PALYGORSKITE FROM PADASJOKI, SOUTHERN FINLAND

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Monoclinic palygorskite with the unit cell $a_0 = 12.689$ Å, $b_0 = 17.845$ Å, $c_0 = 5.119$ Å and $\beta = 91.22°$ has been found at Padasjoki, southern Finland. The mineral is thought to be of hydrothermal origin. Monoclinic symmetry is connected with an ordered Mg-Al substitution, although owing to the low $\triangle d_{12\bar{1}-121}$ value observed a low degree of ordering is suggested.

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Introduction

The first reliable find of palygorskite, $(Mg,Al)_2Si_4O_{10}(OH) \cdot 4H_2O$, in Finland has been made at Padasjoki, southern Finland. Although Kazakov (1911) reported that palygorskite had been found in a museum sample from Stansvik, Finland, later investigations of the Stansvik quarry (Aurola 1956) indicated the existence of only sepiolite. Within the scope of the present study the Stansvik mountain leather and asbestos minerals were re-investigated, but no palygorskite could be found.

Uusinoka (1975, p. 82) reported that no sepiolite-palygorskite was encountered in his study of rock-gouge in fractures of Finnish bedrock.

White mountain leather occurs as thin (about 1 mm) sheets (Fig. 1) in opened fissures in a road cut north of the lake Mäkientaus-tanjärvi at Padasjoki (map sheet 214307; coordinates x = 6801.62, y = 561.08). X-ray diffraction studies proved the mountain leather to be palygorskite. The granitic host rock is partly altered and yellowish green due to epidotization.
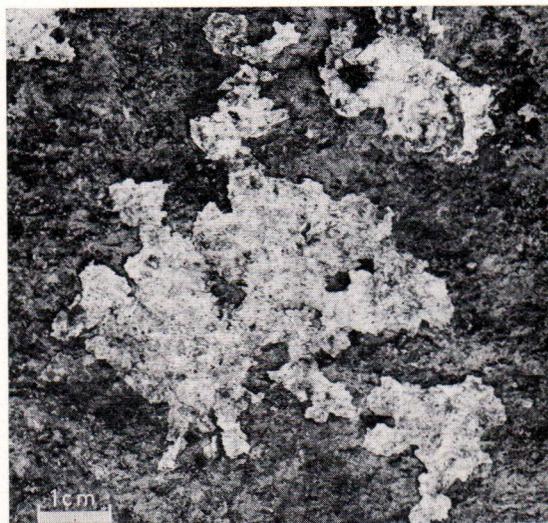
Fig. 1. Palygorskite as thin sheets on granitic host in an opened fissure.

Fig. 2. Slickensides in the fault zone at Padasjoki.

Geological setting

The bedrock of the area is part of the deep-eroded base of the Svecokarelides. WSW from Padasjoki there is a fault zone striking N 65° E. Several outcrops show mylonitization, quartz-epidote dykes and slickensides (Fig. 2). According to Laitakari (1971), the zone can be traced for several kilometres along the contact between porphyritic granodiorite and biotite gneiss. Some small granite areas have also been met with in the region. Morphologically the fault zone manifests itself as the straight valley- and watercourse nearby (Rautajärvi-Pintalammi-Särsjärvi). In a road cut close to the lake Pintalammi a diabase dyke was found that is thought to belong to the roughly 1600-Ma-old olivine diabase dyke swarm of Häme (cf. Laitakari 1969). Small quantities of palygorskite were also identified in fissures of this dyke. Quartz-epidote dykes in the diabase indicate that movements took place in the fault zone after the emplacement of the diabase. Lau-montite-leonhardite-, calcite- and montmorillonite-bearing veins are met with in the fault zone.

Texture and chemical composition

Scanning electron microscopy showed that the palygorskite occurs as interwoven fibres (Fig. 3), the same texture as is exhibited by the mineral in other parts of the world, for example in the Puente Hills in U.S.A. (Henderson et al. 1973), at Stjernøy in Norway (Salter and Appleyard 1974) and at Fergana in U.S.S.R. (Mironenko 1970). This texture is responsible for the leathery character of the sample. The observed indices of refraction are $\alpha' = 1.520 \pm 0.005$ and $\gamma' = 1.545 \pm 0.005$.

Table 1 gives the chemical composition determined by XRF methods (water by the Penfield method). The low total is believed to be due to a deficiency of water, because rechecking of the composition by OES methods did not show any further elements.

There are eight tetrahedral and five octahedral sites in the palygorskite structure. Of the octahedral sites 4—4.25 are filled. Aluminium occupies 28—59 % and magnesium 29—76 % of the occupied sites (Zelazny and Calhoun 1977). The structural formula for the palygorskite from Padasjoki, calculated in accordance with Tien (1973) on the basis of 21 oxygens of dehydrated material is

$$Si_{7.47}Al_{0.53}(Al_{2.03}Fe^{3+}_{0.18}Mg_{1.36}Ti_{0.04}Mn_{0.01})O_{21}-Ca_{0.15}Na_{0.16}K_{0.30}P_{0.05}.$$
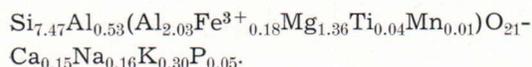
According to Church and Velde (1979), some of the zeolitic Ca, and possibly Na and K,

Table 1. Chemical composition of palygorskite from Padasjoki (analyst V. Hoffrén).

SiO_2	52.95	%
TiO_2	0.33	»
Al_2O_3	15.38	»
Fe_2O_3 *	1.72	»
MnO	0.08	»
MgO	6.46	»
CaO	1.00	»
Na_2O	0.59	»
K_2O	1.66	»
P_2O_5	0.44	»
$H_2O_{tot.}$	15.80	»
CO_2	0.33	»
Ga_2O_3	0.004	»
Sc_2O_3	0.008	»
CeO_2	0.25	»
La_2O_3	0.12	»
Nb_2O_5	0.007	»
	97.129 %	

Number of main ions calculated on the basis of 21 oxygens of dehydrated material

Si	7.47
Ti	0.04
Al	2.56
Fe^{3+}	0.18
Mn	0.01
Mg	1.36
Ca	0.15
Na	0.16
K	0.30
P	0.05

* Total Fe as Fe_2O_3

Fig. 3. Interwoven fibres of palygorskite. Scanning electron micrograph by R. Törnroos.

substitute for Mg in the octahedral position. This very likely applies to the palygorskite from Padasjoki, because octahedral Al seems high (about 56 % of the occupied sites) without these elements substituting for Mg.

X-ray diffraction studies

The studies were conducted with a Philips wide-angle goniometer and Ni-filtered Cu radiation. Several sample preparation techniques, including a Lakeside resin preparation used by Salter and Appleyard (1974), were tested, but the best results were obtained by backloading pure mineral powder in an aluminium specimen holder. For cor-

Table 2. X-ray data on palygorskite from Padas-
joki.

hkl	d (obs.)	d (calc.)	I/I_0
110	10.365	10.340	100
200	6.336	6.343	10
130	5.391	5.386	8
040	4.465	4.461	17
300	4.244	4.229	7
12$\bar{1}$	4.210	4.215	6
121	4.158	4.166	5
20$\bar{1}$	4.033	4.025	2
211	3.929	3.927	2
24$\bar{0}$	3.646	3.649	6
23$\bar{1}$	3.341	3.334	10
311	3.175	3.175	15
440	2.583	2.585	10
002	2.559	2.559	7
	2.542		9
16$\bar{1}$	2.527	2.526	9
302	2.168	2.169	2
	2.128		3
600	2.113	2.114	3
480	1.821	1.825	2
570	1.798	1.798	3
1,10,1	1.670	1.669	3
801	1.506	1.506	2
253 ⎫ 403 ⎭	1.489	1.489	2
861	1.344	1.343	3

Lattice constants:

$$a_0 = 12.689 \text{ Å}$$
$$b_0 = 17.845 \text{ Å}$$
$$c_0 = 5.119 \text{ Å}$$
$$\beta = 91.22°$$

rect peak positions, NaCl was used as internal standard. X-ray data on the mineral studied are presented in Table 2.

Splitting of the 121 peak indicates a monoclinic unit cell (Christ et al. 1969). The extinction for hkO reflections (h + k = 2n + 1) observed by Christ et al. (op.cit.) was considered in indexing the pattern. Two of the peaks (d = 2.542 Å and d = 2.128 Å) are possibly caused by illite impurities. Glycolation of the sample did not reveal an expanding component.

When the sample had been heated at 200°C, 300°C and 400°C for one hour the 10.365 Å peak became more and more faint and diffuse. At the same time a new peak appeared at about 9 Å. Van der Wel (1972) has reported disappearance of the 10.365 Å peak on heating at 400°C but no new peak at 9 Å. According to VanScoyoc et al. (1979), the occurrence of the new 9 Å peak is due to folding of the palygorskite structure on dehydration. Thus the folded structure represents the »anhydride» form (VanScoyoc et al., op.cit.). On heating palygorskite at 550°C, Molloy and Kerr (1961) established almost total collapse of the structure.

Discussion and conclusions

The palygorskite from Padasjoki is thought to be of hydrothermal origin as a result of direct precipitation from a hydrothermal solution like the palygorskite from the Day Book dunite (Furbish and Sando 1976). The geology of the area shows several signs of hydrothermal activity, one of the more notable being the epidotization of the granitic rock on which the palygorskite is found. Alteration and epidotization of palygorskite-bearing syenite on the Shetland Isles is regarded to be due to hydrothermal activity (Stephen 1954). At Stjernøy magnesium was leached from basaltic dykes during hydrothermal alteration (Salter and Appleyard 1974). A similar mode of formation is suggested for Padasjoki. Thus the magnesium needed for the formation of palygorskite originates from hydrothermal reactions in the diabase.

According to Nathan et al. (1970), the hydrothermal palygorskites seem to be monoclinic, but the sedimentary ones orthorhombic. The present study is consistent with this theory. The cooling rate seems to be much more critical for the symmetry than the temperature of formation. Furthermore, Nathan et al. (op.cit.) suggest that palygorskites with an ordered Mg-Al octahedral substitution

have monoclinic symmetry whereas disordered palygorskites have orthorhombic symmetry. Although Christ et al. (1969) proposed that the structure reflects the chemical composition, the present authors have not found any general correlation between symmetry and composition. We believe that there is a continuous series from the orthorhombic state with $\beta = 90°$ to the monoclinic state with a variable β-angle. As proposed by Nathan et al. (1970), this is probably due to the Mg-Al order-disorder structure. Finally, we suggest that the degree of

ordering can be estimated from the splitting of the 121 peak. A high $\triangle d_{12\bar{1}-121}$ value, for example 0.232 (cf. Christ et al. 1969), would reflect a high degree of ordering, whereas a value of, say, 0.156 (cf. Tien 1973) reflects a medium degree of ordering. The value of 0.052 shown by the palygorskite from Padasjoki reflects a low degree of ordering.

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