



Quantitative Estimation of Palygorskite using thermogravimetric Analysis in Paleosols from Sepahanshahr, Isfahan, Iran.

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1 Abstract

Palygorskite accounts for a major portion of the minerals present in paleosols in the central Iranian plateau. The identification and quantitative determination of this clay mineral is of great importance. Among the techniques being used for the identification of soil minerals, the thermogravimetric analysis (TGA) has a long history and provides rather high accuracy. However, its application highly depends on the composition of the minerals in the soil. The present study was carried out to estimate palygorskite contents in the paleosols in Sepahanshahr, Isfahan, using TGA. In order to understand the formation processes of palygorskite, its distribution was also examined in the soils under study. The TGA was applied in combination with XRD and SEM analyses. The results indicate the presence of palygorskite with contents from 22% to 39% in the clay fraction of older horizons of these soils. No trace of this mineral was found in younger horizons. Absence of palygorskite in the parent material and the arrangement of this mineral indicates its pedogenic formation in the past when favorable conditions in terms of pH value and Mg/Ca ratio prevailed. Other clay minerals such as kaolinite, chlorite, and illite were inherited from parent materials.

2 Introduction

The presence of palygorskite has been reported in a great number of soils in arid and semi-arid regions, such as those in Saudi Arabia [Viani et al 1983; Shadfan & Mashhady, 1985], Iraq [Aqrawi, 1993], Syria [Muir, 1951], and Egypt [Hassouba & Shaw, 1980]. In Iran, palygorskite was first reported by Henderson and Robertson (1958). Other workers [Mahjoory, 1979; Abtahi, 1980; Khademi & Mermut, 1998] have also discussed the distribution and genesis of this mineral in Iranian soils. Palygorskite makes up a great portion of the soils, particularly paleosols, in the central Iranian plateau.

Thermal analyses are among the oldest of the various techniques currently being used to identify minerals and to determine their quantity. It includes a group of techniques whereby one physical parameter of the material or a product is measured as a function of heat [Lombardi, 1980]. Thermogravimetric analysis is one such thermal analysis used for the quantitative analysis of clay minerals [Todor, 1976; Paterson & Swaffield, 1987].

The objectives of the present study were to determine palygorskite contents using the TG analysis, and to explain the formation processes of palygorskite in paleosols of SepahanShahr area, Isfahan region, central Iran.

3 Materials and Methods

The study area is located between $51^{\circ} 38' 59''$ and $51^{\circ} 39' 40''$ latitude and $32^{\circ} 52' 25''$ and $32^{\circ} 53' 05''$ longitude, on an old alluvial-colluvial fan 5km south of Isfahan along the southern slopes of the Soffeh mountain range in SepahanShahr, Isfahan. The average annual rainfall in the study area is 95 mm and its average annual temperature is 15°C . The paleosols under study are buried under a thin layer of younger deposits. For the purpose of the mineralogical analyses, soil samples were taken from various depths of two profiles dug out in the area. Samples were also taken from parent materials including Cretaceous limestone, Cretaceous conglomerates and sandstone as well as Jurassic shale in the region.

For clay mineral analysis, soil samples were first air dried after having been passed through a 2 mm sieve and later washed in special containers in distilled water over a period of two weeks in order to remove all the gypsum from the soils. The required pretreatments were performed in order to separate different fractions including organic matter removal by 10% H_2O_2 , carbonate removal using sodium acetate at $\text{pH}=5$, and

the removal of iron oxides using Dithonite-Citrate- Bicarbonate (CBD) , [Jackson, 1979]. Samples from parent materials were also subjected to pretreatments after crushing. The clay fraction of the soil and parent material samples were separated using the centrifuge technique [Jackson, 1979]. For the X-ray diffraction analysis according to Dümmler & Schroeder (1965), the clay samples were first saturated in 1 N solution of potassium chloride and magnesium chloride. Similar to the method of Dümmler & Schroeder (1965), the preferential orientation of the layer silicates was obtained by suction through a porous ceramic plate. The clay suspension was prepared at uniform density (0.2 mg/cm^3) and subjected to ultra-sonic treatment prior to suction in order to achieve optimum orientation and thickness and also to make comparisons of mineral compounds among the different samples possible.

To avoid disturbance of the orientation during drying, the samples were equilibrated for 3 days over saturated NH_4NO_3 solution [Tributh, 1970]. Expansion tests were carried out by solvation with ethylenglycol and DMSO (dimethylsulfoxide). Finally, heating tests were carried out at successively higher temperatures (300°C and 550°C). The treated samples were X-rayed, using a Philips PW-1830 Diffractometer equipped with a graphite monochromator at 45 kV, and 40 mA.

Thermogravimetric analyses were performed using a thermal analyzer Model NET-ZSCH (STA, 409, Luxx PC) at a temperature range of 20°C to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ on a sample already oven-dried at 100°C . Soil aggregates and parent rocks were further studied by scanning electron microscopy (SEM). Dried samples were mounted on Al stubs, then coated with Au and examined using a Philips SEM (XL 30, ESEM).

The quantitative determination of palygorskite was accomplished on the basis of variations in TG curves. With attention to mineralogy of the soils under study, the weight loss at a temperature range of 100°C to 300°C is due to water losses in palygorskite, thus making it possible to estimate its quantity. At this temperature range, the pure palygorskite shows a weight loss of 12.96% [Deer et al, 1971; Olphen & Fripiat, 1979]. The percentage of palygorskite has, therefore, been calculated on the basis of weight loss obtained from TG curves.

4 Results and Discussion

Peaks obtained from XRD of the clay fraction of the limestone, sandstone, and red conglomerate and shale samples indicate the presence of illite, kaolinite, and chlorite. The presence of these minerals in the above formations had also been reported by

other workers [Khademi & Mermut, 1998]. As indicated by the results from XRD, no trace of palygorskite is recorded in parent material samples.

X-ray diffractograms of the soils show that chlorite, illite, and kaolinite are present in surface horizons with no trace of palygorskite. The application of TGA in the qualitative estimation of minerals highly depends on the composition of the mineral contents of the sample [Schultze, 1969; Deer et al., 1971; Todor, 1976]. Along these lines, the composition of the soil minerals has been determined using the XRD method prior to other processes. As shown above, the main minerals in the sample included illite, kaolinite, chlorite, and palygorskite. Palygorskite is the main mineral of the clay fraction in the underlying horizons. This is also supported by the fibrous shapes observed under the electron microscope.

Table 1: Quantitative estimation of palygorskite in the carbonate free clay fraction of paleosols studied using thermogravimetric analysis

Horizon	Depth (cm)	Reduced mass % (100 °C-300 °C)	Palygorskite mass %
A	0-15	0	0
2Btk2	60-80	2.88	22
2Btky2	115-145	3.88	30
2Btky4	175-210	4.15	32
3Btky5	210-250	4.42	34
4Btky7	285-305	4.00	31
4By	305-345	4.54	35
4Btk	365-385	5.05	39

Endothermic peaks at temperatures below 300 °C are due to the release of adsorbed and free water, known as zeolitic water in the case of palygorskite [Deer et al., 1971]. Among the minerals common in soils, smectite, vermiculite, palygorskite and gypsum show identical endothermic peaks at this temperature range [Deer et al., 1971; Olphen & Fripiat, 1979; Paterson & Swaffield, 1987]. The results from XRD analyses show the absence of smectite and vermiculite in the soils studied. On the other hand, the gypsum in the samples had been removed prior to mineralogical analyses. Organic matter, which might have interfered with the results, had also been oxidized and removed. Therefore, the endothermic peaks at the temperature range of 100 °C - 300 °C can be ascribed to the presence of palygorskite and the weight loss of the sample shown in the TG curve can be ascribed to the loss of zeolitic water of this mineral.

The percentage of palygorskite has thus been determined quantitatively on the basis

of the above assumptions. The results from the calculations for the soils are reported in Table 1. Palygorskite forms a major portion of the soils studied.

As also indicated by other workers [Buol et al 1989], the mineralogy of the soils in arid and semi-arid zones is mostly affected by related parent materials. It may therefore be concluded, that the clay minerals such as illite, chlorite, and kaolinite in the soils under study were inherited from parent materials as evidenced by their even distribution throughout the soil. The presence of palygorskite, however, requires a different explanation. This is mainly because neither in the upper young sediments (A horizon) nor in parent material any trace of this mineral can be found. The lack of this mineral in the parent material samples, the elongated morphology of the palygorskite fibers and their radiate arrangement in relation to aggregates and porous and its co-occurrence with secondary calcium carbonate and gypsum indicate the pedogenic origin of palygorskite in the older horizons of these soils [Monger & Dangherty, 1991; Khademi & Mermut, 1998]. Due to evapotranspiration conditions and the formation of gypsum, the high ratio of Mg/Ca and high pH values, favorable conditions existed in the past for the formation of palygorskite [Singer, 1989]. The present arid conditions create favorable circumstances for its stability.

5 References

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