

Michał SKIBA¹

THE ORIGIN OF KAOLINITE FROM THE TATRA MTS. PODZOLS

Abstract. Quartz, plagioclases and micas are the main minerals of all the studied Tatra podzols. K-feldspar, chlorite and kaolinite can be identified in smaller amounts. The clay (<2 µm) fractions of the studied soils contain mica, chlorite, kaolinite and mixed-layer mica-vermiculite minerals. Feldspars and quartz occur in minor amounts. The studied soils represent three stages of mineral alteration. The increase in the amount of kaolinite and vermiculite interlayers as well as the decrease in the amount of chlorite and mica describe best the alteration. Weathering and/or pedogenic origin of the kaolinite is most probable. The exact mechanism of mica/vermiculite formation is unclear, but the alteration of mica is most probable.

Key-words: kaolinite, mica-vermiculite, podzols, weathering, the Tatras

INTRODUCTION

Podzolisation is one of the soil-forming processes. It includes acidification of upper soil horizons, destruction of some components of the parent material in the albic (E) horizon as well as transport of the products of destruction towards the lower, spodic (B) horizon, where new phases also precipitate. Thus, the environment of podzol soils is characterised by strong acidification of the upper part of the soil profile (pH < 4.5) and strong leaching. Podzolisation is controlled by mineral composition and texture of parent material, climate and vegetation (e.g. Skiba 1977, 1997; Lundström et al. 2000).

Several authors identified kaolinite in podzols from different localities (e.g. Wilson et al. 1984; Gustafsson et al. 1995; Righi et al. 1999; Melkerud et al. 2000; Weber et al. 2000). The origin of kaolinite from podzols is not widely discussed. In most cases, the kaolinite reported from podzols is thought to be of non-pedogenic origin (e.g. Wilson et al. 1984; Gustafsson et al. 1995; Melkerud et al. 2000). Wilson (1984) suggested that the kaolinite found in the podzols developed on Scottish till materials is a relict from pre-glacial weathering. The difficulties in explaining the presence of kaolinite in Scandinavian podzols were stressed by Gustafsson et al. (1995). The origin of kaolinite in

¹ Jagiellonian University, Institute of Geological Sciences, Oleandry 2a, 30-063 Kraków, Poland; e-mail: skiba@geos.ing.uj.edu.pl

podzols developed on glacial sediments in Finland (Righi et al. 1997) and Switzerland (Righi et al. 1999) was not discussed.

The occurrence of kaolinite in the podzols from the Tatra Mts. was suggested previously by Kubisz and Oleksynowa (1972) and Oleksynowa and Skiba (1976). This contribution presents preliminary data on mineral changes during the podzolisation process in the Tatra Mts., confirms the presence of kaolinite in the Tatra podzols, and discusses its possible origin.

MATERIAL

The samples were collected in the Polish part of the Tatra Mts. (Fig. 1). Three selected soil profiles were investigated (Fig. 2):

- GM-1, situated on a rock bar near the Czarny Staw Gąsienicowy lake and developed at the altitude 1600 m asl from granitic parent rock,

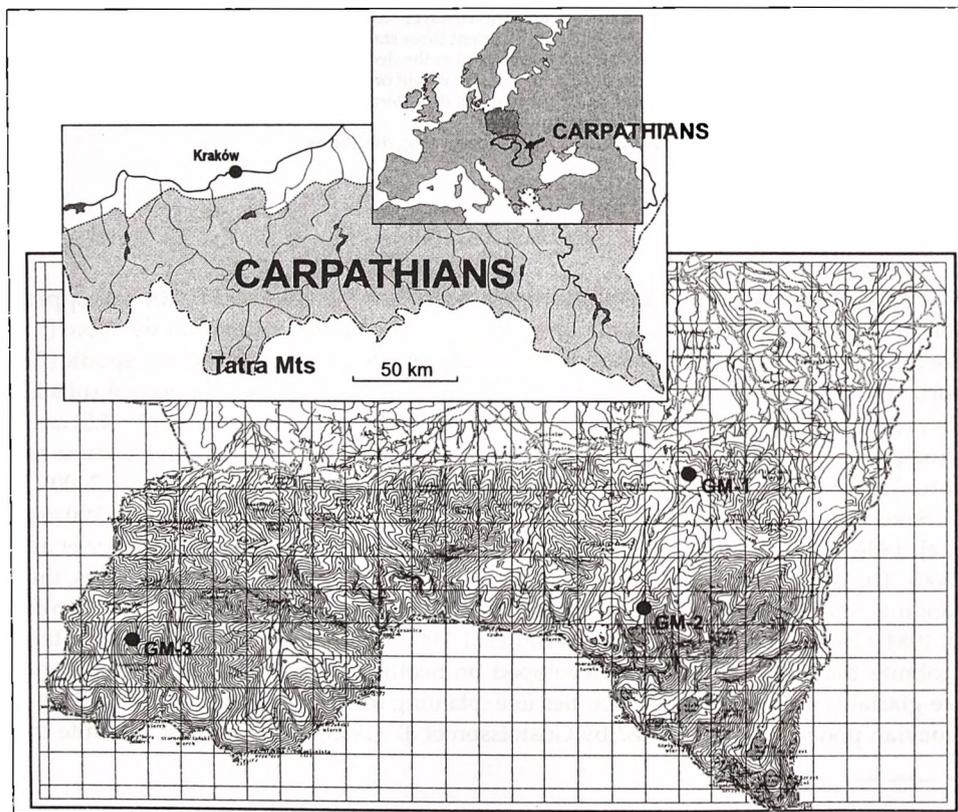


Fig. 1. Location of the investigated soil profiles

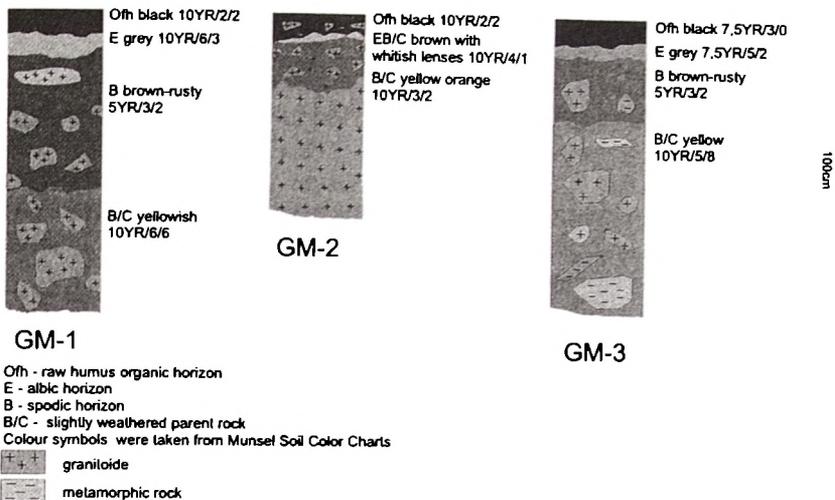


Fig. 2. Schematic drawings of the studied soil profiles

- GM-2, developed at the altitude of 950 m asl from an unconsolidated granitic moraine. This profile is situated in the lower part of the Dolina Suchej Wody valley,
- GM-3, developed at the altitude of 1200 m asl from an unconsolidated moraine, consisting of fragments of gneisses, mica schists and greenstones. This profile is situated in the lower part of the Dolina Jarzabcza valley.

METHODS

Soil fraction (<2 mm) was analysed using the XRD method. Clay (<2 μm) fractions were separated by centrifugation preceded by the following chemical treatment:

- removal of the organic matter with the use of 30% H₂O₂ solution,
- removal of Fe³⁺ oxides performed according to Mehra and Jackson (1960) method,
- Na saturation with the use of NaCl solution, followed by centrifugation and dialysis.

Oriented X-ray samples were obtained by evaporating the water suspensions of the clay fractions on glass slides. XRD analysis of a clay fraction was performed on the samples which were air-dried, ethylene glycol vapour-solvated and heated to 550°C. The infrared spectra of clay fractions were recorded using a Fourier transform infrared spectrometer. The samples were prepared as KBr discs (0.6 mg sample + 300 mg KBr).

RESULTS

Mineral composition of <2 mm fractions

GM-1 profile

Quartz, plagioclases and micas are the main minerals of all horizons of this profile. K-feldspar, chlorite and kaolinite can be identified in smaller amounts. In the upper (E) soil horizon there seems to be more quartz in relation to the other minerals than in the lower horizons. Chlorite accumulates in the lower (B) horizon.

GM-2 profile

Quartz, plagioclases and micas are the main minerals in this profile. K-feldspars, chlorite and kaolinite were identified in smaller amounts. In the upper Ebs/C soil horizon there seems to be more plagioclases in relation to other silicates than in the lower horizons. Chlorite accumulates in the lower (Bs/C) horizon.

GM-3 profile

Quartz and micas dominate in this profile. Plagioclases and K-feldspars were noted in smaller amounts. In the lower horizon (Bs/C) a small amount of chlorite was observed.

Mineral composition of <2 μm fractions

The clay fraction contains mica, chlorite, kaolinite and mixed-layer minerals with swelling interlayers. Feldspars and quartz occur in minor amounts (Fig. 3–5).

Kaolinite is present in the clay fractions of all three profiles studied. In XRD patterns it was identified by the presence of its basal 002 reflections (3.58 Å) in air-dried conditions which do not shift after the treatment with ethylene glycol vapours and disappear after heating to 550°C. Kaolinite identification was confirmed with the use of infrared spectroscopy by the presence of the absorption band at 3697 cm^{-1} (Fig. 6–8). Kaolinite occurs in all the horizons of the GM-1 and GM-2 profiles. In the GM-3 profile, kaolinite is present only in the albic E and the spodic Bfe horizons. The amount of kaolinite increases toward the top of the profiles with respect to chlorite and mica.

Mica is present in all the samples studied, its content decreases toward the upper horizons. Chlorite occurs only in the lower B and B/C horizons.

The mixed-layer minerals are characterised by the presence of basal 001 reflections between 10 Å and 13 Å in air-dried samples which shift to near 14 Å after glycol vapour treatment and disappear after heating to 550°C. According to the criteria given by Brindley (1980), the mixed-layer minerals show the mica/Na-vermiculite characteristic. Intensity and sharpness of the mixed-layer mineral low angle reflection increase toward the top of the soil profiles studied. In X-ray patterns of the GM-1E sample the higher order reflections of the mica/vermiculite mineral can also be seen (Fig. 3).

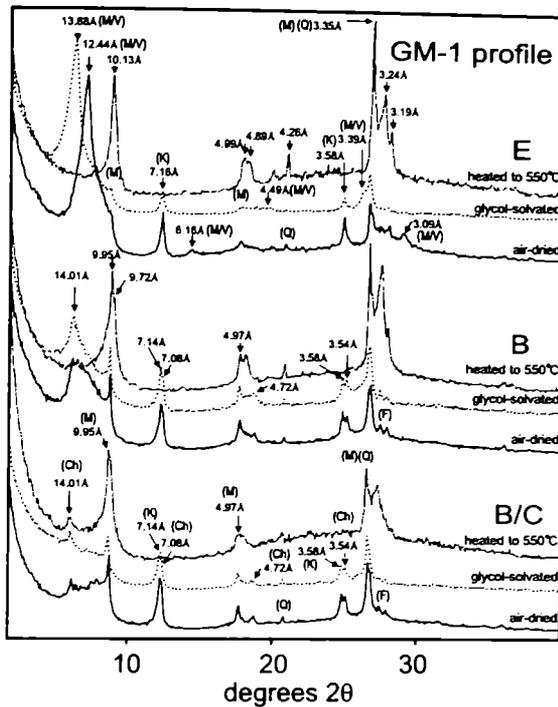


Fig. 3. X-ray diffraction patterns of <2 μm fractions separated from GM-1 profile
 Ch — chlorite, F — feldspars, K — kaolinite, M — mica, M/V — mica-vermiculite, Q — quartz

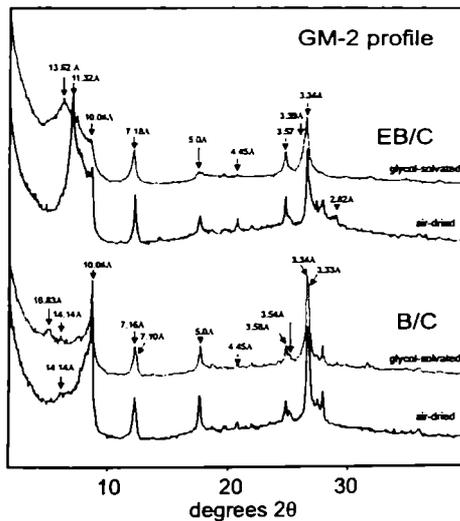


Fig. 4. X-ray diffraction patterns of <2 μm fractions separated from GM-2 profile

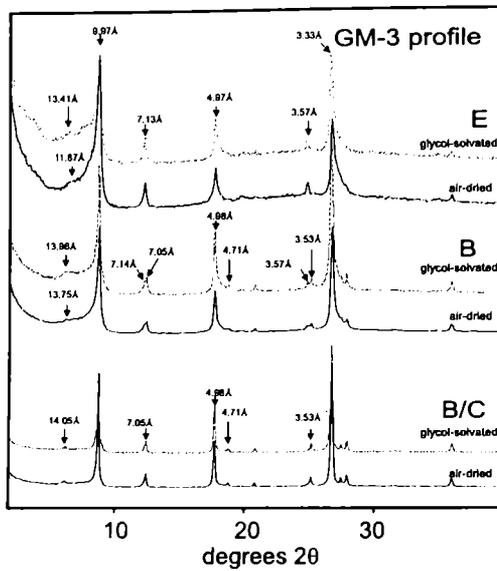


Fig. 5. X-ray diffraction patterns of <2 μm fractions separated from GM-3 profile

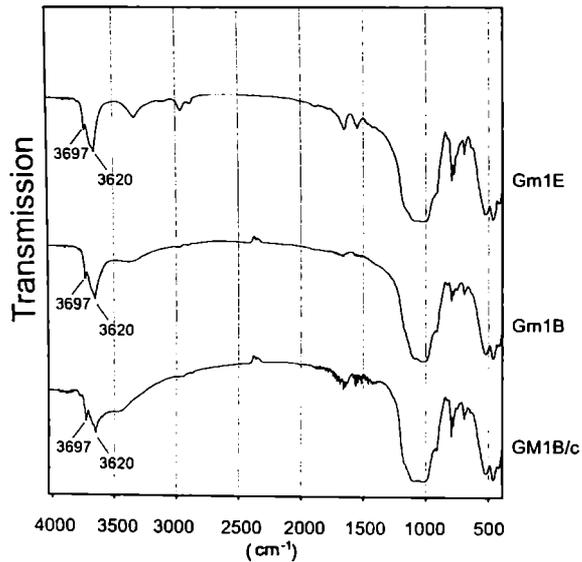


Fig. 6. Infrared spectra of <2 μm fractions separated from GM-1 profile

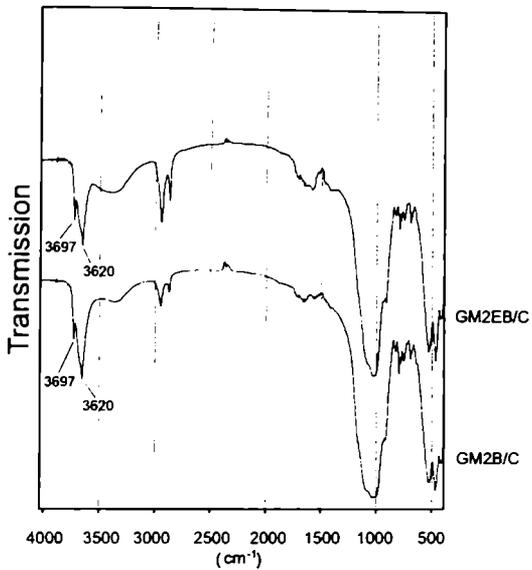


Fig. 7. Infrared spectra of <2 μm fractions separated from GM-2 profile

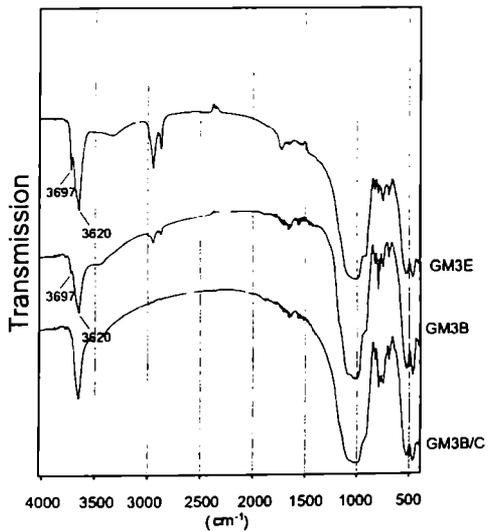


Fig. 8. Infrared spectra of <2 μm fractions separated from GM-3 profile

DISCUSSION OF THE RESULTS

The soils studied represent three stages of mineral alteration (initial, moderate and the most advanced). The increase in the amount of kaolinite and vermiculite interlayers as well as the decrease in the amount of chlorite and mica describe best the alteration. The earliest stage of the alteration can be observed in the GM-3 profile and the most advanced stage can be observed in the GM-1 profile. According to Wilson (1999), vermiculites in podzols are formed by transformation of micas or chlorites. In the soils studied chlorite occurs in minor amount. Additionally, progressive development of the mica/vermiculite minerals in the profiles studied can be observed. Thus, the transformation of micas seems to be the most probable mechanism of mica/vermiculite mixed-layer minerals formation.

Several possible hypotheses of the origin of kaolinite in the profiles studied have to be considered. They are: the eolian deposition; the inheritance from the parent material, weathered during the Tertiary or affected by hydrothermal kaolinitisation; and the formation in cold climate by weathering and/or podzolisation.

Eolian deposition

The eolian contamination of the soils studied with kaolinite, however possible, has been excluded. Kaolinite was reported from atmospheric dusts collected from a snow cover in the Tatras (Maneckí et al. 1978). Eolian deposition of kaolinite was also noted in Slovakia by Šucha et al. (2001). Airborne dust described in this paper contains kaolinite, micas and <2 µm quartz grains. The increasing amount of kaolinite in the soils studied is not accompanied by increasing amount of micas and quartz. Thus, the process of eolian contamination is not a feasible mechanism which could control the presence of kaolinite in the Tatra podzols. It is also difficult to imagine the process of the transport of eolian kaolinite toward the lower part of the soil profile through the cemented spodic (B) horizon.

Inheritance from the Tertiary weathering crust/or hydrothermally kaolinitised bedrock

The other possibility of the kaolinite origin is its inheritance from the material weathered during the Tertiary when the climate was warm and humid (e.g. Klimaszewski 1988; Pasendorfer 1971). But the occurrence of kaolinite in the GM-2 profile, which was developed on the rock bar after the Quaternary glaciation, cannot be explained by this hypothesis, which is also excluded by the occurrence of kaolinite only in the upper horizons of the GM-3 profile.

On the other hand, no hydrothermal kaolinitisation was reported from the Tatra granitoides (e.g. Durman et al. 2001).

Possible formation of kaolinite during the weathering and/or the podzolisation processes

According to Dixon (1989) and Weaver (1989) kaolinite can form in cold temperate climates, providing adequate rainfall. Also stable isotopic studies of kaolinites from different localities indicate widespread cold climate formation of kaolinite (Środoń 1999 and literature cited therein). Kaolinite can also be a product of lichens/granite or fungi/rock interactions (e.g. Adamo, Violante 2000; Chen et al. 2000 and literature cited therein).

The occurrence of kaolinite in the soil profiles studied might be explained by the transformation of primary aluminosilicates or the neoformation in the acidic and strongly leached environment. Wilson (1999) regards both neoformation and transformation as feasible mechanisms of the formation of kaolinite in soils.

According to the presence of kaolinite in the lower part (B/C horizons) of the GM-1 and GM-2 profiles, unaffected by the podzolisation, it is difficult to say that the formation of kaolinite is strictly connected with the podzolisation process. Kaolinite can be formed during early weathering of a parent material, before the stage of soil formation. Intensive chemical weathering in initial soils from the Alpine environment was described by Reynolds (1971). The occurrence of kaolinite in the GM-3 profile implies the possibility of kaolinite formation during podzolisation within the albic E horizon.

It is possible, but not confirmed, that the formation of kaolinite from the soils studied took place with significant participation of micro-organisms (lichens and fungi).

CONCLUSIONS

1. Kaolinite is quite common mineral in the Tatra podzols.
2. Weathering and/or pedogenic origin of the kaolinite is most probable.
3. The exact mechanism of mica/vermiculite formation is unclear, but the alteration of primary mica is most probable.

Acknowledgments. The author would like to thank very much to Dr. Marek Michalik, Prof. dr. hab. Jan Środoń and Prof. dr. hab. Stefan Skiba for reviewing this text and for the helpful suggestions.

REFERENCES

- ADAMO P., VIOLANTE P., 2000: Weathering of rocks and neogenesis of minerals associated with lichen activity. *Applied Clay Science* 16, 229–256.
- BRINDLEY G.W., 1980: Order-disorder in clay mineral structures. In: G. W. Brindley, E. H. Brown (eds.), *Crystal Structures of Clay Minerals and Their X-ray Identification*. Mineralogical Society Ed., London.
- CHEN J., BLUME H. P., BEYER L., 2000: Weathering of rocks induced by lichen colonization — a review. *Catena* 39, 121–146.
- DIXON J. B., 1989: Kaolin and serpentine group minerals. In: Dixon J. B., Weed s. b., (ed.) *Minerals in Soil Environments*. 2nd edn Soil Science Society of America, Madison, WI. 467–525.

- DURMAN M., JACHER K., KAMIENSKA I., MICHALIK M., 2001: Przeobrażenia hydrotermalne w granitoidach Tatr Wysokich. *Przeegl. Geol.* 49, 339.
- GUSTAFSSON J.P., BHATTACHARYA P., BAIN D.C., FRASER A.R., MCHARDY W.J., 1995: Podzolisation mechanism and the synthesis of imogolite in northern Scandinavia. *Geoderma* 66, 167–184.
- KLIMASZEWSKI M., 1988: Rzeźba Tatr Polskich. PWN, Warszawa, 668 pp.
- KUBISZ J., OLEKSYNOWA K., 1972: Produkty przeobrażenia minerałów krzemianowych w glebie z Krzyżnego (Tatry). *Spraw. z Pos. Kom. Nauk. Oddz. PAN w Krakowie XVI/2*, 530–531.
- LUNDSTRÖM U.S., van BRAMEN N., BAIN D., 2000: The podzolisation process. A review. *Geoderma* 94, 91–107.
- MANECKI A., MICHALIK M., OBIDOWICZ A., WILCZYŃSKA-MICHALIK W., 1978: Charakterystyka mineralogiczna i palinologiczna pyłów eolicznych z opadów w Tatrach w latach 1973 i 1974. *Prace Miner.* 57, 19–60.
- MEHRA O.P., JACKSON M.L., 1960: Iron oxide removal from soils and clays by dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, Sixth National Conference, Pergamon Press, 317–327.
- MELKERUD P.A., BAIN D.C., JONGMANS A.G., TARVAINEN T., 2000: Chemical, mineralogical and morphological characterisation of three podzols developed on glacial deposits in Northern Europe. *Geoderma* 94, 125–148.
- OLEKSYNOWA K., SKIBA S., 1976: Geochemical characterization of a polygonal soil on the flattening of Krzyżne Pass in the Tatra Mts. *Studia Geomorphologica Carpatho-Balcánica X*, 27–47.
- PASENDORFER E., 1971: Jak powstały Tatry. Wyd. Geol., Warszawa.
- RIGHI D., RÄISÄNEN L., GILLOT F., 1997: Clay mineral transformations in podzolized tills in central Finland. *Clay Minerals* 32, 531–544.
- RIGHI D., HUBER K., KELLER C., 1999: Clay formation and podzol development from postglacial moraines in Switzerland. *Clay Minerals* 34, 319–332.
- REYNOLDS R.C., 1971: Clay mineral formation in an alpine environment. *Clays and Clay Minerals* 19, 361–374.
- SKIBA S., 1977: Studies on mountain soils formed in various phytoclimatic zones of the crystalline part of the Polish Tatra Mts. *Roczniki Gleb.* 27, 205–241.
- SKIBA S., 1997: Środowisko geograficzne gleby. In: *Encyklopedia Geograficzna Świata* 10, Polska, 102–110.
- ŚRODOŃ J., 1999: Use of clay minerals in reconstructing geological processes: recent advances and some perspectives. *Clay Minerals* 34, 27–37.
- ŠUCHA V., ŚRODOŃ J., CLAUER N., ELSASS F., EBERL D. D., KRAUS I., MADEJOVA J., 2001: Weathering of smectite and illite-smectite under temperate climatic conditions. *Clay Minerals* 36, 403–419.
- WEAVER C.E., 1989: *Clays, Muds and Shales. Developments in Sedimentology* 44. Elsevier, Amsterdam, Netherlands.
- WEBER J., GARCIA-GONZALES T. M., DRADRACH A., 2000: Skład mineralogiczny bielic wytworzonych z granitów w karkonoskim piętrze subalpejskim w rejonie występowania kłęski ekologicznej. *Zeszyty Problematy Postępów Nauk Rolniczych* 464, 251–259.
- WILSON M.J., BAIN D.C., DUTHIE D.M.L., 1984: The soil clays of Great Britain: II. Scotland. *Clay Minerals* 19, 709–735.
- WILSON M.J., 1999: The origin and formation of clays minerals in soils: past, present and future perspectives. *Clay Minerals* 34, 7–25.

POCHODZENIE KAOLINITU WYSTĘPUJĄCEGO W TATRZAŃSKICH GLEBACH BIELICOWYCH

Streszczenie

Głównymi minerałami występującymi w badanych tatrzańskich bielicach są kwarc, plagioklasy i miki. W mniejszych ilościach występują w nich także skalenie potasowe, chloryt i kaolinit. We frakcji pelitycznej ($<2 \mu\text{m}$) badanych gleb występują mika, chloryt, kaolinit i minerały mieszanopaketowe typu mika/wermikulit. We frakcji $<2 \mu\text{m}$ obecne są również niewielkie ilości skaleni i kwarcu. Występujący w badanych glebach kaolinit powstał najprawdopodobniej w procesie przemian w kwaśnym i silnie przemywanym środowisku gleb bielicowych. Minerale mieszanopaketowe typu mika/wermikulit są przypuszczalnie produktem transformacji pierwotnych minerałów mikowych. Badane gleby reprezentują trzy stadia zaawansowania procesów kaolinityzacji i wermikularyzacji.