*Thermochimica Acta*, 13 (1975) 223–230


# THERMAL ANALYSIS OF PALYGORSKITE

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(Received 16 May 1975)

## ABSTRACT

Slickensides and fissures in a fresh outcrop of silicified limestones at the Bürgenstock (Switzerland) contained palygorskite. According to TG, DTA and heating X-ray experiments, dehydration of the palygorskite took place in four steps. Each step clearly showed an alteration in the unit cell dimensions. Exothermic reactions which occur at higher temperatures resulted in the formation of a Mg–Al-silicate high phase together with some clinoenstatite and the formation of $\beta$-cristobalite with some cordierite, respectively.

## INTRODUCTION

Müller-Vonmoos and Schindler[1] described palygorskite on slickensides and in fissures of silicified limestones at the Bürgenstock (Switzerland). The palygorskite formed dirty white to yellowish coatings (Fig. 1). In thin sections the mineral could

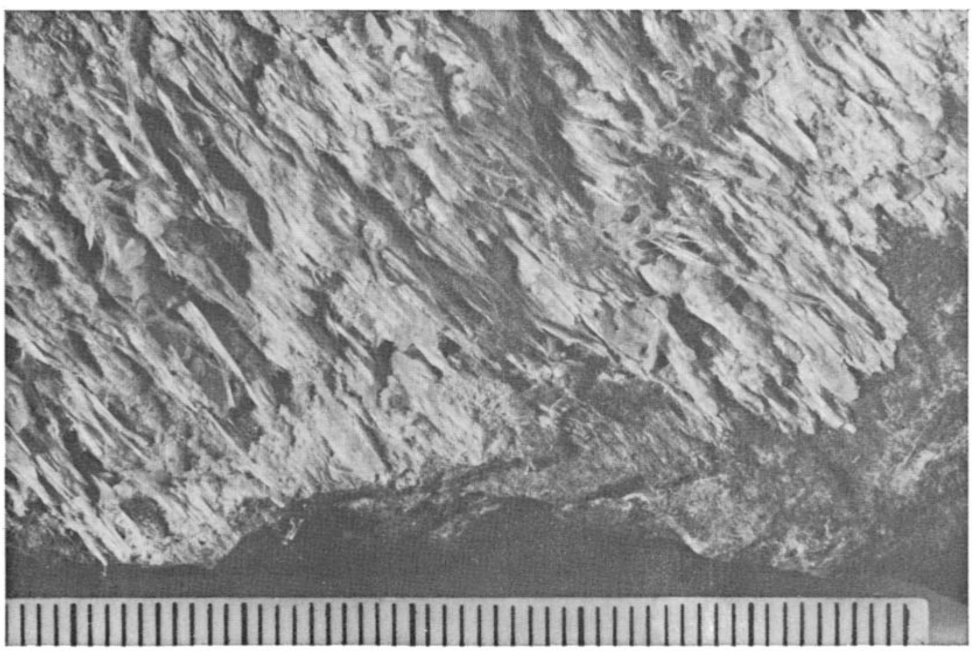

Fig. 1. Palygorskite forming coatings on silicified limestone (scale divisions 1 mm).

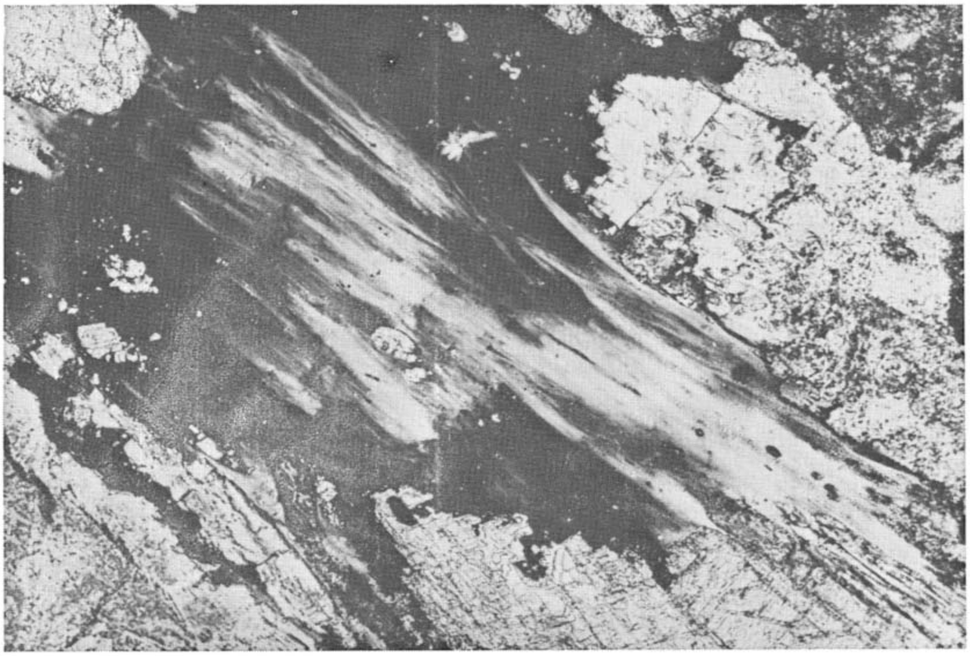

Fig. 2. Palygorskite in a fissure of silicified limestone (thin section, 80 ×).

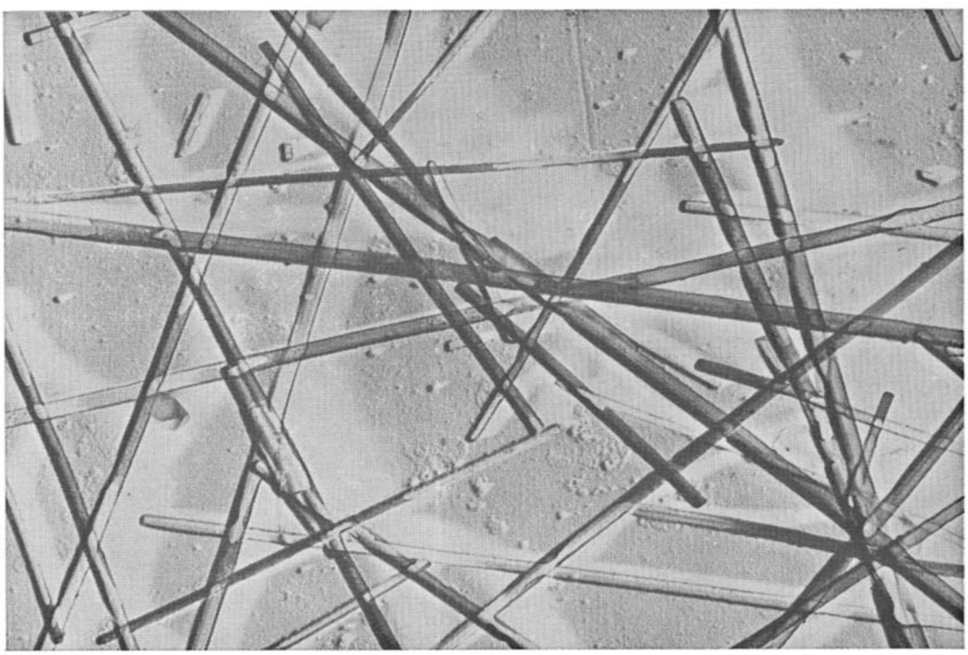

Fig. 3. Electron micrograph of palygorskite (22500 ×).

be observed in fissures, mostly containing calcite (Fig. 2). Electron micrographs revealed the typical lath-shaped units (Fig. 3). The rock belongs to Lower Cretaceous (Hauterivian) of a non-metamorphic helvetic nap. Probably the palygorskite grew during the last orogenic phase (Pliocene) in low temperature solutions. According to chemical analysis and thermogravimetric investigations, the following composition can be given:

$$(Si_{7.88}Al_{0.12})_{8.00}(Al_{1.55}Mg_{1.92}Fe_{0.46})_{3.93}(OH)_{1.95}(OH_2)_{4.13}\cdot 3.90H_2O,$$
$$Ca_{0.06}K_{0.03}Na_{0.10}$$

Thermal analysis (TG–DTA) of this palygorskite indicated four endothermic reactions and corresponding weight loss steps and three exothermic reactions. The interpretation of these reactions given by Müller-Vonmoos and Schindler[1] could be proved by X-ray investigations.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

For TG and X-ray investigations the palygorskite was purified from calcite and quartz by hand picking . For the simultaneous TG–DTA the calcite was removed by boiling in an acetate-buffer (15 min, pH 5) followed by changing the palygorskite into the Ca-form.

TG and TG–DTA were carried out with a Mettler-thermobalance[2] which permitted simultaneous recording of weight changes, DTA-curves and the actual temperature during the test. The sample weight was 50 mg. For TG and TG–DTA we

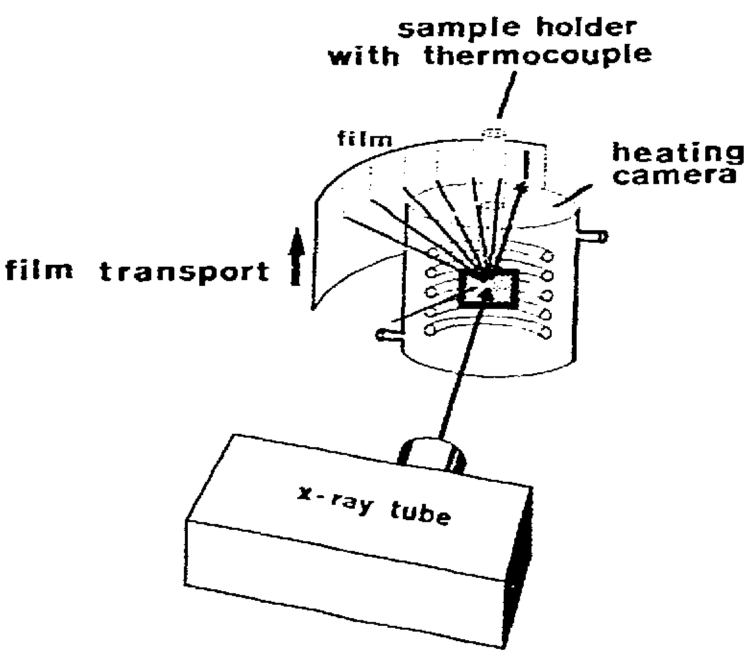


Fig. 4. Schematic sketch of X-ray high temperature camera and X-ray tube.

heated in flowing air at heating rates of 0.5°C $min^{-1}$ and 6°C $min^{-1}$, respectively. The reference material in DTA-runs was dead burnt palygorskite.

An Enraf Nonius high temperature X-ray camera (system Lenne-de Wolff) was used to follow the decomposition of palygorskite. This method has the advantage that the sample can be mounted in the sample holder of the X-ray camera and be heated up continuously during exposure of the film without changing its position (Fig. 4). The X-ray camera is equipped with a quartz monochromator. A special film holder allows a transport of the film at various rates. Time marks are printed automatically on the film for correlating the X-ray patterns to the specific times in the simultaneously recorded temperature curve[3]. The palygorskite was heated in flowing air at a heating rate of 0.5°C $min^{-1}$.

## RESULTS AND DISCUSSION

Heating the palygorskite at 0.5°C $min^{-1}$, the dehydration took place in three steps (Fig. 6). If it is assumed that the three steps correspond to the loss of zeolithic water, bonded water and the dehydroxylation, respectively, the value obtained for the bonded water is too low, whereas the OH-content turns out to be too high (Table 1). However, when heating at a rate of 6°C $min^{-1}$, the third step of weight loss clearly separated into two steps and the simultaneous DTA indicated two endothermic reactions, at 525 and 598°C. Assuming the dehydration of the bonded water in two steps (TG 0.5°C $min^{-1}$, 85–195°C and 195–~480°C), the loss of bonded water and the dehydroxylation amounts to 8.8 and 2.1% ,respectively.

TABLE 1

DEHYDRATION OF PALYGORSKITE HEATED AT 0.5°C $min^{-1}$ (TG) AND 6°C $min^{-1}$ (TG–DTA), RESPECTIVELY, AND THE VALUES FOR THE IDEAL UNIT CELL $Si_8Mg_5O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ AFTER BRADLEY[8]

| *Water content of the ideal unit cell* | | *TG* | | *TG–DTA* | |
|---|---|---|---|---|---|
| Zeolithic water | 8.6% | up to 85°C | 7.9% | up to 195°C | 8.5% |
| Bonded water | 8.6% | 85–195°C | 4.3% | 195–322°C | 4.7% |
| | | | | 322–530°C | 4.3% |
| Hydroxyl water | 2.15% | 195–640°C | 6.6% | 530–820°C | 2.1% |
| Total | 19.35% | | 18.8% | | 19.6% |

When heating at a rate of 0.5°C $min^{-1}$, the loss of zeolithic water took place at temperatures up to 85°C (Fig. 6). By X-ray between 35 and 55°C, a distinct change of the lattice constants, especially a contraction in the direction of the a-axis, could be observed (Fig. 5, Table 2). According to this unit cell deformation, the zeolithic water should be released completely at 55°C. On the other hand, the loss of the zeolithic water observed by TG was completed only at 85°C. An explanation for this delay may be a readsorption of the zeolithic water on the external surface. A loss of zeo-

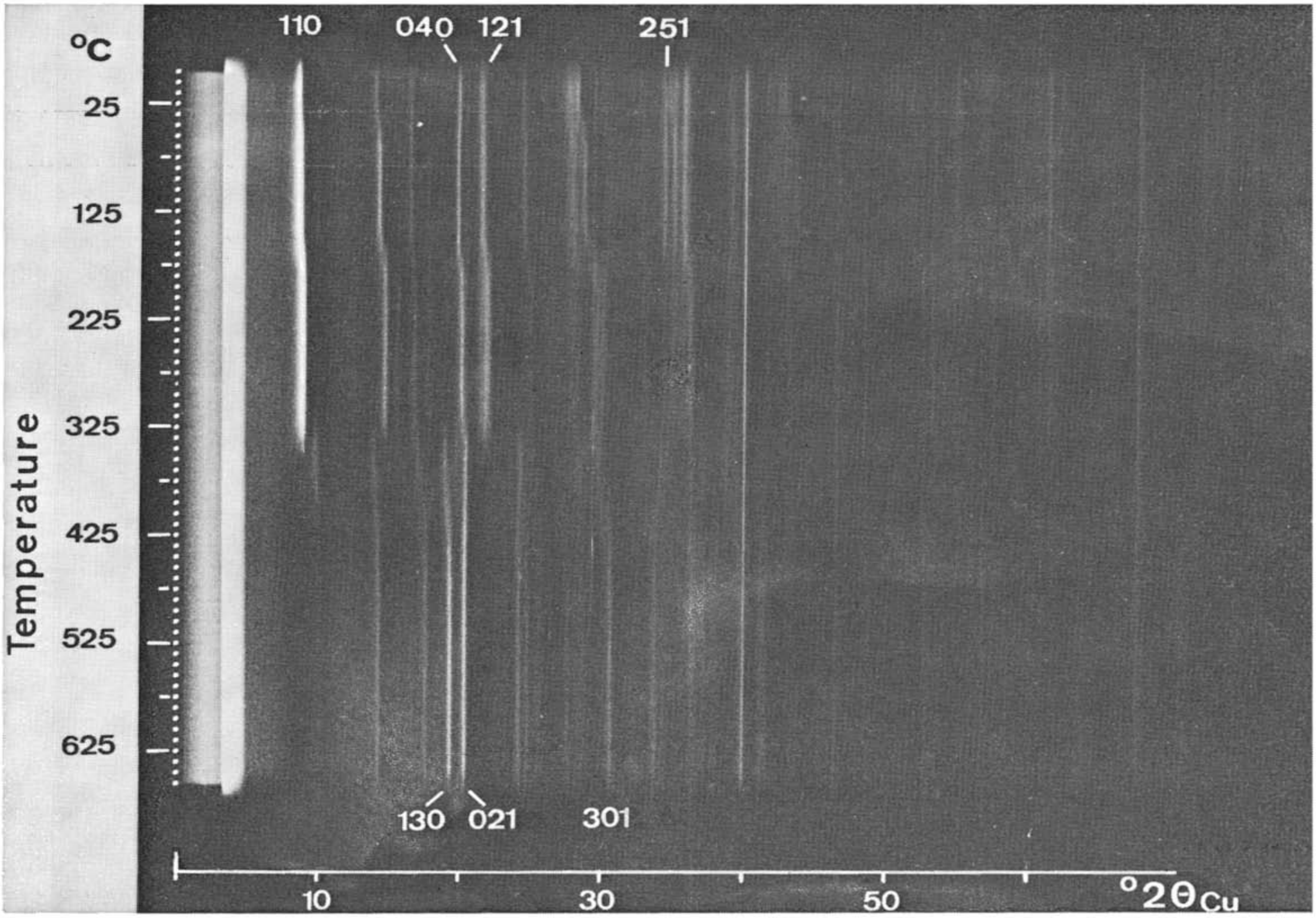


Fig. 5. X-ray film showing the thermal dehydration of palygorskite. Cu-$K_\alpha$ radiation; film speed, 5 mm $h^{-1}$; heating rate, 0.5 °C $min^{-1}$.

TABLE 2

*d*-VALUES, ESTIMATED INTENSITIES AND INDICES OF REFLECTIONS OF PALYGORSKITE AT 25, 55, 195 AND 475 °C

Copper-$K_\alpha$-radiation, heating rate 0.5 °C $min^{-1}$. Impurities: C = calcite, M = muscovite.

| *Temperature* | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *25 °C* | | | *55 °C* | | | *195 °C* | | | *475 °C* | | |
| *d* | *I* | *hkl* | *d* | *I* | *hkl* | *d* | *I* | *hkl* | *d* | *I* | *hkl* |
| 10.254 | 100 | 110 | 10.178 | 100 | 110 | 9.889 | 100 | 110 | 8.640 | 10 | 110 |
| 6.302 | 40 | 200 | 6.204 | 50 | 200 | 6.001 | 40 | 200 | 6.186 | 60 | 120 |
| | | | | | | 5.679 | 20 | 210 | 5.023 | 50 | 011 |
| 5.371 | 30 | 130 | 5.368 | 30 | 130 | 5.268 | 30 | 130 | 4.583 | 100 | 130 |
| | | | 4.986 | <10 | M | 4.976 | 20 | 001/M | 4.354 | 100 | 021 |

TABLE 2 *(continued)*

| *Temperature* | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *25°C* | | | *55°C* | | | *195°C* | | | *475°C* | | |
| *d* | *I* | *hkl* | *d* | *I* | *hkl* | *d* | *I* | *hkl* | *d* | *I* | *hkl* |
| 4.451 | 60 | 040 | 4.462 | 60 | 040 | 4.395 | 60 | 040 | 3.674 | 40 | 031 |
| 4.353 | 10 | 121 | 4.341 | 10 | 121 | | | | 3.590 | 20 | 140 |
| | | | | | | 4.340 | 20 | 021 | | | |
| | | | | | | | | | 3.466 | 10 | 131 |
| | | | | | | 4.127 | 30 | 140 | | | |
| | | | | | | | | | 3.223 | 10 | ? |
| 4.126 | 60 | 121 | 4.116 | 60 | 121 | 4.071 | 50 | 121 | | | |
| | | | | | | | | | 3.135 | 10 | 041 |
| | | | | | | 4.012 | 20 | 300 | | | |
| | | | | | | | | | 3.04 | 10 | C |
| 3.637 | 30 | 240 | 3.627 | 30 | 240 | 3.555 | 20 | 240 | | | |
| | | | | | | | | | 2.916 | 40 | 301 |
| 3.45 | <10 | 150 | | | | | | | | | |
| | | | | | | | | | 2.651 | 30 | 051 |
| 3.221 | 50 | 231 | 3.198 | 40 | 231 | | | | | | |
| | | | | | | | | | 2.443 | 10 | 122 |
| | | | | | | 3.166 | 10 | 141 | | | |
| | | | | | | | | | 2.358 | <10 | 032 |
| | | | | | | 3.029 | 20 | 250/C | | | |
| | | | | | | | | | 2.266 | 10 | 222 |
| 3.158 | 60 | 400 | 3.102 | 40 | 400 | 3.000 | 20 | 400 | | | |
| | | | | | | | | | 2.181 | 20 | 042 |
| 3.028 | 10 | C | 3.025 | 10 | C | | | | | | |
| | | | | | | | | | 1.723 | 10 | 264/540 |
| | | | | | | 2.957 | 30 | 410/340 | | | |
| 2.604 | 40 | 251 | 2.599 | 40 | 251 | 2.598 | 20 | 251 | | | |
| | | | | | | 2.558 | 20 | 411 | | | |
| 2.576 | 40 | 440/061 | | | | 2.480 | 40 | 440 | | | |
| 2.551 | 40 | 161 | 2.555 | 40 | 161 | | | | | | |
| 2.502 | 60 | 161 | 2.505 | 50 | 161 | | | | | | |
| | | | 2.295 | 10 | 212 | | | | | | |
| | | | 2.280 | 10 | 232 | | | | | | |
| | | | 2.242 | 10 | 222 | | | | | | |
| 2.122 | | 271? | | | | | | | | | |
| | | | 2.107 | 10 | 280 | | | | | | |
| 2.104 | 20 | 600 | 2.067 | 10 | 600 | | | | | | |
| | | | | | | 1.946 | 10 | 620 | | | |

*Dimensions of the elementary cells*

| *Monoclinic* | *Monoclinic* | *Orthorhombic* | *Orthorhombic* |
|---|---|---|---|
| a = 12.65 Å | a = 12.43 Å | a = 12.00 Å | a = 10.45 Å |
| b = 17.80 Å | b = 17.86 Å | b = 17.59 Å | b = 15.28 Å |
| c = 5.22 Å | c = 5.21 Å | c = 4.98 Å | c = 5.32 Å |
| $\beta = 95°30'$ | $\beta = 95°33'$ | | |

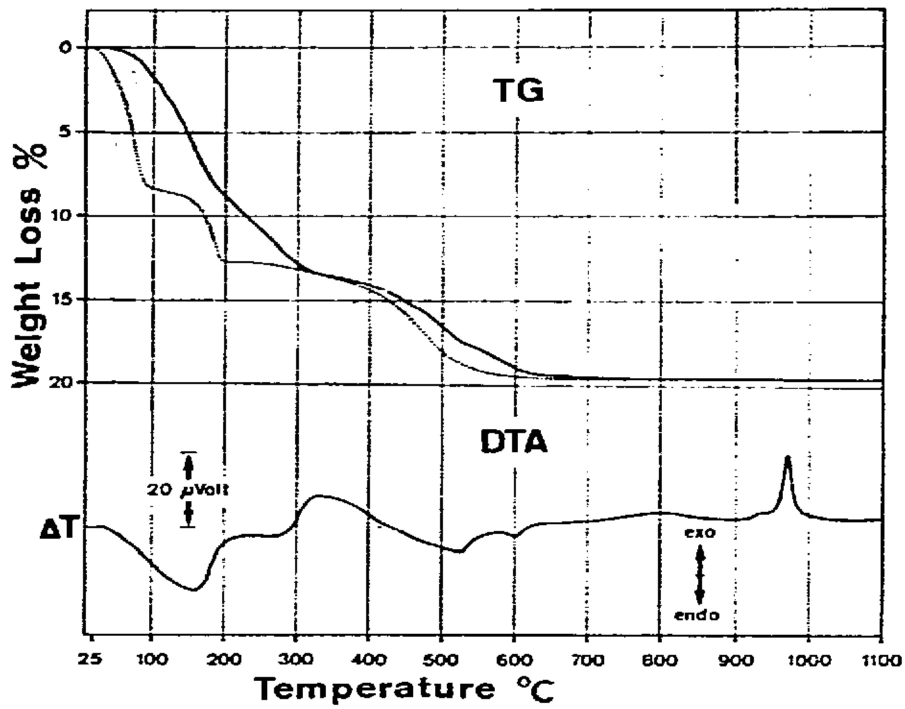


Fig. 6. TG and DTA curves of palygorskite.
······, TG-curve, heating rate 0.5°C min$^{-1}$, air flow 3 l h$^{-1}$.
———, TG–DTA curves recorded simultaneously, heating rate 6°C min$^{-1}$, air flow 6 l h$^{-1}$.
▬▬, regions of structural changes during the dehydration of palygorskite.

lithic water in two steps was also observed by Veniale[4] investigating palygorskite from Attapulgus.

Based on TG (heating rate 0.5°C min$^{-1}$), the first loss of bonded water took place between 150 and 195°C. In the same temperature range a change could be observed in the X-ray pattern. According to TG, the second loss of bonded water started gradually above 200°C. Between 335 and 450°C, the lattice changed due to the formation of palygorskite-anhydrite. The two steps of dehydration might be attributed to the different bond strength of the water to Mg and Al, respectively. Between 645 and 675°C the anhydrite decomposed into an amorphous phase.

Between 740 and 885°C X-ray photographs indicated the crystallisation of a Mg–Al-silicate phase ($Mg_2Al_4Si_5O_{18}$) with high quartz structure[5] besides some clinoenstatite. In the same temperature range DTA revealed a weak exothermic reaction. Additional exothermic peaks at 930 and 975°C corresponded to the formation of β-cristobalite and some cordierite.

According to our investigations, each of the four dehydration steps of the palygorskite were clearly correlated to structural changes. This is not in agreement with the investigations of Hayashi et al.[6] and Preisinger[7], where no changes were observed in the structure of palygorskite during dehydration up to 210° and 350°C, respectively.

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