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Environmental signals in palaeosols: mineralogical and stable isotope evidence

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The south-western South Carpathians represent a nappe pile which is mainly composed of pre-Alpine basement nappes separated by the ophiolitic Severin unit. Within the Haţeg basin the late Cretaceous was divided by Stilla (1985) into sedimentary groups, separated by local unconformities. From Maastrichtian to Early Paleogene two different continental formations are known: the Densuş-Ciula and the Sânpetru formations both represented by continental deposit. The late Cretaceous basin subsidence correlates with the stacking of the Getic nappe on the top of the Danubian realm, as well as uplift of the surrounding areas and orogenic collapse (Bojar et al., 1998; Willingshofer et al., 2001). Burial of the Maastrichtian strata by younger deposits was limited to a few hundred meters.

At Tustea quarry, situated at the northern border of the basin, the 10 m vertical escarpment comprises two levels of massive red mudstones intercalated with conglomerates and cross-stratified sandstones. The bottom of the sequence is represented by a massive red mudstone followed by 4 m coarse grained, poorly sorted deposits with trough-cross to parallel stratification. The channel bodies show laterally crosscutting and alternating sandstones and conglomerates, which indicate unstable channelized flow with discharge fluctuations. The inter-channel areas, starved of coarse sediment supply, were site of pedogenesis. The soils show: a red mud horizon with blocky structure characterised by the presence of well developed vertical roots and burrows and a level with calcareous concretions. There are several levels of calcretes with thickness and lateral continuity indicating moderately developed soils (Retalak, 2001). Paleosols can be classified as calcisols (Mack and James, 1994). Associate with some of concretion layer, just above of them, dinosaurs nesting sites together with embryonic/hatchling skeletal remains were found. Based on these remains, the eggs are thought to belong to a hadrosaurid *Telmatosaurus transsylvanicus* (Grigorescu et al., 1994).

X-Ray analyses show that all paleosol samples have a bulk mineralogy dominated by layer silicates. In the fraction less than 2µm, smectite, dominates with up to 94 mass %. Other clay of minerals present in very small amounts are: illite in the range of 4 to 10 mass %, and kaolinite 2 to 4 mass %. The position of the OH band of the infrared spectrum indicate that the smectite is montmorillonite. The smectite fraction less than 0.2µm was separated from different paleosol levels were separated in order to make additional chemical analyses and determine the isotopic composition of smectites. For isotopic composition measurements Hydrogen from the OH position and Oxygen from the OH and SiO_4 positions, absorption and interlayer water were removed by heating the samples at 200 °C for ~24 hours. Preliminary heating tests were done on STX 1 smectite standard. The samples were heated to 200°C and after each heating step an infrared spectrum and a x-ray diffraction were performed. X-ray diffraction of heated STX 1 standard shows the collapse of the (001) layer. Unheated smectite shows a (001) d-spacing of about 14.7 Å. After 5 hours at 200 °C the d-spacing is 9.74 Å. Further heating does not change the layer distance. The collapse of the layer is due to the removing of interlayer water. Infrared spectra show that only after 24 hours heating practically all interlayer water is removed, 12 hours heating was insufficient.

Stable isotope measurements on oxygen were performed using a classic silicate line with Nickel bombs. The samples were firstly heated under vacuum c. 1 day at 200°C and than fluorinated with BrF_5 at 550°C for ~ 1 day. The $\delta^{18}O$ compositions are around 19 ‰ (SMOW). For the hydrogen isotopic measurements the samples were also heated under vacuum one day at 200°C, and than measured on a TC/EA device in continuous flow. The δD values vary from –143 to -166 ‰ (SMOW). Also for the Hateg basin, measurements on the isotopic composition of the rainwater have been started in August 2006.

The calcretes show a narrow range of isotopic compositions, with $\delta^{18}O$ values between 24.1 and 25 ‰ and $\delta^{13}C$ between 8.1 and –8.9 ‰ (PDB)

At Tuştea, the red colour and the presence of calcretes with micritic texture indicate that the soils formed above the water table under oxidizing, alkaline conditions. The deeply penetrating vertical root traces also suggest well-drained soils. These conditions were favourable for the preservation of egg and bone material. The thickness and distribution of the calcrete levels indicate multiple buried, moderate to strong developed soils, most probably developed on a stable terrace, close to the basin border. The coarse sequence is interpreted as deposited in a feeder zone of an alluvial fan during flooding events. The high content in smectite, up to 98 mass %, was favored by the presence of the volcanoclastic material present at this site. Using appropriate fractionation factors, the isotopic data indicate that the smectite are in equilibrium with the local present meteoric water line. This fact was also put in evidence by early workers (Savin and Epstein, 1970, Lawrence and Taylor, 1971). In contrast, the stable isotopic composition of calcrete are preserved reflecting the composition of paleosol water at the time of Late Cretaceous..

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