

MINERALOGY OF PALAGONITIC MATERIAL FROM THE GOLAN HEIGHTS, ISRAEL

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Abstract—Sideromelane in Pleistocene lapilli-tuff rocks from the Golan Heights had partly altered into palagonite. X-ray and electron diffraction showed that the major part of the clay alteration product is composed of a dioctahedral micaceous mineral with well organized crystallinity along the *a*- and *b*-axes. Very poor basal reflections as well as incomplete expansion upon glycerolation and incomplete collapse upon heating were interpreted as being due to random interstratification with chlorite. Electron microscopy showed the particles to be very similar to montmorillonite tactoids. The thermal behavior as well as surface properties were similar to those of montmorillonite. Differential dissolution analysis and infrared spectroscopy failed to indicate amorphous constituents to any significant extent. Chemically the material was enriched in iron, aluminum and titanium and depleted in alkali and alkaline earth cations.

A minor component of the clay was found to consist of 'onion-like' halloysite. It is suggested that palagonite is a natural precursor for montmorillonite in the volcanic glass-montmorillonite alteration series.

INTRODUCTION

Though in use for a long time, the term 'palagonite' is fairly ill-defined and still seems to cause confusion. Peacock (1926) described it as a highly hydrated volcanic glass, usually with a low index of refraction (1.46–1.49). Hay and Iijima (1968) characterized it as a vitreous waxlike or resinous alteration product of sideromelane, that is generally yellow or orange, isotropic to weakly birefringent, with refractive indices ranging from 1.46 to 1.70. According to Kerr (1959) the indices of refraction of sideromelane and palagonite frequently overlap and the only distinguishing feature is the different water content.

Palagonite has only rarely been isolated and few clay mineralogical analyses have been carried out on that material. Hay and Jones (1972) reported the silica content of palagonite samples from Hawaii to be highly variable, with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios ranging from about 0.1–3.6. The same authors also noted that a relatively pure palagonite sample was characterized by a very weak X-ray diffraction peak at 4.43 Å, probably the (020) reflection of a poorly ordered phyllosilicate. X-ray analysis of Columbia River Plateau, Oregon Coast and Iceland samples of palagonite revealed the presence of smectites as the only crystalline components (Bonatti, 1965). Is palagonite then a semi-amorphous material with incipient crystallization into montmorillonite or an essentially amorphous aluminosilicate with admixtures of small amounts of crystalline montmorillonite?

This paper presents the results of some observations

on palagonitic material separated from altered pyroclastic rocks in the Golan Heights, northern Israel.

MATERIALS

The samples were collected from exposures of pyroclastic material south and west of Qnaitra (35° 47' 20"/33° 07' 30") and close to Tel Avital, one of the major volcanic cones in the northern Golan Heights. This volcanic cone and several others are part of a series arranged along two major lines of weakness and were formed during a period of volcanic activity in the Pleistocene. The ejected material consists of a variety of pyroclastics, including scoriae, lapilli and ash, all of a basic composition. While most of this material was deposited close to the ejection sites, part of it was carried eastward by the prevailing westerlies and sedimented in lower depressional areas.

The area has a subhumid Mediterranean type of climate. A long and dry summer follows a mild winter with an average rainfall of 900 mm p.a. a small fraction of it in the form of snow.

The pyroclastic material in one of the major deposition sites, the Qnaitra depression, is quarried from open-cut pits. Three samples were taken from the exposed wall of one of these quarries situated 3 km west of Qnaitra, at three different levels: T1—at 20 m from the surface; T2—at 17 m and T3—at 4 m.

METHODS

Rocks were indurated and thin sections were prepared for their optical examination. The < 2 μm frac-

tion from the rock samples was collected by the sedimentation method after an initial procedure of gentle crushing and then shaking in distilled water for 24 hr. This fraction was subdivided by centrifugation into fine ($< 0.2 \mu\text{m}$) and coarse ($0.2\text{--}2 \mu\text{m}$) clay.

Specific surface area of both rock and $< 2 \mu\text{m}$ material was determined by the ethylene glycol method of Carter *et al.* (1965). The differential dissolution technique of Hashimoto and Jackson (1960) was applied in order to determine the quantities of silica and alumina soluble in alkaline solution. These would then permit an estimate of the amount and composition of amorphous material. Cation exchange capacities were determined at a pH of 7. Separate determinations were also made at pH 3.5 and 10.7 in order to assess the CEC Δ value.

The chemical composition of relatively fresh rock and $< 2 \mu\text{m}$ material was determined by X-ray spectroscopy on a Philips model 1010 apparatus. Free iron oxides in the $< 2 \mu\text{m}$ material were obtained by the modified Aguilera and Jackson method (1959) and determined by atomic absorption.

Mineralogical determinations of the $< 2 \mu\text{m}$ material were carried out by X-ray, electron microscopy, thermal analysis and i.r. spectroscopy. For X-ray analysis a Philips model 1010 diffractometer was used, in addition to transmission cameras of the Debye-Scherrer type. Analyses were carried out on both dry and glycerolated, heated, oriented and unoriented samples, before and after treatment for the removal of amorphous material. The dry samples were equilibrated and run in a 65 per cent r.h. atm.

Electron micrographs were obtained on a JEOL, model Jem T7 electron microscope, with a beam voltage of 50 kV. Drops from suspensions of untreated $< 2 \mu\text{m}$ material were allowed to dry on grids. Whenever flocculation occurred, very dilute Calgon was added to the suspension. Exposure times were 5 sec. In order to avoid excessive dehydration during photography, examination and focusing were done on separate particles. Electron diffraction grids were partly covered with aluminum.

DTA and TGA curves were obtained on an apparatus with a 9°C min^{-1} heating rate and photographic recording, and a Stanton 1 mg thermobalance, respectively. For the i.r. spectroscopy a 237 Perkin-Elmer spectrometer was used.

RESULTS AND INTERPRETATION

Optical examination of rock thin sections

All the samples could be classified as scoriated, vitric lapilli-tuff. Olivine and pyroxene phenocrysts were imbedded in a matrix composed of microlites of basic

plagioclase interspersed in volcanic glass (sideromelane) with a refractive index of 1.60–1.61.

Part of the sideromelane had undergone alteration into weakly birefringent, yellowish-gold palagonite, with a refractive index varying between 1.52 and 1.57. The alteration appeared to be particularly well developed along the vesicle rims. Aside from the palagonite, no other clay mineral material could be observed.

The rock samples differed among themselves in the degree of alteration. While in sample T1 only a small part of the glass had undergone alteration, nearly all the glass in sample T3 had turned into palagonite.

Electron microscopy

In micrographs the general aspect of the clay from all samples was that of a uniform, well-dispersed montmorillonite (Fig. 1e). The shape of the particles was reminiscent of bentonite tactoids, of a uniform thickness. Frequently the particles were so strongly folded as to render them a shredded appearance (Figs. 1a–c).

Another mineral, of an oval, concentric shape, appeared to be halloysite, similar to the 'onion-like' halloysite described by Minato and Utada (1969) and Siefferman and Millot (1968) (Fig. 1b). The mineral was present in small quantities only and seemed to be more frequent in the fine ($< 0.2 \mu\text{m}$) clay fraction.

Well-defined amorphous minerals like allophane and imogolite were not identified but occasionally clusters of very small, spheroidal particles linked together to form chains that branch out and intertwist, were observed (Fig. 1d). Similar shapes had been reported by Besoain (1969) for amorphous minerals in many parts of the world.

X-ray and electron diffraction

In Fig. 2 are given the diffraction tracings for the whole clay fraction from sample T2. They were obtained from oriented material, which had not received any pretreatment except Mg-saturation, deposited on porous ceramic plates. Very similar tracings were obtained from the other samples also. Except for some weak reflections indicative of the presence of kaolinite or halloysite, no other diagnostic reflections could be identified. Glycerolation did not improve the quality of the diffraction peaks, nor did K saturation.

For the detection of weak reflections photographic methods were employed. Prior to examination the samples were subjected to various pretreatments.

In dry, Mg-saturated, otherwise untreated samples, powder photographs for the identification of basal spacings revealed the presence of clear but weak reflections at 7.07 \AA and weak and very diffuse reflections at $14.2\text{--}14.8 \text{ \AA}$ (Table 1). Barely discernible, diffuse 003

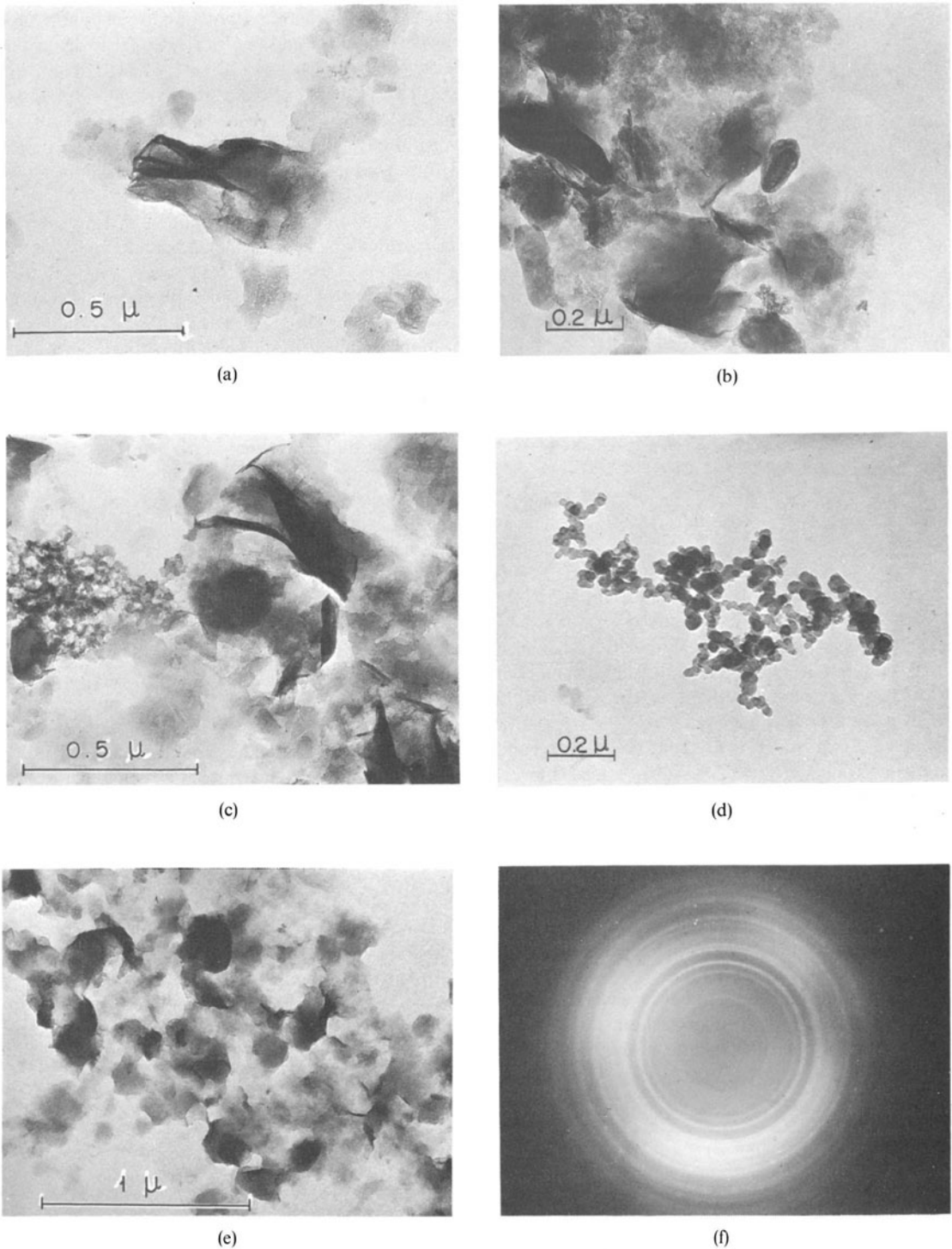


Fig. 1. Electron micrographs of the $< 2 \mu\text{m}$ palagonitic material from altered pyroclastic rocks, Golan Heights, Israel. (a) Strongly folded particle, similar to a dispersed montmorillonite tactoid. (b) Dispersed, folded particles and at center right one concentric, oval shaped halloysite particle. (c) Dispersed, folded particles and at center, left unidentified, amorphous(?) material. (d) Amorphous(?) material consisting of clusters of small, spheroidal particles linked into intertwisting chains. (e) Group of evenly dispersed, montmorillonite-like palagonite particles. (f) Electron diffraction of a group of palagonite particles from previous picture.

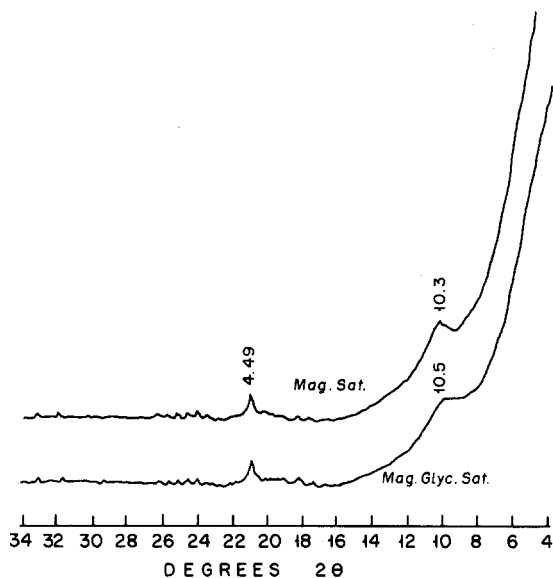


Fig. 2. X-ray diffraction tracings for $< 2\mu\text{m}$ palagonitic material from altered, pyroclastic rocks, cobalt radiation.

and 004 reflections of the 14 \AA mineral were also present at 5.06 and 3.52 \AA , respectively.

On samples which had been subjected to the differential dissolution technique and from which iron oxides had been removed, slight improvements in the 7.07 \AA reflections were achieved.

Upon heating to 550°C for 2 hr, one diffuse band, extending from 9.50 to 14.2 \AA was obtained. Further heating up to 700°C did not significantly alter the shape or position of the reflections.

Maximum orientation and glycerolation of otherwise untreated samples, which had not been dried, did not improve the intensity of the reflections, but only increased the 14.8 \AA spacing to a diffuse $15.5\text{--}16.8\text{ \AA}$ reflection. Another diffuse reflection appeared at 10.5 \AA , while the 7.07 \AA reflection became very weak.

The 7.07 \AA lines appeared to be somewhat more distinct in the fine ($< 0.2\mu\text{m}$) clay fraction.

In contrast to the poor quality of the basal reflec-

tions, Debye-Scherrer photographs of unoriented powders in untreated samples yielded fairly distinct hk lines, notably (11,02); (13,20); (31, 15,24), (26, 40), and (35,17,42) (Table 2). From a strong, slightly diffuse 060 line at 1.495 \AA the dioctahedral character of the mineral was deduced. The 02,11 line had a sharp peak with a gradual tailing off, characteristic for a two-dimensional lattice.

Trace amounts of accessory minerals identified from the photographs were calcite and apatite.

Excellent resolved hk rings were obtained from selected area electron diffraction photographs of sheet-like, folded particles (Fig 1 f). In addition to the hk reflections obtained from X-ray diffraction, the weaker 22,04 line was also identified (Table 2). Only the 11,02 reflections were strong. All the others including the 06,33 line were weak and somewhat diffuse.

From the diffraction analysis the a and b dimensions were determined by the interplanar spacings d_{400} and d_{600} , respectively. Measurements were on at least five different ring patterns of both the X-ray and the electron diffraction photographs. Values of $8.970\text{--}9.012\text{ \AA}$ for b and $5.144\text{--}5.220\text{ \AA}$ for a were obtained.

The diffraction results indicate the presence of two distinct clay mineral species in the clay fraction separated from the altered pyroclastic rocks:

(a) The major part of the clay is composed of a dioctahedral micaceous clay mineral with well organized crystallinity along the a and b axes. The very poor basal reflections, as well as the incomplete expansion upon glycerolation is interpreted as being due to random interstratification with a non-expanding 14 \AA mineral. The incomplete collapse to 9.5 \AA upon heating suggests that this interstratified component is aluminous or iron-rich chlorite. Iron-rich chlorites are known to give very weak 001 and 003 reflections (Brown, 1961). The stronger 002 reflection overlaps with and therefore could be mistaken for kaolinite.

(b) A minor component in the clay is a mineral from the kaolinite group. This mineral appears as b -axis disordered kaolinite or halloysite, depending on whether the clay had been dried prior to examination.

Table 1. 001 reflections from northern Golan palagonitic material ($< 2\mu\text{m}$), Mg saturated

Indices	Untreated, slightly oriented		Glycerolated, max. oriented		DDA pretreated		Preheated to 550°C	
	d (\AA)	I	d (\AA)	I	d (\AA)	I	d (\AA)	I
001	14.2–14.8	w., diff.	15.5–16.8	w., band	14.2–14.8	w., diff.	9.5–14.2	w., band
001	7.07	w., diff.	7.10	v.w., diff.	7.07	w.		
002			10.8	v.w., diff.				
003	5.06	v.w., diff.			5.06	v.w., diff.		
004	3.52	v.w., diff.			3.52	v.w., diff.		

Table 2. *hk* reflections from X-ray and electron diffraction of palagonitic (< 2 μ m) material from the Golan Heights (T-2)

Indices	X-ray		Electron	
	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
11, 02	4.54	s., with tail	4.52	m., with tail
13, 20	2.56	s.	2.58	s.
22, 04			2.26	m.
31, 15, 24	1.67	w., diff.	1.70	w.
33, 06	1.495	s.,	1.502	w.,
26, 40	1.28	w., diff.	1.29	w.
35, 17, 42	1.23	v.w., diff.	1.25	w., diff.
Calcite	3.02	v.v.w.		
Apatite	2.81	v.v.w.		

Differential-thermal analysis (DTA) and thermo-gravimetric analysis (TGA)

In Mg-saturated, otherwise untreated samples, the large endotherm at 150°C (Fig. 3) indicates the presence of a swelling mineral or possibly of an amorphous substance like allophane. The unsymmetrical endotherm at 550°C and the small exotherm at 900°C both point to the presence of a *b*-axis disordered kaolinite, or halloysite. The relatively low temperature of the exotherm, and its small size attest to the small particle size and disordered structure of the mineral (Mackenzie, 1957). The shape of the curves for the different materials was nearly identical, but the size of the 550°C endotherm differed. Arranged according to their size, the T3 sample contained the largest amount of kaolinite-halloysite (approx. 26 per cent), about twice more than sample T1 which contained the lowest (approx. 13 per cent).

Weight losses at different temperatures (Fig. 4) allow similar conclusions to be drawn from the TGA.

I.R. spectroscopy

The most prominent absorption peaks in all untreated samples were observed at 910–920 cm^{-1} (Fig. 5). This absorption is to be attributed to the stretching frequency of Si—O bonds.

Less developed were the absorption bands associated with stretching vibrations of the OH groups. Absorption bands at 3700–3710 cm^{-1} indicate the presence of OH groups belonging to kaolin type minerals. The absorption peaks at 3620 cm^{-1} , indicative of internal hydroxyl groups, were barely discernible. This latter absorption could be assigned to kaolin type minerals, but also to aluminous montmorillonite or chlorite (White, 1971).

Absorption in the 880–900 cm^{-1} range, fairly well developed in all samples might be attributed to OH bending frequencies of montmorillonite with trivalent ion occupancy in the octahedral sites.

Most of these absorption peaks appeared to be more developed in the fine (< 0.2 μ m) clay fraction.

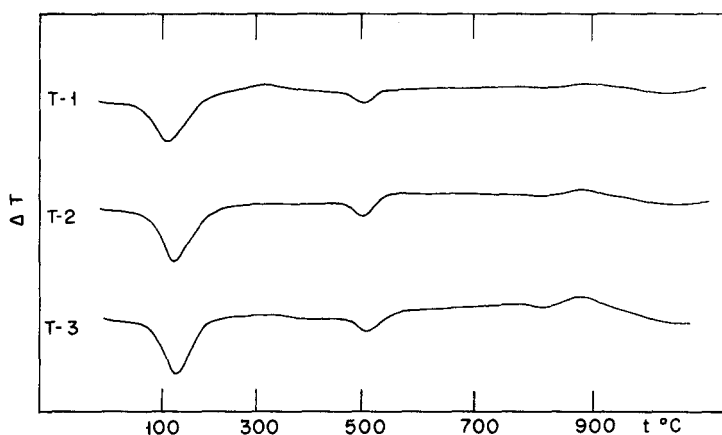


Fig. 3. Differential thermal analysis of < 2 μ m palagonitic material.

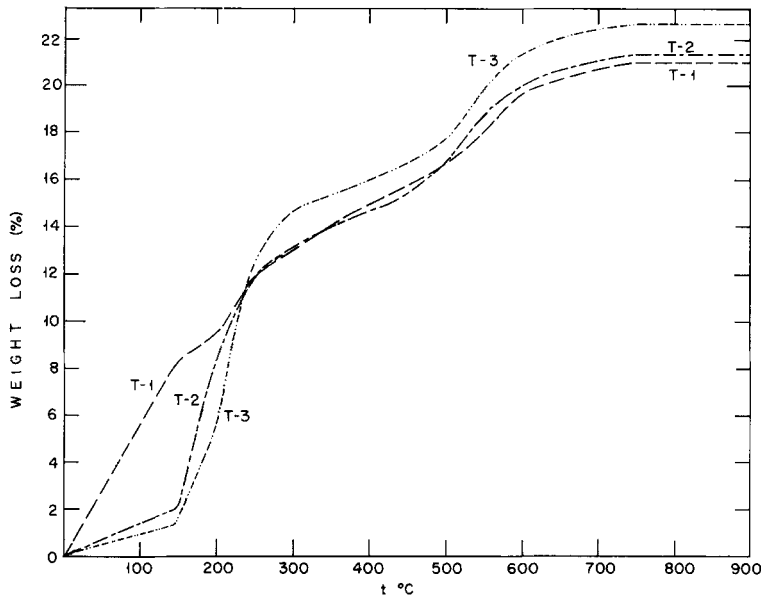


Fig. 4. Thermogravimetric analysis of $< 2 \mu\text{m}$ palagonitic material.

The lack of any absorption at 800 cm^{-1} suggests the lack of quartz or amorphous Si-O groups.

From these spectra it can be deduced that at least a large fraction of the clay is in a well organized crystalline state.

Chemical determinations

The chemical composition of the altered lapilli-tuff rock T2 and the $< 2 \mu\text{m}$ material collected from it is

given in Table 3. No unaltered material was present to serve as reference for calculating the chemical alteration. Chemical changes during alteration could only be estimated by comparison with a nearby unaltered magmatic rock of basic composition.

Depletion in alkalis appears to be nearly complete. Also alkaline earth cations had been depleted to a large extent. The small amounts of Ca and Mg persisting in the $< 2 \mu\text{m}$ material are probably present largely in the adsorbed form and possibly as carbonates. Manganese had also undergone depletion and, to a much more limited extent, also silica. Changes in iron and titania are insignificant.

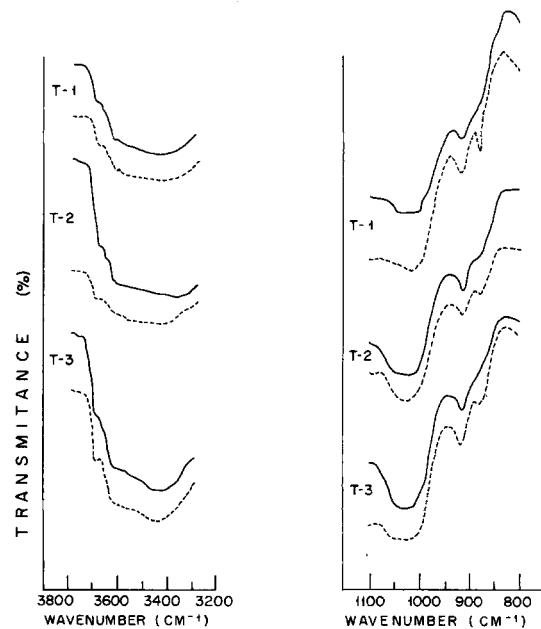


Fig. 5. I.R. spectra of $< 2 \mu\text{m}$ palagonitic material.

Table 3. Chemical composition of the altered lapilli-tuff rock T2 and the $< 2 \mu\text{m}$ palagonitic material separated from it. For reference the chemical composition of a nearby, unaltered basic rock is given (ignited basis)

	T2 rock	T2 < $2 \mu\text{m}$	Unaltered rock
SiO ₂	47.05	49.10	45.52
Al ₂ O ₃	18.31	23.15	16.35
Fe ₂ O ₃	14.68	16.55	13.29
MnO	0.19	0.12	0.20
TiO ₂	4.39	4.32	3.14
CaO	8.34	4.33	8.08
MgO	3.78	1.15	7.32
P ₂ O ₅	2.16	1.08	1.36
K ₂ O	0.69	0.19	0.98
Na ₂ O	0.65	0.31	3.95
	100.25	100.30	100.19

Table 4. Free iron oxides and differential dissolution analysis of palagonitic alteration material (< 2 μm) from altered lapilli-tuff rocks (in % by wt)

	DDA					
	Free Fe ₂ O ₃ (%)	SiO ₂	Al ₂ O ₃	SiO ₂ /Al ₂ O ₃	After heating	
					SiO ₂	Al ₂ O ₃
T1	2.25	9.6	4.9	3.3	12.8	6.4
T2	3.92	10.6	7.1	2.5	8.3	6.8
T3	3.51	9.8	6.9	2.5	7.4	4.1

Only a small fraction of the iron is present in the 'free' state (Table 4). Since mineralogical analysis did not reveal any iron or titania ore minerals in the < 2 μm material, most of these elements must be included within the clay mineral lattice.

The differential dissolution analysis was carried out to examine whether any amorphous aluminosilicates were present in the < 2 μm material. From the results in Table 4 it can be seen that the total amounts of silica and alumina brought into solution are small relative to the weathering products of many other volcanic materials. The SiO₂/Al₂O₃ molar ratio of the material in solution is high and uncharacteristic for most of the amorphous alteration products of pyroclastic rocks. Rather, this ratio suggests partial breakdown of mica-type clay minerals. Heating of the samples to 400°C prior to the DDA treatment did not significantly alter the extent of the solution, thereby excluding the presence of amorphous interlayer alumina (Dixson and Jackson, 1962).

Surface properties

Specific surface areas (SSA), cation exchange capacities (CEC) and hygroscopic moisture values for the whole rocks and the < 2 μm material are given in Table 5. Specific surfaces of the fine material are very high (500–600 m² g⁻¹). Only swelling 2:1 clay

minerals of the montmorillonite group and also allophane (Besoin, 1969) are known to possess comparable specific surface area.

The surfaces appear to be highly charged and active as evidenced from the high CEC and hygroscopic moisture values. Again these results are comparable to those obtained from montmorillonite, or allophane at high pH. Cation exchange capacities as determined at low and high pH values were not significantly different from those obtained at pH 7.

The SSA of the whole rocks is considerably smaller. The rock SSA: < 2 μm SSA ratio can be taken as a measure of the argillation degree. Using that method, the T1 rock contains the least amount of clay (~16 per cent) while T3 is the most argillized, with ~75 per cent.

DISCUSSION

A frequent stumbling-block in the interpretation of alteration phenomena and clay mineral formation is the correct identification of the processes involved as authigenic. The possible sources of error are numerous. In sedimentary materials the most common is to accept detrital minerals as authigenic. Igneous rocks may have undergone more than one cycle of weathering and alteration. Probably the most frequent and serious source of error is to include contaminants

Table 5. Specific surface areas (SSA), cation exchange capacities (CEC) and hygroscopic moisture values for whole lapilli-tuff rocks and their palagonitic < 2 μm alteration products

	SSA (m ² g ⁻¹)	CEC (m-equiv. 100 g ⁻¹) at pH 7	(-) H ₂ O (%)	Argillation* (%)
T1 rock	76.4		2.16	~16
T1 < 2 μm	503.3	118	12.82	
T2 rock	277.0		8.88	~50
T2 < 2 μm	563.5	106	13.93	
T3 rock	413.6		13.22	~75
T3 < 2 μm	579.7	101	13.35	

* Assuming the SSA of the perfectly unaltered rock to be negligible.

with the alteration products. Therefore, prior to the interpretation of the Golan Heights alteration phenomena, the possible interference of contamination deserves some consideration.

The exposures of pyroclastic material that were sampled form part of a massive deposit of ejecta, exceeding 20 m in depth. Though variation in grain size and vesicularity do exist within this deposit, thorough petrographic examination of various cross-sections (Mor, 1973) did not reveal the presence of any non-pyroclastic material. Moreover, the sedimentation pattern strongly suggests that though deposition into a shallow body of water may have occurred, the means of transport of the pyroclastic material was wind alone. Therefore the addition of materials of alluvial origin is highly improbable.

The admixture of clay material by alluviation from the soils covering the deposits is hardly feasible because of the considerable depth from which some of the samples were taken. Also, the composition of the clay fraction from soils formed contemporaneously on the pyroclastic material is very much different from the alteration products described (Singer, 1972).

In the Near East, including Israel, contamination by wind is a particularly potent factor. Aeolian material depositing throughout the Quaternary invariably contains quartz. This fact has been used successfully to prove the aeolian contamination of basaltic soils in the Galilee (Singer, 1967). While nearly all the contemporaneous soils in the Golan Heights do contain some quartz and therefore very probably are contaminated, the alteration products described are remarkably free of quartz, suggesting absence of any aeolian contamination.

The microscopic observation of the palagonitic alteration can serve as positive evidence for the authigenic formation of the clay. The palagonitic alteration material appeared to develop gradually from the unaltered glass, and not to represent an added coating. Finally, the degree of alteration, as observed visually in thin sections of various rocks, seemed to be well related to the specific surface areas as measured in these rocks and to the amount of clay extracted from them.

The alteration of pyroclastic material has been given ample attention both because of the abundance of that material and the frequently unusual alteration products. While the alteration series: volcanic glass-allophane or imogolite-halloysite-kaolinite, seems to represent the most common alteration course in humid climates, both cold and hot (Besoain, 1969) drier conditions appear to foster a variety of other secondary minerals, the principal among them being montmorillonite. Kanno (1961) reports from Japan the transformation of allophane into montmorillonite as a result

of intermittent imperfect drainage and addition of soluble bases and silica. Poorly crystalline montmorillonite has been identified in ash-derived soils from the Antilles and Nicaragua and attributed to alternating dry and humid conditions (Colmet-Daage, 1969). Retention of the soil solution by internal capillary channels of vesicular pumice and alternate wet and dry conditions are the two factors instrumental in the genesis of montmorillonite in the pumice soils of Oregon, according to Chichester *et al.* (1969).

Very little information is available on the transition stages in the volcanic glass-montmorillonite alteration. Pettapiece and Pawluk (1972) propose that the montmorillonite is formed by synthesis from components derived from the hydrolysis of the volcanic glass, passing through a stage of poor crystallinity and random interstratification. Precursors of an allophanic nature for the montmorillonite formation are given by Chichester *et al.* (1969).

Palagonite is frequently regarded as the amorphous analogue of montmorillonite in volcanic glass alteration. When not formed under submarine conditions, palagonite paragenesis from volcanic glass is attributed to conditions created by impeded drainage (Fieldes *et al.*, 1956) similar to those of montmorillonite.

In nearly all the related reports, occurrences of palagonite are associated with those of montmorillonite. According to some authors (Hay and Iijima, 1968; Hay and Jones, 1972) montmorillonite is a separate mineral phase precipitated from solutions saturated with regard to components brought into solution during the sideromelane-palagonite alteration.

From the results of X-ray analyses, Bonatti (1965) appeared to regard palagonite as mixtures of montmorillonite with largely amorphous hydrated glass. Though Hay and Iijima (1968) and Hay and Jones (1972) in their descriptions of palagonite from Hawaii mention the occurrence of X-ray diffraction peaks which could be associated with montmorillonite, they commonly distinguish between palagonite proper which is largely X-ray amorphous, and more or less crystalline montmorillonite.

The present investigation does not indicate that the palagonite from the Golan Heights can be defined as amorphous by any of the accepted standards. Both X-ray and electron diffraction showed the distinct development of a dioctahedral sheet silicate structure. Layer stacking, admittedly, appears to be less perfect and to consist of a random interstratification of expanding mica type- non-expanding chlorite layers. Infrared spectroscopy indicated the existence, at least to a limited degree, of crystalline arrangements.

Electron micrographs revealed the essentially mica-

aceous external morphology of the particles while surface properties are very similar to those usually associated with montmorillonite. Neither did the differential dissolution technique treatments release into solution significant amounts of amorphous components.

As shown by Jackson (1968) aluminous chlorite commonly occurs together with montmorillonite and has a possible role in the crystal nucleation of that latter mineral. Interstratified chlorite–montmorillonite would be a probable intermediary product in that process.

The present investigation has shown that the so called palagonite from the Golan Heights is a mineral having a close resemblance to interstratified montmorillonite–chlorite. It is therefore suggested that palagonite is a natural precursor for montmorillonite in the volcanic glass–montmorillonite alteration series. This suggestion is supported by the study of the artificial alteration of basic volcanic glass, in which Trichet (1969) obtained a dioctahedral mineral (060 reflection = 1.48 Å) that presented characteristic features of Al–montmorillonite and Al–swelling chlorite.

The alteration of the Golan Heights palagonite had been accompanied by a nearly complete depletion in alkali and alkaline earth cations and a slight depletion in silica. According to Hay and Jones (1972) the content of silica in palagonite varies as a function of climate, and they report $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios differing as much as 0.1–3.6 in palagonites from Hawaii. But again, as with the mineralogical data, it is not clear whether these data refer to palagonite per se or to mixtures of alteration products that include also montmorillonite.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the Golan Heights palagonitic material is 3.6 and is close to that obtained for the alteration products of atmospherically weathered basalt in the Galilee, under a similar rainfall (Singer, 1970). While according to Bonatti (1965) palagonite formation requires relatively high temperatures and therefore takes place mainly during the effusion and cooling of subaquatic lava, Hay and Iijima (1968) present evidence that palagonite may also form by the reaction of glass with percolating ground-water. When sufficiently high pH values are attained, glass is altered into palagonite. Some sedimentological evidence indicates that the alteration of Golan Heights palagonite may have taken place under shallow subaquatic conditions such as marshes or intermittent lakes, created by temporary water logging (Mor, 1973). Therefore, alteration conditions created primarily by percolating ground-water, similar to those reported from Oahu, Hawaii (Hay and Iijima, 1968) can be assumed also to have prevailed here.

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Résumé—La sideromélane contenue dans les lapilli-tuffs du Pleistocène provenant des hauteurs du Golan est partiellement altérée en palagonite. La diffraction des rayons X et des électrons montre que la plus grande partie du produit argileux d'altération est composée d'un minéral micacé dioctaédrique ayant une cristallinité bien organisée le long des axes *a* et *b*. Des réflexions basales très médiocres, un gonflement incomplet au glycérol et une fermeture incomplète lors du chauffage ont été interprétés comme dus à une interstratification au hasard avec de la chlorite. La microscopie électronique montre que les particules sont très semblables à des tactoïdes de montmorillonite. Le comportement thermique et les propriétés de surface sont semblables à ceux de la montmorillonite. L'analyse par dissolution différentielle et la spectroscopie infrarouge se sont révélées impuissantes pour déceler des constituants amorphes en quantité significative. Chimiquement, le matériau a été enrichi en fer, aluminium et titane et appauvri en cations alcalins et alcalino-terreux.

On a découvert qu'un composant mineur de l'argile consiste en de l'halloysite en 'bulbe d'oignon'. On suggère que la palagonite est un précurseur naturel de la montmorillonite dans les séries d'altération verre volcanique-montmorillonite.

Kurzreferat—Sideromelan in pleistozänen Lapilli-Tuff-Gesteinen von den Golan-Höhen hat sich teilweise in Palagonit umgewandelt. Röntgen- und Elektronenbeugung zeigten, daß der größte Teil des Tonumwandlungsproduktes aus einem dioktaedrischen, glimmerartigen Mineral mit gut ausgebildeten Kristallitschichten der *a*- und *b*-Achse besteht. Sowohl die sehr dürrtigen Basisreflexe als auch unvollständige Aufweitung nach Glycerinbehandlung und unvollständige Kontraktion nach Erhitzung wurden als Folge einer zufälligen Wechsellagerung mit Chlorit interpretiert. Die Elektronenmikroskopie zeigte, daß die Teilchen Montmorillonittaktoiden sehr ähnlich sind. Das thermische Verhalten und die Oberflächeneigenschaften waren denen des Montmorillonits ähnlich. Die Analyse des Lösungsverhaltens und die Infrarotspektroskopie ergaben keine Hinweise darauf, daß amorphe Bestandteile in irgend einem bedeutsamen Ausmaß vorlagen. Chemisch war das Material an Eisen, Aluminium und Titan angereichert und an Alkali- und Erdalkalitionen verarmt.

Ein Nebenbestandteil des Tons besteht aus 'zwiebelartigem' Halloysit. Es wird vorgeschlagen, den Palagonit als einen natürlichen Vorläufer des Montmorillonits in der Umwandlungsreihe vulkanisches Glas-Montmorillonit aufzufassen.

Резюме — Сидеромелан в горных породах плейстоцинского шлакового туфа из Голановых Хайтс частично изменился в палогонит. Рентгенография и дифракция электронами показали, что большая часть продукта изменения глины состоит из диоктаэдрального слюдистого минерала с хорошо организованной кристалличностью по осям *a* и *b*. Очень плохие базальные отражения, неполное расширение при обработке глицерином и неполное осаждение при нагреве приписали произвольному перемежающемуся напластованию хлорита. Под электронным микроскопом видно, что частицы очень похожи на тактоиды монтмориллонита. Термическое поведение и характеристики поверхности подобны характеристикам монтмориллонита. Анализ дифференциальной диссолюцией и ИК-спектроскопия не показали значительного количества аморфных составных частей. Материал был химически обогащен железом, алюминием и титанием и истощен щелочью и катионами щелочной земли.

Нашли, что небольшая часть глины состоит из «лукообразного» галлуозита. Полагают, что палогонит является естественным предвестником монтмориллонита в вулканическом стекле — последовательность изменения монтмориллонита.