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PALEOENVIRONMENT INTERPRETATION OF THE CARPATHIAN KEUPER ROCKS AS REVEALED BY CLAY MINERAL ANALYSIS

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Abstract: The results of the qualitative and semiquantitative determination of clay minerals in the Keuper clastics and carbonate rocks (sandstones, shales and dolostones) are presented and their depositional environments deduced. Well crystallized illite, and chlorite are the most predominant clay minerals in the Keuper rocks, followed in amount by very well crystallized kaolinite, and palygorskite. It is suggested that kaolinite was formed in a fluvial environment, illite and chlorite were formed under marine to shallow-marine conditions, or perhaps were derived from older sedimentary rocks. Palygorskite was formed under arid evaporatic conditions. The clay minerals were most probably formed either from the weathered products of the parent rocks (i.e. igneous and metamorphic rocks of the crystalline cores of the Western Carpathians, and/or from the foreland of the Bohemian Massif) or as a result of change in conditions of depodition.

Key words: clay minerals, paleoenvironment, Carpathian Keuper, Western Carpathians, Czecho-Slovakia.

Introduction

The Carpathian Keuper rocks of probably Upper Triassic, Norian age (Rakús et al. 1990) outcrops both in the Krížna (Fatric) and Envelope (Tatric) tectonic units as well as in the former Klippen Belt, within the mountain ranges of the Central Western Carpathians of Czecho-Slovakia (Fig. 1). In general, the Carpathian Keuper is composed of intercalated sandstones, siltstones, shales and dolostones with occasional breccias and conglomerates. The keuper of the Envelope unit contains as a rule, a greater portion of clastic materials and that of the Krížna unit more dolostone intercalations.

A detailed sedimentologic and petrographic study of the Carpathian Keuper rocks by Al-Juboury (1992) has revealed that the paleoenvironment of the Keuper is a generally, continental, littoral environment changed to those of shallow-marine, lagoonal with hypersaline conditions for the deposition of dolostones. The area of Keuper deposition was affected by sea level changes and oscillations.

The purpose of this study is to determine the qualitative and semiquantitative distribution of the clay minerals present in both the clastic and carbonate Keuper rocks and to interpret their environment of deposition. Samples were selected from representative Keuper profiles in the Western Carpathian mountain ranges (Fig. 1).

Methods and results

The clay fraction of (28) samples of clastics and carbonates as separated using the standard sedimentation methods to obtain the less than 2 microns fraction following the procedures recommended by Carver (1971) for the clastic rocks and by Jackson (1975) for the carbonates. The samples selected from the Keuper profiles studied, included 20 of sandstones and silty shales, 8 of dolostones. Samples were prepared for X-ray diffraction (XRD) analysis by the oriented aggregate techniques according to the method of Gibson (1966). Mineral identification was further facilitated by the ethylenglycolation method and heating treatment. A Dron-3 diffractometer (cooper radiation) was used to make the X-ray diffraction scans.

Differential thermal analysis was done by heating the samples at the rate of 20 °*C/min.*, using a MOM 1500 Q (Paulik-Erdey, Budapest) electric furnace. Calcium aluminium oxide was used as an inert material.

Transmission electron microscopy pictures were made of dispersed clay samples with a Tesla BS 242 B electron microscope after sedimentation of ultrasonically dispersed samples and drying on a carbon coated copper grid. Scanning electron pictures were made of rock fragments, using a JEOL JSM 840 scanning microscope. Biscaye's method (1965) of approximate calculation of the quantity of clay as revealed by peaks of height ratios has been used in this study.

Tab. 1 shows that illite and chlorites are the most predominant clay minerals in the Keuper rocks, followed by kaolinite and traces of palygorskite. Crystallinity measurements were made, using the method of Jacobs (1974).

This measurement was done by determining the ratio of the width of the (001) peak at half-height of the peak above background, thus a sharply resolved peak of high intensity characteristic of good crystallinity, would have a small value. This method show that the observed kaolinite is very well crystallized when compared to the other clays present in the same rocks (Tab. 1).

Illite was identified by the distinct peak 10.0 Å and weak 5 Å peak in the air dried sample, that are unaffected either by the standard heating or by expansion (glycolation) treatments. Chlorite is identified on the basis of a strong 14.73 Å peak which is intensified by heat treatment up to 550 °*C* and the 7.14 Å peak which is the occupational place for kaolinite. However, distinction between kaolinite and chlorite can be decided by heating to 550 °*C* for 1 hour, giving rise to collapsed kaolinite peaks at this point (Brown & Brindley 1980). Palygorskite was determined by its 10.5 Å peak which is unaffected by glycolation but disappears with 450 °*C* heating, however, long XRD pattern (Fig. 2) shows

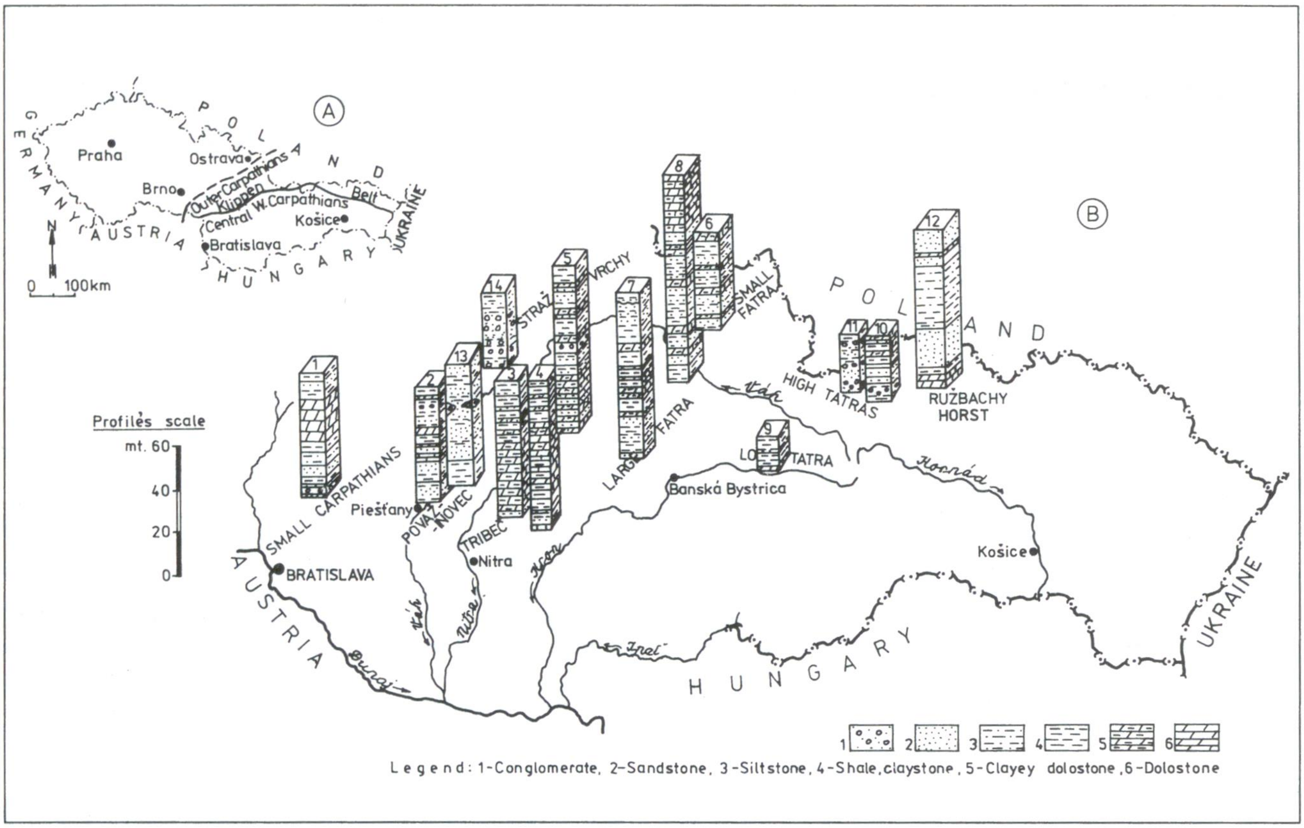

Fig. 1. A - map of Czecho-Slovakia. **B** - Slovak part and the location of Keuper profiles in the mountain ranges of the Central Western Carpathians.

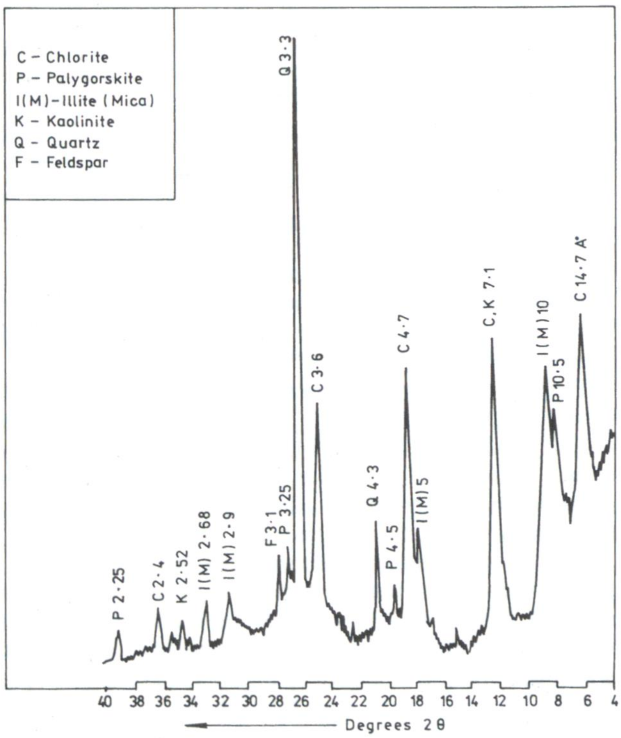

Fig. 2. XRD pattern of oriented preparation of < 2 μm fractions of clay from the Keuper sandstones at Drietoma, showing different reflections of palygorskite.

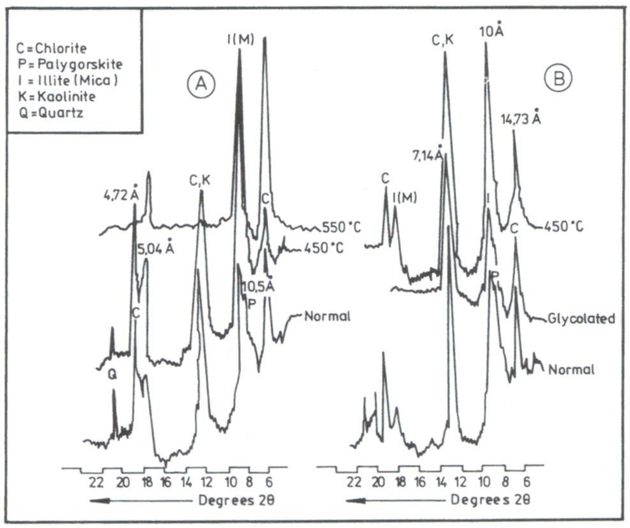

Fig. 3. X-ray diffractions pattern of oriented Keuper clay minerals.
A - clay minerals from the sandstones, the Klippen Belt.
B - clay minerals from the dolostones, the High Tatra Mts.

the different reflections of palygorskite. Fig. 3 shows the characters of the diffractograms for Keuper clay minerals. Mixed-layer clays and montmorillonite were not identified. The differential thermal analysis curves of some selected clay samples fail to indicate the presence of kaolinite, and all the observed reactions are the endothermic reactions for illite. The identification of palygorskite was further confirmed by chemical microanalysis.

Table 1: Summarized qualitative and semi-quantitative determination of clay minerals present in the Keuper rocks (representative samples).

Sample No. Profile	Clay Minerals				Crystallinity measurements based on the adapted methods of Biscaye (1965) and Jacobs (1974)		
	Illite	Chlorite	Kaolinite	Palygorskite	Illite	Chlorite	Kaolinite
4 Vysoká 754	abundant	rare	abundant	no	perfectly	poorly	very well
6 Banka	extremely abundant	trace	no	no	"	"	"
15 Veľké Pole	abundant	abundant	abundant	no	poorly	poorly	very well
16 Zázrivá	extremely abundant	abundant	abundant	no	well	"	"
49 Ždiar (dolostone)	abundant	abundant	rare	trace	"	"	"
4 Široké Sedlo	abundant	extremely abundant	abundant	trace	"	well	very well
7 Drietoma	abundant	abundant	abundant	trace	poorly	poorly	"
3 Beckov	rare	extremely abundant	abundant	no	"	"	very well

Discussion

Keller (1970) has shown in detail the suitable environmental conditions for the genesis of clay minerals. He indicated that illite develops from the weathering of igneous rocks that are rich in potassium feldspars. These rocks are present in the crystalline core mountains of the Western Carpathians (Maheľ & Buday 1968). Furthermore, Engelhardt (1977) has concluded that illite may be derived from reworked sedimentary rocks and from muscovites that sustain for many sedimentary cycles. These sediments may exist in the older Lower and Middle Triassic quartzites and carbonates of the Western Carpathians.

Crystallinity measurements (Jacobs 1974) show that the observed illite is generally well crystallized as revealed by the sharp XRD 10 Å peak. Well crystallized illite is a good indication of better preservation of rock-derived minerals in older colder or dryer climates with less hydrolyzing conditions on land (Chamley 1989). Electron micrographs revealed well-edged illite sheets (Fig. 4) with well defined grain boundaries. O'Brien & Burrell (1970) concluded that the relatively good crystallinity of the clay size detritus is well displayed by sharp X-ray peaks and by the well defined grain boundaries in electron micrographs.

Chlorite is derived from the weathering of rocks rich in ferromagnesian minerals that contain high content of Mg, Fe and Ca,

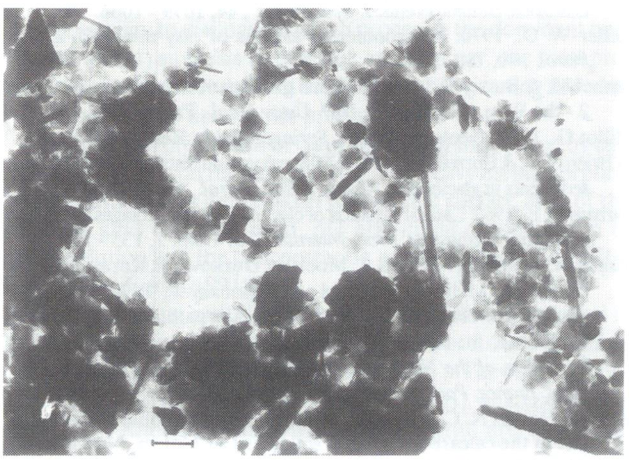

Fig. 4. Electron micrograph of clay size fraction < 2 μm of the sandstones at the Drietoma profile of the Klippen Belt. Short palygorskite fibres and little well-edged illite sheets are clearly observed (b=μm).

and that is excellent in the basic igneous and metamorphic rocks (Millot 1970). These rocks are also common in the crystalline cores of the Western Carpathians.

The present chlorite is believed to be Mg-rich chlorite, according to the estimation method of Weiss (1991), that is based on the intensity of basal diffractions 002 and 004 of chlorite. The petrographic study of both the sandstones and dolostones of the Carpathian Keuper revealed the presence of diagenetic chlorites in the form of either fine patchy rims enclosed other grains, or occupy voids between the grains. These are indications of a diagenetic formation of chlorite which are locally abundant in the local abundance of ferromagnesian minerals (e.g., biotite) or of shallow marine to brackish environment (Chamley 1989).

Keller (1970) also indicated that kaolinite most probably develops from weathering of pre-existing rocks such as granite, mafic rocks and volcanic ash. Grim (1968) has shown that kaolinite may be of a detrital origin derived from the weathering of igneous rocks that are rich in potassium feldspar. The above rocks are mainly present in the older crystalline core rocks of the Western Carpathians.

Weaver (1960) stated that kaolinite is dominant in sediments of fluviatile environments, a partly indicated environment for the Keuper sandstones as revealed by the grain size analysis and interpretation. Furthermore, Parham (1966) has mentioned that kaolinite frequently tends to increase in abundance in a near-shore facies, while illite reaches maximum abundance seaward of kaolinite. The kaolinite of the Keuper sediments is indicated as very well crystallized when compared to the other clays present in the same sediments, and this confirms its formation in a nonmarine environment.

Well defined pseudo-hexagonal kaolinite plates are recorded from the clay fraction electron micrographs. Halloysite with a tubular shape from the sandstone of the High Tatra Mts. Keuper has been detected in the scanning electron images (Fig. 5).

Palygorskite was firstly observed in the Keuper sediments through the present work. This mineral has a fibrous texture and chain structure and is commonly associated with dolomites and other Mg-rich minerals. Arid climatic conditions favor the formation of palygorskite in desert soils. Attapulgite (palygorskite) was described by Elgabaly (1962) in the desert soils of Egypt, Al-Rawi et al. (1969) in the arid region of Iraq, and Van den Heuvel (1966) in the calcareous desert soils of New Mexico, USA.

Chamley (1989) has shown that palygorskite derives from chemical precipitation in evaporative basins, other studies, however, have shown that this mineral may also form under subarid

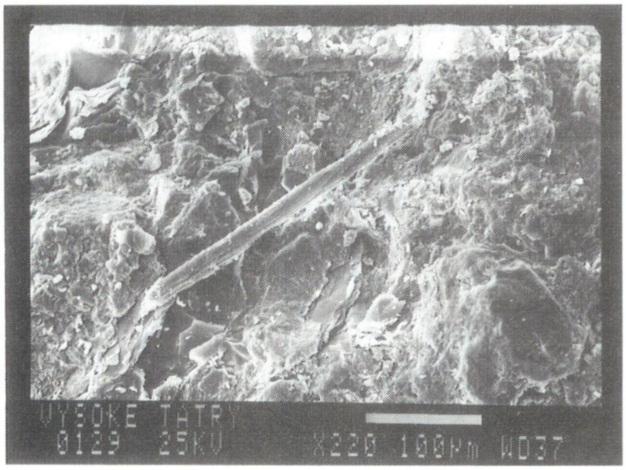

Fig. 5. Scanning electron microscopy (SEM) image of halloysite (kaolinite) tube in the sandstone of High Tatra Mts. Široké Sedlo Keuper profile.

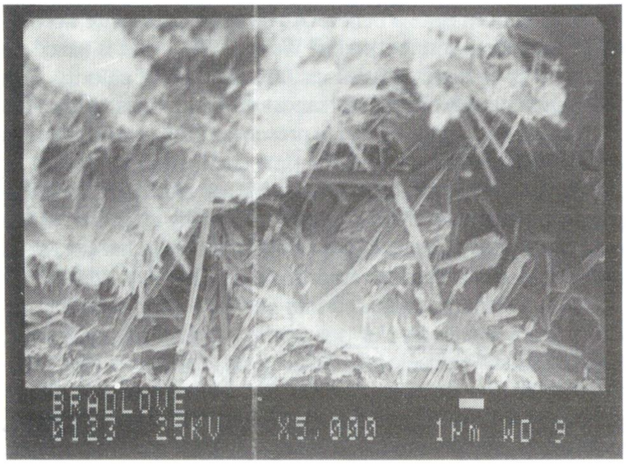

Fig. 6. SEM image of long and short fibres of palygorskite. Sandstone of the Klippen Belt Keupe

conditions in calcareous pedogenic crusts, and that the fibrous clays may be easily reworked by wind or water from these subaerial, lacustrine, or peri-marine environments. Fibrous clays may therefore be either authigenic or detrital in a given sedimentary environment. Short and broken fibres as a typical morphological form of palygorskite are clearly seen in the electron micrographs (Fig. 4). Some of these fibres were examined chemically, showing that the MgO content reaches up to 4.13 %. These broken fibres are an indication of reworking from exposed areas which may consist of evaporative sediments (Chamley & Müller 1991). These sediments probably occurred in the Lower Permian and Middle Triassic dolomites of the Western Carpathians. Scanning electron image reveals short and long fibres of palygorskite (Fig. 6) in the carbonate-rich sandstones of the Keuper in the Klippen Belt, as well as those from the Široké Sedlo Keuper profile in the High Tatra Mts. (Fig. 3). The dominating carbonate-rich sandstone (calclithic arenite) as well as the presence of intraformational carbonate breccias in the above profiles (Al-Juboury 1992) may indicates the intensively weathered carbonate rocks from a pre-existing carbonate rich formations.

Chamley (1989) summarized the conditions for palygorskite formation as "alkaline conditions in restricted basins subject to marine transgressions, limited water exchange, warm and humidity, contrasted climate and strong evaporation". These conditions are exactly suitable for the Keuper dolostones as indicated by many features characterized the hypersaline (lagoonal) restricted basin, the probable basin for these dolostone deposition.

Conclusions

Illite, chlorite, kaolinite and palygorskite are the clay minerals association of the Keuper rocks (both clastic and carbonates). This association reveals that continental (fluvial), shallow marine, lagoonal (hypersaline) paleoenvironments are supposed for Keuper deposition. These results are confirmed by detailed petrographic and sedimentologic studies of both clastic and carbonate Keuper rocks in the Western Carpathians of Czecho-Slovakia.

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