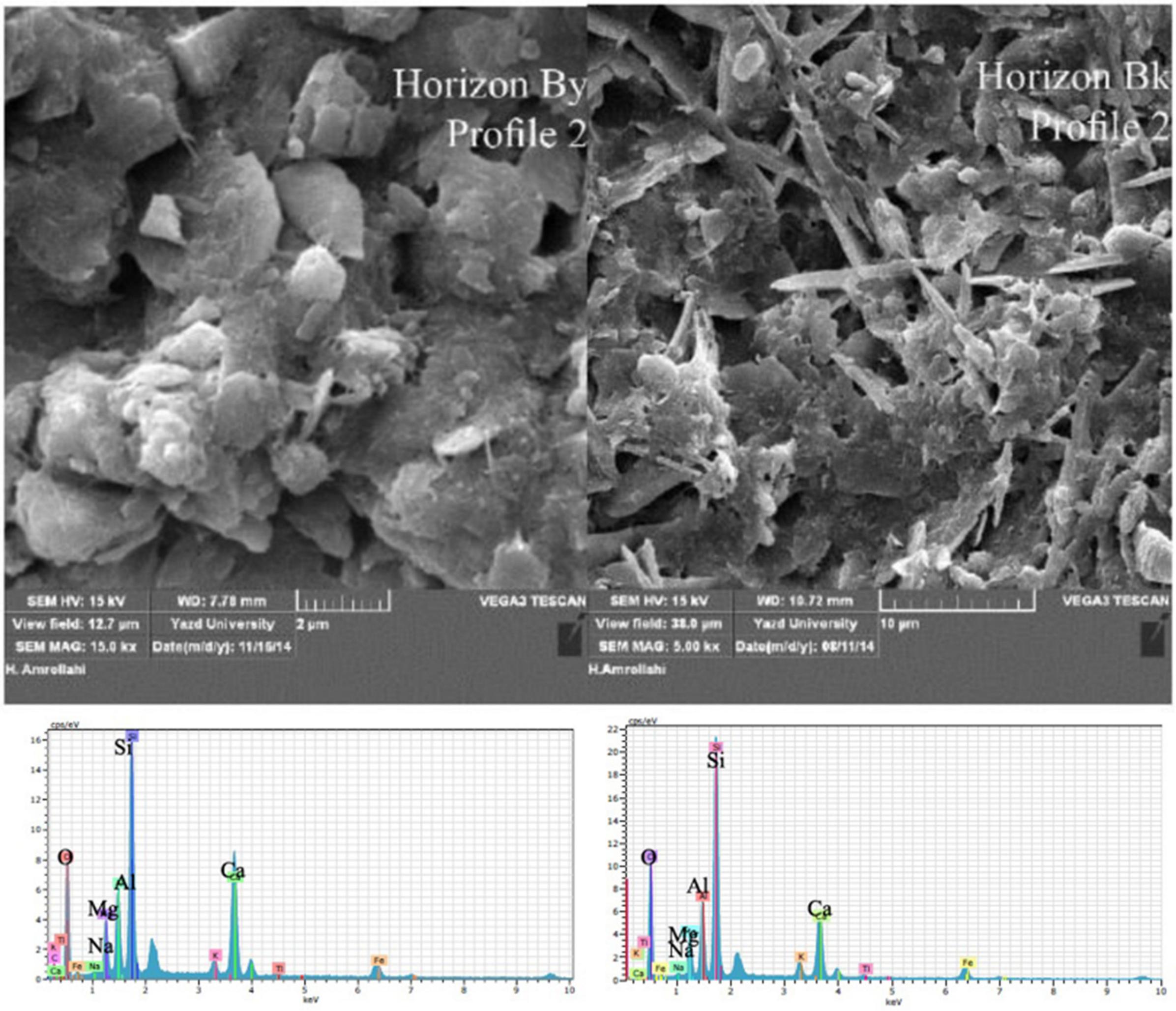
performed using an optical microscope. For scanning emission microscopy (SEM), the soil samples were placed onto glass slides and coated with gold. Then, microscopy analyses were performed using a SEM TESCAN instrument. Energy dispersive X-ray spectrometer (EDS) test was performed on the SEM images. The element analyses on the SEM images were done with EDS mapping, Bruker X Flash 6/10. The EDS-analyzed elements were compared with calculated soil elements of few ratios (90:10, 80:20 and 60:40) of calcite to palygorskite by formula (calcite: palygorskite as $CaCO_3$: $(Mg, Al)_2\ Si_4\ O_{10}$).

Results

All soil horizons, except for the gypsic horizon (Cy), showed low salinity in 1:5 soil/water extracts. The soil reaction in the 1:1 soil/water suspension in all the horizons, except for the Cy horizon, is alkaline ($pH > 8.0$). Minimum quantity of lime (21.75%) was calculated in the A horizon of profile 1 on upper landform and maximum quantity of lime (38.75%) was calculated in calcic horizon (Ck in profile 1) and AC horizon of profile 3 on the Soltanieh formation (Table 1). The ratio of Ca^{2+}/Mg^{2+} in 1:5 soil/water extracts in Bk1 and Bk2 horizons (in profile 1) were less than other horizons (Table 2). Soluble calcium/magnesium ratio in profile 2 was observed with the minimum quantities in Cy and Bk horizons due to relatively higher Mg concentration in these horizons (Table 2). Dry Munsell color in A horizon of profile 1 was brown (7.5YR5/3). In the horizons of Bk1 and Bk2 of profile 1, dry colors were changed from brown to reddish yellow (7.5YR6/6), whereas Ck horizon was pink (7.5YR7/4). Dry Munsell colors in A, B and Cy horizons of profile 1 were light brown (7.5YR6/4). Dry soil Munsell colors of topsoils on Soltanieh formation and detritus were brown and light brown, respectively.

An increased content of lime can be observed in the Bk horizons. In the Cy horizon, the content of gypsum significantly increases. Secondary calcite in Bk (25–80 cm) was occured in powder regular masses averaging 5 to 15 mm in diameters and 2–20% in area of the horizon in profile 2. This profile has developed from Nayband formation detritus. Secondary gypsum in the gypsic horizon (Cy) of profile 2 was observed with a massive structure where it diffused in all parts of the horizon. Table 3 shows total element in some of the horizons in study profiles. The amount of magnesium oxide in the solid phase of the soil profiles does not change significantly. However, the relative content of magnesium in comparison with calcium oxide tends to decrease within depth. The content of silicon in profile 2 is considerably higher than that in profile 3. The ratio of silica to alumina tends to increase with the depth, although this increase is small. Slight changes in the bulk contents of the major elements attest to a relative homogeneity of profiles. Against this background, the pedogenic accumulation of lime and gypsum in the Bk and Cy horizons, respectively, is clearly seen (Table 1).

Fig. 8. The SEM images with EDS spectrometers from calcic (Bk) and gypsic (By) horizons of profile 2. [Colour online.]



Among, palygorskite was detected in the samples according to strong reflection peaks at 1.06 nm and moderate reflection peaks at 0.64 nm in profiles 1 and 2 (Fig. 3). Illite and palygorskite in the soils developed from the Nayband formation constitute 40.64 and 39.30% in the clay fractions (<1 µm), respectively, in P1 (calculated by method of Biskaye 1964). In the soil developed from the Nayband detritus (P2), the content of palygorskite has increased up to 43.00% with a simultaneous relative decreasing of the content of illite. Along with palygorskite and illite, chlorite and smectite minerals were identified as 18% and 9%, respectively. X-ray diffraction data did not show the presence of palygorskite crystals in the soils on the Soltanieh formation (Fig. 4).

The photos of thin sections indicate that the major minerals in the bedrock R horizon in profile 1 are calcite, dolomite and quartz (Fig. 5).

The scanning electron microscopy (SEM) of parent materials from profiles 1 and 3 did not show the presence of palygorskite (Fig. 6).

The results of SEM analysis of profile 1 are shown in Fig. 7. It can be seen that the calcic Bk1 horizon contains a higher amount of palygorskite than the underlying Bk2 horizon; however, there was not palygorskite in the A horizon.

The soil samples in the calcic B horizon of profile 2 showed the presence of fibrous palygorskite crystals, but in the gypsic By horizon of this profile, such long crystals are absent (Fig. 8).

In the SEM images from Bk1 and Bk2 horizons of profile 1 (Fig. 7) and Bk horizon of profile 2 (Fig. 8), palygorskite crystals of 10 µm and longer can be seen on the secondary lime. This suggests the neoformation of palygorskite as authigenic mineral on calcite crystals upon increasing in the concentration of magnesium accompanying precipitation of secondary lime. The SEM from the secondary gypsum (By horizon in profile 2) shows the presence of very fine (<2 µm) palygorskite crystals (Fig. 8). The appearance of palygorskite in the gypsic horizon can be related to physical weathering and illuviation of palygorskite from the upper horizons

Fig. 9. EDS results on the electron microscope images of A, Bk, By and C horizons related to calculated elements from formula of palygorskite and calcite mix minerals.

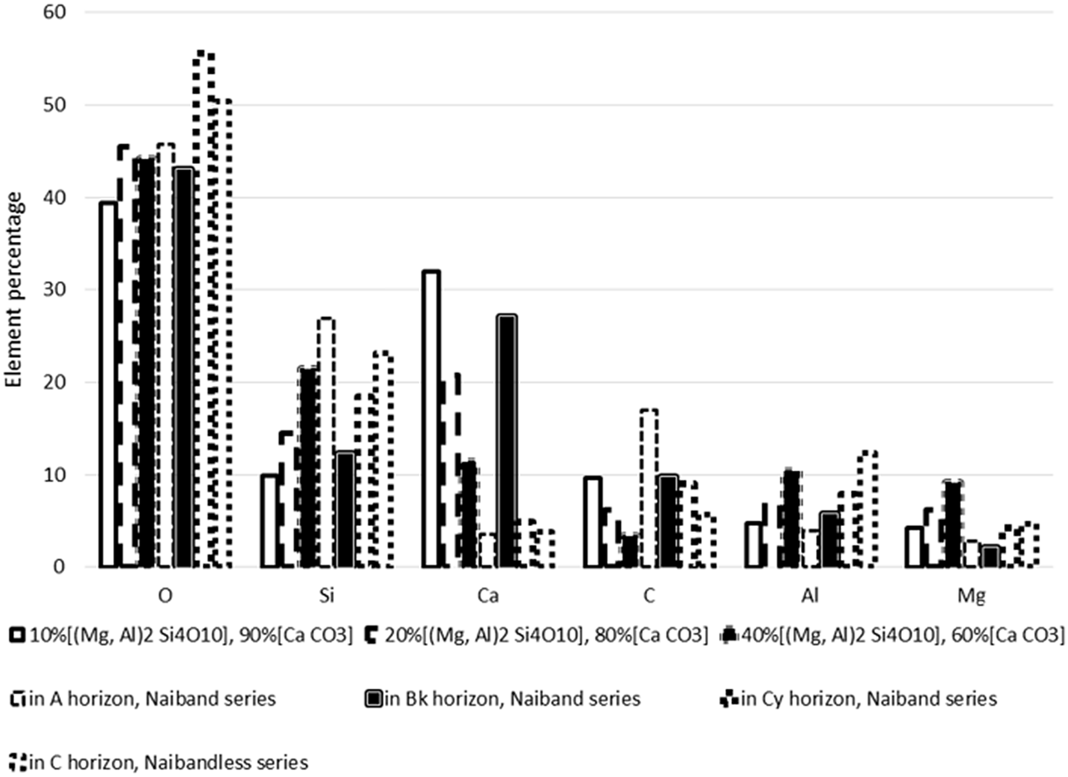
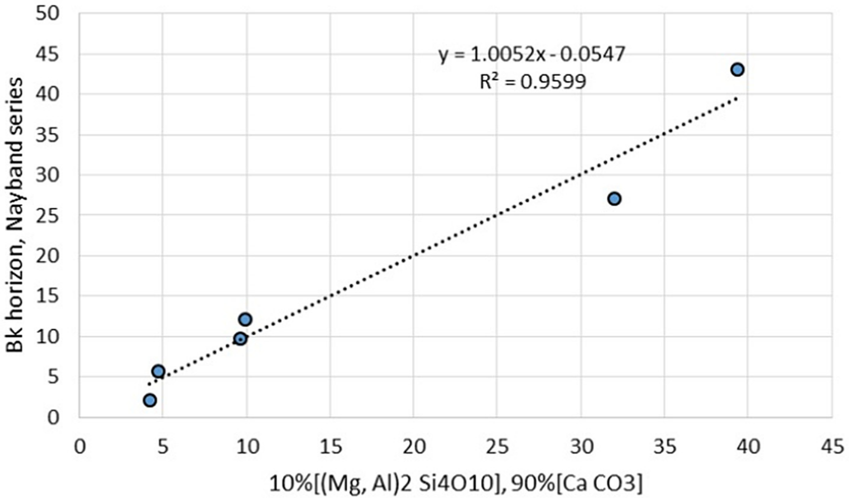


Fig. 10. A high coefficient of determination between determined elemental percentage of palygorskite (EDS analyses) and calculated mixed proportional (10:90) palygorskite and calcite. [Colour online.]



to smaller sizes. The SEM images of the C (profile 1) and AC (profile 3) horizons (Fig. 6) did not show the presence of palygorskite, suggesting that the lithogenic palygorskite is absent in these profiles. Also, the absence of palygorskite in the A horizon of profile 1 (Fig. 7) suggests the lack of plausible eolian origin of palygorskite in this profile. Thus, we concluded that palygorskites in the Bk horizons of the studied soils have formed from pedogenic origin. To further support such neoformation in calcic horizon, it has shown EDS results taken from electron microscopy samples in Figs. 6, 7 and 8. The EDS analyses were confirmed proximity of some elements percentages in formula (calcite: palygorskites, 90:10) and Bk horizon in P2 on Naiband detrition (Figs. 9

and 10). The ratio in formula (90:1) is close to the approximate ratio of 40:4 for the percentages of lime and palygorskite, respectively, in Bk horizons of the profiles 1 and 2. This ratio estimated from approximately 40% of lime in the calcareous horizons (Table 1) and 4% of palygorskite from multiplying 10% of the clay fraction and about 40% palygorskite in clay fraction.

Discussion

In the study area, palygorskite after ethylene glycol treatment expanded to about 17.5 Å, in accordance with Nordmeyer (1966) related to the [001] crystal lattice. Similar results with the use of the XRD analysis were earlier obtained for some samples from Mangyshlak Peninsula by Jeffers and Reynhold (1987). They reported on palygorskite that expanded upon ethylene glycol solvation. Kadir and Eren (2008) reported palygorskite associated with Quaternary caliches on the coastal landforms of Mersin, in Turkey, with Mediterranean climate. Also, Hojati et al. (2010) reported neoformation of palygorskite crystals under the influence of a saline and alkaline ground water in Central Iranian soils. The difference between the present study and others as Kadir and Eren (2008) and Hojati et al. (2010) is that the present study indicates the neoformation of Paligorskite crystals in the soils with Mesozoic parent materials on highlands of Central Iran. Palygorskite crystals of large (up to 20 μm and more) sizes were formed in situ in the calcic horizon that this phenomenon is adapted by Martin-Vivaldi and Craig (1972) that the length of palygorskite fibers varies greatly from <1 μm up to 20 μm. Smaller palygorskite crystals appeared in a deeper gypsic (By) horizon as the products of palygorskite weathering in the upper horizons. Although the formation of secondary gypsum in the By horizon could also provide a higher concentration of magnesium ions, the formation of palygorskite in this horizon could not be justified due to the less alkaline reaction.

Conclusion

The neoformation of palygorskite in the calcic horizon probably took place upon an increase in the relative concentration of Mg in the course of precipitation of secondary calcite with abundant silica, as confirmed by Scholtz (1968), Millot et al. (1969), Parquet (1970), and Lamouroux et al. (1973). They also reported palygorskite in calcareous horizon in chestnut and brown soils are important in better development and management of such soils. Proving of neoformation of Palygorskite in an aridic soil moisture regime is important, since this mineral has roles in soil fertility and stability (Singer 1992 and Shariatmadari 1998). Due to the similarities in soil parent materials of the study area in Iran and in the earlier study soils developed from calcareous rocks in the former Soviet Union in Central Asia, it would be recommendable to further investigate the occurrence and authigenic formation of palygorskite in the soils of Asia.

References

Akhavan Ghalibaf, M., and Chizhikova, N. 1998. Clay mineralogy, physical and chemical properties of some soils on the aeolians in Central Iran 1988. International symposium of Arid land soils, Turkey.

Akhavan Ghalibaf, M., and Chizhikova, N. 1999. Mineralogical properties of soils formed on Tertiary geological deposits in the north of Yazd. 7th Symposium of Crystallography and Mineralogy of Iran.

Akhavan Ghalibaf, M., and Chizhikova, N. 2000. Effect of subterranean (Qanat) water in desert soil mineralogical characteristics of Yazd. International Conference of Qanat, Yazd, Iran.

Akhavan Ghalibaf, M., and Mohammadi, S. 2011. *Quantitative clay mineralogy of Yazd-Ardakan plain with a scale of 1:500,000*. The Final Report of the Project in Faculty of Natural Resources in Yazd University.

Akhavan-Ghalibaf, M., and Rahbar-Alam-Shirazi, F. 2013. The origin, genesis and evolution of the clay minerals of palygorskite in the sediments and soils of Yazd Plain. 21th Symposium of Crystallography and Mineralogy, Zahedan, Iran.

Altaha, A. 1997. Effect of saline and alkaline ground water on soil genesis in semiarid southern Iran. Soil Sci. Soc. Am. J. **41**: 583–587.

Bailey, S.W. 1980. Structures of layer silicates. Pages 2–123 in G.W. Brindley and G. Brown, eds. Crystal structures of clay minerals and their X-ray identification. Mineralogical Society, London.

Bigham, J.M., Jayhes, W.F., and Allen, B.L. 1980. Pedogenic degradation of sepiolite and palygorskite on the Texas high plains. Soil Sci. Soc. Am. J. **44**: 159–167.

Biskaye, P.E. 1964. Mineralogy and sedimentology of the deep sea sediment fine fraction in the Atlantic ocean geochemistry. Tech. Rep. **8**: 86.

Brinkman, R. 1979. Clay transformations: aspects of equilibrium and kinetics. Pages 433–457 in G.H. Bolt, ed. Soil chemistry B. Physico-chemical models, Vol. 5, Part B. Elsevier Science Publishing Co., Amsterdam, Developments in Soil Science.

Dixon, J.B., and Weed, S.B. 1989. Minerals in soil environments. Soil Science Society of America, 1244 pp.

Elprince, A.M., Mashhady, A.S., and Abahusayn, M.M. 1979. The occurrence of pedogenic palygorskite (Attapulgite) in Saudi Arabia. Soil Sci. **128**: 211–219.

Golden, D.C., Dixon, J.B., Shadfan, H., and Kippenberger, K.A. 1985. Palygorskite and sepiolite alteration to smectite under alkaline conditions. Clays Clay Miner. **15**: 77–83.

Gradusov, B.P. 1992. Genetic-geographic patterns in the composition of soil-forming parent materials on the world map. Pages 196–301 in Globalnaya geografia pochv i faktorov pochvoobrazovania (The global geography of soils and soil-formation factors). Moscow.

Haghipour, A., and Aghanabati, A. 1989. Geological map of Iran. Ministry of Mines and Metals. Geological survey of Iran. 2nd ed.

Hashemi, S.S., Baghernejad, M., and Ghiri Najafi, M. 2013. Clay mineralogy of gypsiferous soils under different moisture regimes in Fars province, Iran. J. Agric. Sci. Technol. **15**: 1053–1068.

Hojati, S., Khademi, H., and Faz Cano, A. 2010. Palygorskite formation under the influence of a saline and alkaline ground water in central Iranian soils. Soil Sci. **175**: 303–312.

Jeffers, J.D., and Reynhold, R.C. 1987. Expandable palygorskite from the Cretaceous-Tertiary boundary, Mangyshlak peninsula, U.S.S.R. Clays Clay Miner. **35**: 473–476.

Kadir, S., and Eren, M. 2008. The occurrence and genesis of clay minerals associated with Quaternary caliches in the Mersin area, Southern Turkey. Clay Miner. **56**: 244–258.

Kaplan, Y.M., Eren, M., Kadir, S., Kapur, S., and Huggett, J. 2014. A microscopic approach to the pedogenic formation of palygorskite associated with Quaternary calcretes of the Adana area, southern Turkey. Turk. J. Earth Sci. **23**: 559–574.

Khabarov, A.V., and Chizhikova, N.P. 1984. Genetic and geochemical characteristics of soil forming parent materials and soils in the eastern Ustyurt. Pages 71–95 in Priroda, pochvy i problemy osvoyenia pustyni Ustyurt (Nature, soils and reclamation problems in the Ustyurt desert)'. Pushkin Institute.

Khitrov, N.B., and Ponizovskii, A.A. 1990. Practical *m*anual on the *a*nalysis of *i*onic–*s*alt *c*omposition of *n*atural and Alkaline *m*ineralsoils. Moscow (in Russian).

Kittrick, J.A., and Hope, E.W. 1983. A procedure for the particle size separation of soils for X-ray diffraction analysis. Soil Sci. **95**: 218–227.

Lamouroux, M., Parquet, H., and Millot, G. 1973. Evolution des mineraux argileux dans les sols du Liban, 23: 53–71.

Martin-Vivaldi, J.L., and Craig, J.R. 1972. Paligorskite and sepiolite (The hormites). Pages 255–275 in J.A. Gard, ed. The electron optical investigation of clays. Mineralogical Society, London.

Millot, G., Parquet, H., and Ruellan, A. 1969. Neoformation de l'attapolgite dans les sols a de la Basse Mouloya, Maroc Oriental, C.R. Acad. Sci. Ser. 2771–2774.

Minashina, N.G., and Gradusov, B.P. 1973. The mineralogy of clay in certain desert soils. Pochvovedeniye. **7**: 123–136.

Monger, C.H., and Daugherty, L.A. 1991. Neoformation of palygorskite in a southern New Mexico Aridisols. Soil Sci. Soc. Am. J. **55**: 1646–1650.

Nordmeyer, H. 1966. The retention of organic and inorganic compounds on clay minerals. Organic Chemistry Service, Chemistry department, Joint Nuclear Research Center, Ispra Establishment, Italy, 122 pp.

Page, A.L., Miller, R.H., and Keeney, D.R. 1982. Methods of soil analysis. Part 2-chemical and microbiological properties. ASA, SSSA, USA, 1159 pp.

Parquet, H. 1970. Evolution Geochimique des mineraux argileux dans les alterations et les sols des climats mediterraneens tropicaux a saisons contrastees. Mem. Serv. Carte. Geol. Alsace Lorraine, Strasbourg no. 30.

Rahbar-Alam-Shirazi, F., and Akhavan-Ghalibaf, M. 2014. The geological formations as a major factor of soil evolution in semi-arid vertical zones of Iran. Pages 117–120 in Materials on the study of Russian soils, Proceeding of the conference in Saint Petersburg State University, Saint Petersburg, Russia.

Scholtz, H 1968. Die boden der feuchten Savanne Sudwestafricas. Planzeneernaehr. Bodenkd. **120**: 208–221.

Shariatmadari, H. 1998. Interaction of phosphates and selected organic molecules with palygorskite and sepiolite. A Thesis Submitted to the College of Graduate Studies of the Requirements for the Degree of Doctor of Philosophy in the Department of Soil Science University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Singer, A. 1992. Palygorskite and sepiolite group minerals. Pages 829–873 in Minerals in soil environment. B. Dixonand S.B. Weed), 2nd ed. SSSA Publication, Madison, Wisconsin, USA.

Singer, A. 2002. Palygorskite and sepiolite–the enigmatic clay minerals. Berichte der Deutchen Ton-und Tonmineralgruppe **9**: 203–216.

Soil Survey Staff. 2014. Keys to Soil Taxonomy, A basic system of soil classification for making and interpreting soil surveys, 12nd ed..US Government Printing Office. USDA. NRCS, Washington DC, 372 pp.

Sosnovskaya, V.P., Chizhikova, N.P., and Antipov, I.K. 1978. Glinistie minerali pochv i pochvoobrazuyushikh porod Beshkentskoy dolini (Clay minerals of soils and soils-forming rocks of the Beshkent valley). Moscow University Bulletin, Moscow, pp. 35–45 (in Russian).

Travnikova, L.S. 1980. The mineral composition of finely dispersed material in grey-brown soils of the Karshin Steppe. In Management of salt-affected soils. Moscow Dokuchaev Soil Institute, Moscow.

Walkley, A., and Black, I.A. 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of chromic acid method in soil analysis. Soil Sci. **79**: 459–465.