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Stable isotopic composition of carbonates in Quaternary sediments of the Skala Podil'ska sequence (Ukraine)

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Abstract

Stable isotopes of carbon and oxygen in carbonates from Quaternary sediments sequence of Skala Podil'ska in Podolia were studied. Samples were collected from two loess with fossil soils packages, from lacustrine loams separated them, and from the underlying alluvium. The isotopic analysis was carried out on the bulk loess, fossil soils and loam samples, calcitic concretions and other detrital and auhigenic forms of carbonates (rhizocretions). These are thin tubes lined by micrite, empty or filled by root fragments with calcified cells and calcified cortex of the roots. Variation in carbon isotopic composition of soil and loess samples depends on the $^{13}C/^{12}C$ ratios of authigenic and detrital $CaCO_3$-containing components. Therefore, the carbon isotopic composition of rhizocretions affected bulk isotopic composition of loess and soils. Likewise, the isotopic composition of lithoclasts and bioclasts influence the isotopic composition of carbonates from the loams of lacustrine-like subsequence. The $\delta^{13}C$ as well as $\delta^{18}O$ values for concretions from all the analysed horizons in the sequence fell within a very narrow range. This suggests that carbonate concretions and rhizocretions were formed under roughly similar conditions, with considerable supply of soil CO_2 to the groundwater bicarbonate. The smallest $\delta^{13}C$ value obtained for calcified root cortex, for calcite precipitated directly inside the root structure, may indicate mineralization of C_3 plants.

1. Introduction

The Skala Podil'ska site is located above the bank of the Zbruč River in the Dniester River basin in the Western Podolia (Ukraine). Geographical coordinates of the site are 48°51'N and 26°11'E. The southern part of the Podolia region, and more exactly the basin of the middle Dniester, is rare among European areas, as it has widespread, well-developed and differentiated deposits of the Lower Quaternary. During a geological field survey by a Polish–Ukrainian group of scientists, the Quaternary sediment sequence was found as the cover of the Silurian limestones exploited in a huge quarry. It consists of a loess series with several fossil soils, and intraloess lacustrine-type loams, lying on alluvial sands and gravels covering the Neogene limestones. The profile was selected as a main object of a joint project concerning the Lower Quaternary paleoclimatic and paleohydrological changes in Southern Podolia. Many horizons with carbonate concretions were observed in the profile as well as differentiated authigenic carbonates dispersed in the important sections of sediments. Study the composition of stable isotopes of oxygen and carbon was conducted to assess the possibility of using them in reconstruction of paleoclimatic changes.

2. Geological and geographical setting

The Podolia Upland is situated in the eastern part of the Meta-Carpathian Uplands, which separate the Peri-Carpathian Foredeep from the Central European Lowlands (Maruszczak, 2001). This is a plateau upland, associated with the Precambrian platform (Hofštejn, 1979), overlain by almost undisturbed Paleozoic and Cretaceous layers and by the Miocene sea deposits left by the epicontinental Paratethys Sea. The patches of alluvial deposits, occurring on the extensive plain of the former sea bottom, were formed by the non-arranged flows of the pre-Dniester

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River in the latter part of the Pliocene. They indicate that this river flowed far to the north of its modern valley. The extensive loess covers form the youngest sedimentary unit.

The Podolia Upland is characterized by distinct features of structural relief conditioned by platy arrangement of rocks and basement tectonics. Its southern part is distinguished as the Peri-Dniesterian Canyon Plateau (Gerenčuk, 1979). This strongly dissected loess plateau reaches an altitude of 310–320 m a.s.l. (Gerasimov, 1972). Until the 1960s, this loess was considered to be of alluvial origin, formed in one sedimentation cycle together with the pre-Dniester alluvia (Sokolovskyj, 1957). Running evenly with a parallel of latitude, the Dniester River valley is a typical canyon (= "jar" in Slav) with large incised meanders. Meridional valleys (of the so-called "Podolian" direction) of several tributaries flowing into the Dniester River from the north run along the basement fractures of N–S orientation (Maruszczak and Sirenko, 1989/1990). Therefore, the landscape is characterized by a regular pattern of flat or slightly undulated interfluve areas, and valleys of canyon type, which are incised even to the depth of 150–200 m in the area adjoining the Dniester River valley. The slopes inside the canyons are terraced in places, and the over-canyon parts of river valleys consist of several wide old terraces, which represent two main accumulation surfaces (Veklič, 1965; Ivanova, 1977). The highest terrace was dated at the Upper Pliocene (Hofštejn, 1979).

The present climate of the Peri-Dniesterian Canyon Plateau is temperate, continental-steppe (Pontian), with rather mild and foggy winters (mean January temperature −5 °C), and warm, sunny summers (mean July temperature about 19 °C). Precipitation occurs as short heavy rainfalls, often storms, with a mean annual total of 625–650 mm (Wróbel and Mrugała, 2001). Before agricultural management of this area, natural vegetation formed meadow steppes with oak forest patches developed on chernozems and gray forest soils.

The examined exposure of the Quaternary deposits occurs in the vicinity of Burdiakivcy near Skala Podil'ska, on the right bank of the Zbruč River, a tributary of the Dniester (Fig. 1). The exposure is situated on a gentle inclined plateau hanging over the deep valley of the Zbruč River. The top of the exposure reaches an altitude of 260 m a.s.l, 65 m above the bottom of the Zbruč River valley, and 150 m above the bottom of the Dniester River valley. The exposure occurs in a quarry of Silurian limestone, which underlies the Badenian marine sediments and the Lower Quaternary series of alluvial and loess-soil deposits. The Quaternary deposits are exposed in back walls of large landslide scars, which intensively develop in the contact zone of the Tertiary and Quaternary layers. Peculiar intra-loess lacustrine deposits indicate a lake basin, about 1 km in diameter and about 6 m thick, clearly visible in the area of the exposure. Its origin has not been explained previously.

Badenian marine sediments and a discordant sequence of Quaternary sediments cover Silurian limestones. Lithothamian limestones with flint concretions, sandstones and clays represent the Badenian. Their thickness uncovered in the quarry is differentiated according to local erosion from 10 to 15 m.

3. Description of Quaternary sediments

The Quaternary sequence embraces four superimposed sedimentary units (Fig. 2):

Unit I—alluvial deposits overlying the Badenian bedrock. They are composed of gravels (flint pebbles, hornstones,

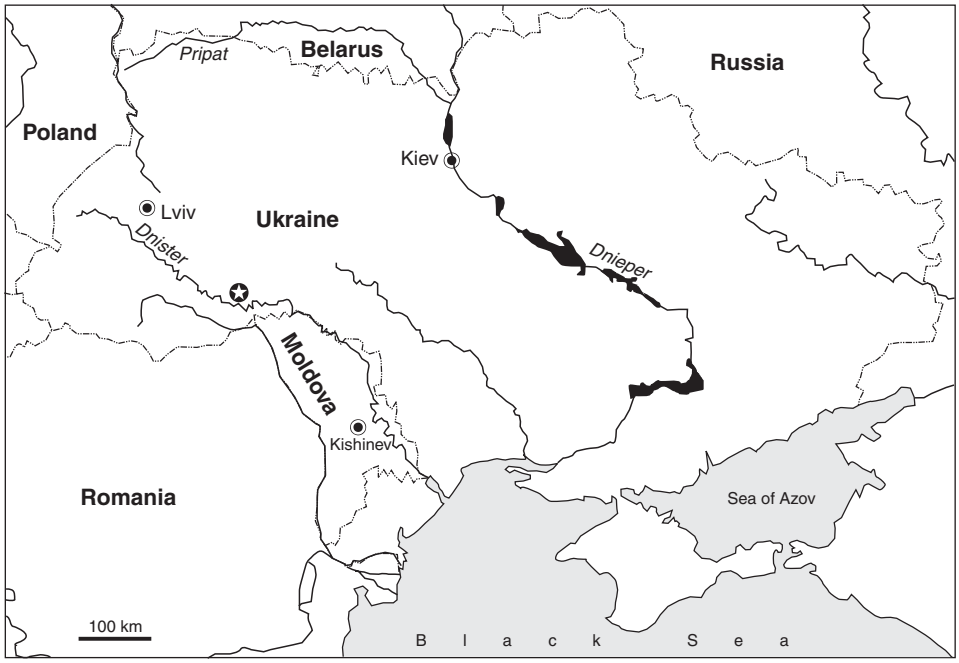

Fig. 1. Location of the Skala Podil'ska site.