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STABLE ISOTOPE COMPOSITION OF CARBONATES IN LOESS AT THE CARPATHIAN MARGIN (SE POLAND)

Bożena Łącka[1], Maria Łanczont[2], Maryna Komar[3], Teresa Madeyska[1]

[1]Institute of Geological Sciences, Polish Academy of Sciences, Twarda 51/55, 00-818 Warszawa, Poland; e-mail: lacka@twarda.pan.pl; tmadeysk@twarda.pan.pl
[2] Department of Physical Geography and Paleogeography, Maria Curie-Skłodowska University, Kraśnicka 2D, 20-817 Lublin, Poland; e-mail: lanczont@biotop.umcs.lublin.pl
[3] Institute of Geological Sciences, National Academy of Sciences of Ukraine, Gonchara str. 55b, Kyiv, Ukraine; e-mail: mkomar@operamail.com

Abstract
Samples for the study were collected from, known from the literature, outcrop profiles in Zarzecze, Radymno, Dybawka, Tarnawce and Pikulice-Nehrybka, situated at the Carpathian border, in the vicinity of the Przemyśl town, close to the San River valley (SE Poland). They represent the Vistulian loess-palaeosol sequences. Carbonates occur mainly in the loesses representing OIS 2 and 3. Pollen analysis, carried out for two profiles (Tarnawce, Radymno), throws light on palaeoecological conditions of loess cover formation and transformation.
Isotopic analysis of authigenic carbonates was carried out on carbonate cemented bodies dispersed throughout the loess in forms of nodule, rhizolith and rhizocretion and on bioclasts, mainly snail shells, ostracod valves, and sparse globules (probably the internal shells of the naked snails).
In the successions studied, the upper Vistulian loess deposited in environment with poor vegetation, contains rhizoliths and rhizocretions mainly, while in the middle and lower Vistulian loess with well developed soils, gley horizons, and intercalations of subaqueous sediments, remains of snail shells and ostracod valves prevail. The two main forms of carbonates differ markedly in isotopic composition from one another. These differences seem to be more important than those between samples of one form of carbonates along particular sections. That is the result of numerous factors affecting the fractionation of carbon and, in particular, oxygen stable isotopes in the environment of precipitation of authigenic calcite. The isotopic composition of carbonates cementing sediments is controlled mainly by biomineralization of organic matter and local climatic parameters which were rather slightly differentiated during the formation of the studied sediments. The $\delta^{13}C$ values for bioclasts vary in a broader range than for calcitic cements. Usually the snail shell carbonate is more enriched with heavier carbon isotope than that from ostracod valves, resulting from the isotopic equilibrium with precipitation and with surface waters, respectively. Basing on our study we can conclude that fluctuations of isotope composition of authigenic carbonates make it hard to apply as a paleoclimatic indicator. However, the general trend of $\delta^{18}O$ variation in analysed carbonate fractions from leoss-palaeosol sequences displays some connections with climatic fluctuations.

Key words: loess, authigenic carbonates, carbon and oxygen stable isotopes, Vistulian

INTRODUCTION

Stable isotope composition of carbon and oxygen in pedogenic carbonates could be used as indicators of climatic conditions during the loess sedimentation and the soil development (Cerling 1984, Nordt *et al.* 1996 etc.). During the study on application of this method for the reconstruction of the Vistulian palaeoclimatic changes basing on loess profiles at the Carpathian Margin, an important differentiation of isotope composition between particular morphological forms of authigenic carbonates was found. Searching for solving the problem of reasons of such differentiation the authoresses decided to study several, known from the literature, loess profiles situated in the vicinity of the Przemyśl town, close to the San River valley (SE Poland). Samples were collected from the outcrop profiles in Zarzecze, Radymno, Dybawka, Tarnawce and Pikulice-Nehrybka (Fig. 1).

The studied loess deposits occur in the eastern part of the Carpathian Foothills, and in the plateaux of the Carpathian Foreland belonging to the Sandomierz Basin (Klimek & Starkel 1972).

Relief of the eastern part of the Carpathian Foothills is rather compact. Its main morphologic elements are remnants of three, step-like arranged surfaces of partial planation. The remnants of the oldest planation surface are preserved at about 500 m a.s.l., in the watershed area of the San and Wiar rivers. The middle (foothill) and lower (near-valley) planation surfaces occur at 380–410 m a.s.l. and 290–320 m a.s.l., respectively. The foothill planation surface dominates in the landscape.

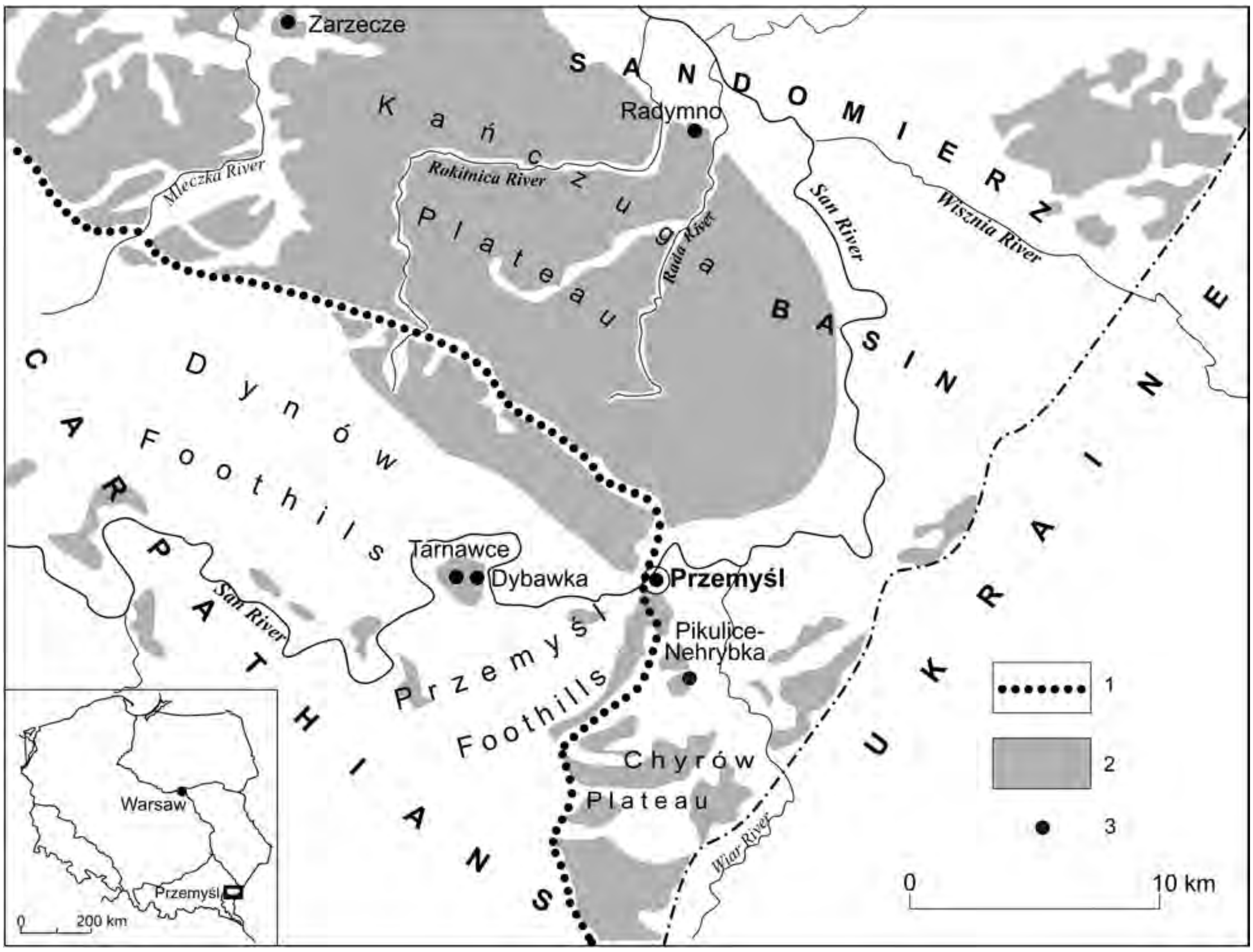

Fig. 1. Sketch map showing locations of the studied profiles. *1* – Carpathian border, *2* – loess distribution, *3* – investigated sites.

The wide and deep valley of the San River is a morphological axis of the area. This meandering valley (with the bottom at about 200 m a.s.l.) divides the eastern part of the Carpathian Foothills into the Dynów Foothills and the Przemyśl Foothills. A step-like system of four Pleistocene terraces (the highest, high, middle, and low) occurs on the valley sides. These terraces occur on flysch rock socles as alluvial and aeolian cover. Loess patches reach a height of 280–320 m a.s.l., and in places their thickness exceeds 20 m. The largest loess patches are associated with the high terrace (Tarnawce profile) and the middle terrace (Dybawka profile). They occur also on slope flats and on the near-valley planation surface.

The plateaux of the Carpathian Foreland rise at 220–300 m a.s.l. The relative heights associated with valleys reach 40–80 m. The undulated plateaux are dissected by river valleys, and form rather narrow ridges running parallel to the Carpathian margin. The plateaux are covered with the loess mantle, in places over 10 m thick, which overlies older fluvial and glacial deposits, and Tertiary marine clays.

The Kańczuga Plateau is an isolated upland fragment of distinctive arc shape, which in the north borders on the depression of the Fore-Carpathian Pradolina, and the valley of the Lower San River is its northeastern boundary (Kondracki 1988). The Zarzecze profile is located in the central part of the widest part of the plateau.

The Chyrów Plateau is situated south of Przemyśl, eastwards of the Lower San River Valley; it is the most southeastern region of the Sandomierz Basin, and only its small part occurs in Poland. The Wiar River valley separates the ranges of hills with tens-meter-high slopes. The Pikulice-Nehrybka profile is located in the Pleistocene terrace of the Wiar River.

INFORMATION ABOUT THE PROFILES

The isotopic analysis was carried out on calcite concretions, rhizocretions and other authigenic and detrital forms of carbonates. These carbonates are present in fragments of the loess profiles only.

Zarzecze

The Quaternary deposits are exposed in the open pit of a brick-yard situated in the northern part of the Zarzecze village, near the road to Przeworsk (49°50’00’’N, 22°32’05’’E). The site is located in the central part of the subcarpathian loess plateau, i.e. the Kańczuga Plateau (Fig. 1). The profile is composed of two loesses and glacigenic deposits which represent the maximum glaciation in Poland (Laskowska-Wysoczańska 1991, Łanczont *et al.* 2000). The loess cover, reaching maximum thickness of about 8 m, con-

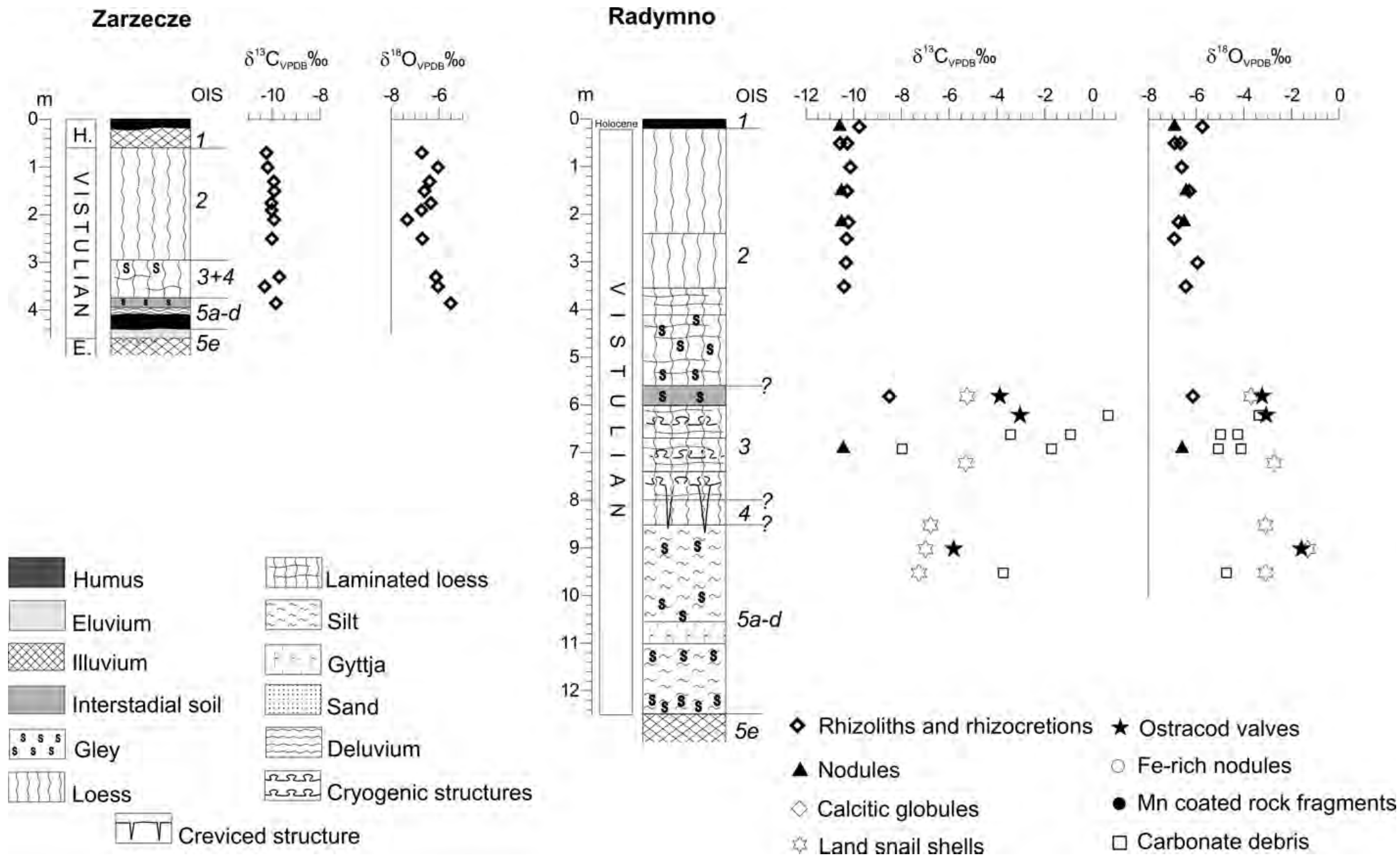

Fig. 2. Geological sections of Vistulian from Zarzecze and Radymno and the variation of $\delta^{13}C$ and $\delta^{18}O$ values along these profiles.

tains, after the mentioned authors, older loesses from the Warta (=Warthe) and Vistula Glacials, which are separated by a thick and well-developed pedocomplex from the Eemian–Early Vistulian. Simplified description of the upper part of the profile (Fig. 2), where carbonates are present, is given below (depth in metres):

0.00 – 0.60	Recent soil.
0.60 – 2.95	Compact carbonate loess.
2.95 – 3.75	Irregularly laminated loess with traces of gleying in the upper part.
3.75 – 3.95	Palaeosol of Early Vistulian Interstadial (Odderade?). Bluish-rust-coloured silt, in the lowest part brown, in the upper part gleying
3.95 – 4.10	Material of humus horizon redeposited by deluvial processes.
4.10 – 4.40	Palaeosol of Early Vistulian Interstadial (Brörup+Amersfoort?) developed as humus horizon of chernozem.
4.40 – 4.60	Eluvial horizon Eet of the Eemian palaeosol.
4.60 – 5.35	The Bt1 horizon of the Eemian palaeosol.
5.35 – 6.15	The Btg2 horizon of the Eemian palaeosol.

The loesses from this profile were TL dated in Lublin and Gdańsk laboratories. The results obtained for the Vistulian part of the profile in both laboratories are convergent. They are used for stratigraphic interpretation of the profile. The ages of four samples of carbonate loess from the near-surface layer (0.60–2.95 m) range from 22.1 to 29.3 ka BP (Łanczont *et al.* 2000, Fedorowicz & Łanczont 2004, Fedorowicz 2006). The obtained dating results can indicate that the youngest layers of loess are absent in this site. They were probably removed by Holocene erosion.

Radymno

The loess profile is situated in the brickyard at the north-eastern part of the Radymno town (49°57’50’’N, 22°48’50’’E). The loess covers the Pleistocene terrace of the San River. The loess profile was examined by several scientists. The main loess beds distinguished by Malicki (1972b), Maruszczak (1991b), Alexandrowicz *et al.* (1989), and Wójcik & Zimnal (2003) can be easily correlated but the published descriptions markedly differ in the detailed lithology and thickness of individual layers.

Our samples were collected from three fragments of brickyard walls situated in its north-western part, accessible to investigations. The Holocene soil during the time of our sampling was destroyed. The loess is carbonate to the depth of about 10.4 m (Fig. 2). Simplified description of the profile (depth in metres) is given below:

0.00 – 0.20	Weakly developed humus horizon of recent soil.
0.20 – 2.40	Buff loess with two horizons of irregular streaks of ferruginous precipitations and crotovinas.
2.40 – 3.55	Dark buff laminated loess.
3.55 – 4.10	Buff loess, slightly horizontally layered.
4.10 – 5.60	Light-greyish, slightly laminated, gleyed loess.
5.60 – 6.00	Gley horizon, probably interstadial palaeosol.
6.00 – 6.70	Stratified, grey and yellow silty loam. It is the upper layer (I) of diapir-type and cryogenic load deformations.
6.70 – 7.40	Stratified, buff loess disturbed with plication structures – it is the middle layer (II) of deformations
7.40 – 8.00	The lower (III) layer of diapir-type deformations, load structures and casts of subvertical fissure structures 1.8 m deep and 0.1 m wide.
8.00 – 8.50	Clayey silt, greyish, weakly deformed.
8.50 – 11.00	Brown-grey loam of flood-boggy origin very compact with sandstone gravels at the depth of 9.8 m. Elongated lense/pocket of gyttja occurs at the depth of 10.6 – 11.0 m. These deposits are rich in humus, the content of which increases to 5.5% in the layer bottom.
11.00 – 12.55	Loam and clayey silt, zonally gleyed.
12.55 – 13.60	Clayey silt, excavation does not reach the lower boundary but according to the description by Maruszczak (1980), the lower part of this layer probably represents the Eemian soil, strongly transformed by subsequent processes associated with flooding. This soil, over 1 m thick and represented by gleyed illuvial horizon, was found in the southern part of brickyard (Radymno 2 site).

The molluscs assemblages described by Alexandrowicz (Alexandrowicz *et al.* 1989) from the middle part of the profile represent rather humid conditions. In the sediments corresponding probably to the fragment in the profile at the depth of 5.80–7.00 m an “assemblage with *Succinea oblonga elongata* which indicates an open, quite humid habitat and cold, subpolar climate” was described. The second assemblage found beneath, with *Gyraulus laevis* and *Lymnaea truncatula* indicates the presence of small water body. “Shells of the land snails found (*Succinea, Vertigo*) come from the margin of the water reservoir into which they were washed (...). The assemblage is typical of a loess valley facies which was accumulated partly in land and partly in water environment” (Alexandrowicz *et al.* 1989). According to stratigraphic interpretation of the profile by the mentioned authors, the palaeosol occurring in the bottom of loess represents a warm period of interstadial type and is related to the Early Vistulian (Oxygen Isotope Stage – OIS 5a–d). Preliminary palynological analysis, which was done for this fragment of the section, suggests another interpretation (M. Komar, unpublished). The vegetation composition points unequivocally for the Eemian Interglacial. Only three local pollen assemblage zones (L PAZ) are distinguished: *Quercus*, *Corylus+Tilia* and *Carpinus*. The mixed forest of temperate climate at the beginning of the *Quercus* zone turned into rich deciduous forests of the interglacial optimum. In contrast to vegetation succession documented in the pollen diagram of Tarnawce (Komar & Łanczont 2002) and some other sites of southern Poland, the phase of development of hornbeam forests in Radymno is very clear.

According to the initial stratigraphic interpretation of the profile, with reference to the results of basic analyses (grain size, contents of calcium carbonate, humus and iron compounds – unpublished data), the loess deposits occurring to the depth of about 5.5 m can be related to the Upper Plenivistulian (compare also Wójcik *et al.* 2003). Subaqueous flood-boggy humus deposits occurring under the loess and over interglacial soil, i.e. from 8.5 to 13.6 m, were formed in the Early Vistulian. Therefore, the loess deposits with cryogenic deformations in the middle part (5.6–8.5 m) of the profile probably represent the middle and lower part of the Plenivistulian (OIS 3, 4). This preliminary stratigraphic interpretation will be verified by additional pollen analysis, TL dating, and other specialized analyses (among others micromorphologic and micropalaeontologic ones) which are in progress.

Dybawka

The Dybawka loess-palaeosols sequence is situated in the Przemyśl Foothills, about 7 km westwards of the city of Przemyśl (49°47'15''N, 22°41'20''E, Fig. 1). It represents loesses forming an eolian cover on the so-called middle (Vistulian) terrace of the San River. The profile is located in the highest point of this terrace. The top of the exposure occurs at 223 m a.s.l., and the San River channel at 196.7 m a.s.l. The Vistulian loess is here extremely thick (over 15 m). Carbonate loess without distinct traces of pedogenesis occurs from a depth of 2.5 m to about 8.6 m (Fig. 3). Simplified description of the profile (depth in metres) is given below:

0.00 – 1.95	Holocene soil complex, very well developed (A-Eet-Bt).
1.95 – 2.50	Silty clay (the B/C horizon of the soil).
2.50 – 3.00	Buff, porous loess.
3.00 – 5.00	Buff loess, with weak traces of lamination.
5.00 – 7.10	Buff silt, striped-laminated.
7.10 – 7.50	Vegetation horizon (?) – yellowish-grey silt.
7.50 – 8.65	Yellowish-grey silt, faintly stratified.
8.65 – 14.50	Series of five interstadial tundra soils, each with one or two horizons, each 0.4–0.6 m thick, separated by layers of clayey silt and silt. This unit of the Dybawka profile is correlated with Inter-Pleniglacial of Vistulian.
14.50 – 15.50	Subaqueous loess – clayey silt and greyish-brown, stratified sandy muds of flood facies correlated with Lower Pleniglacial and Early Vistulian
15.50 – 21.70	Sands and gravels of channel facies (Eemian and Wartanian).
21.70 –	Rock socle of terrace.

In the upper part of the carbonate loess Alexandrowicz (after Łanczont 1991b) found typical assemblage of *Pupilla muscorum*, *P. loessica* and *Vallonia tenuilabris* with species widely distributed in zone of temperate climate: *Clausilla dubia* and *Trichia hispida*. Several TL datings, obtained for the carbonate loess occurring between the Holocene soil and the first/upper interstadial palaeosol of Inter-Plenivistulian, range from 10.4 to 15.8 ka BP, except one sample from the interphase horizon at 7.1–7.5 m (23 ka BP) (Fedorowicz & Łanczont 2004). These small age differences in such thick loess bed probably evidence high intensity of loess dust accumulation on the terrace in the younger part of OIS 2, i.e. in the post-maximum part of the Vistulian Glaciation.

Tarnawce

The loess profile is situated in the Przemyśl Foothills, about 8 km westwards of the city of Przemyśl (49°47'40''N, 22°41'05''E, Fig. 1). The loesses form an eolian cover about 17 m thick on the so-called high terrace (40–60 m) of the San River. The Tarnawce section is situated in a small valley – tributary of the San River. The top of the exposure occurs in a landslide scar at the height of 248 m a.s.l.

M. Łanczont (1991a, 1993, 1995) published description of the Tarnawce profile and the results of lithological analyses. The oldest part of this profile is composed of loess of flood-bog facies correlated with the Odra (=Drenthe) Glacial. An erosion surface separates this deposit from the loess-like layered deposits (about 6 m thick) from the Warta (=Warthe) Glacial, on which the Eemian soil is developed. The Vistulian loess is rather thin (about 4 m) but well differentiated in respect of stratigraphy. Carbonates are present in the uppermost part of the section only (Fig. 3). Simplified description of the profile (depth in metres) is given below:

0.00 – 1.00	Holocene brown soil (cambisol A-Bbr)
1.00 – 2.50	Typical buff loess, slightly laminated.
2.50 – 3.15	Laminated loess with grey streakes of gleyed silt.
3.15 – 3.60	Interstadial subarctic brown soil with denuded upper part (with horizons Bbr-Bbrg) correlated with Inter-Pleniglacial of Vistulian.
3.60 – 3.85	Gleyed loess
3.85 – 4.15	Interstadial soil, with two horizons, probably from Early Glacial
4.15 – 5.05	Clayey loess, in the bottom part it resembles deluvia of humus horizon.
5.05 – 7.75	Eemian palaeosol of brown type.

Pollen analysis was made for the upper part of the section, beginning at the Eemian soil, and ending at the top of the section. The results of the Eemian and Early Vistulian sediments analysis were published (Komar & Łanczont 2002), while the results of the uppermost part of the section have not been published till now. Altogether 39 samples were analysed, and the section has been divided into 14 Local Pollen Assemblage Zones. It is the only palynologically studied loess profile in the vicinity of Przemyśl.

The bottom part of the pollen diagram corresponds to generally accepted scheme of vegetation development during the Eemian interglacial. Floral changes recorded in pollen spectra resemble the Eemian pollen succession found in fossil lacustrine deposits in Poland. Lower boundary of the Eemian interglacial is marked in the profile by the presence of subarctic flora, showing for moderately cold climatic conditions, open landscape with small patches of trees. In the part of the diagram, which corresponds to the Eemian interglacial, the development of birch-pine, followed by deciduous multi-species forest was documented with *Viscum* and *Humulus lupulus*, and then *Corylus avellana* (climatic optimum). The phases of hornbeam, fir and birch-pine forests, typical for Eemian succession, are absent.

The whole Vistulian succession is characterized by continuous occurrence of trees and shrubs pollen. Two interstadials are marked in the diagram. They occur in direct sequence, and are separated by denudation surface and thin layer of loam. The first one (at the depth 3.9–4.1 m from the surface) is characterized by birch-pine forest with small admixture of other trees (*Ulmus, Quercus, Picea*) and shrubs (Caprifoliaceae, Rhamnaceae), documenting boreal climate. During the second, cooler interstadial (3.2–3.6 m) communities of open habitats dominated the birch-pine forest.

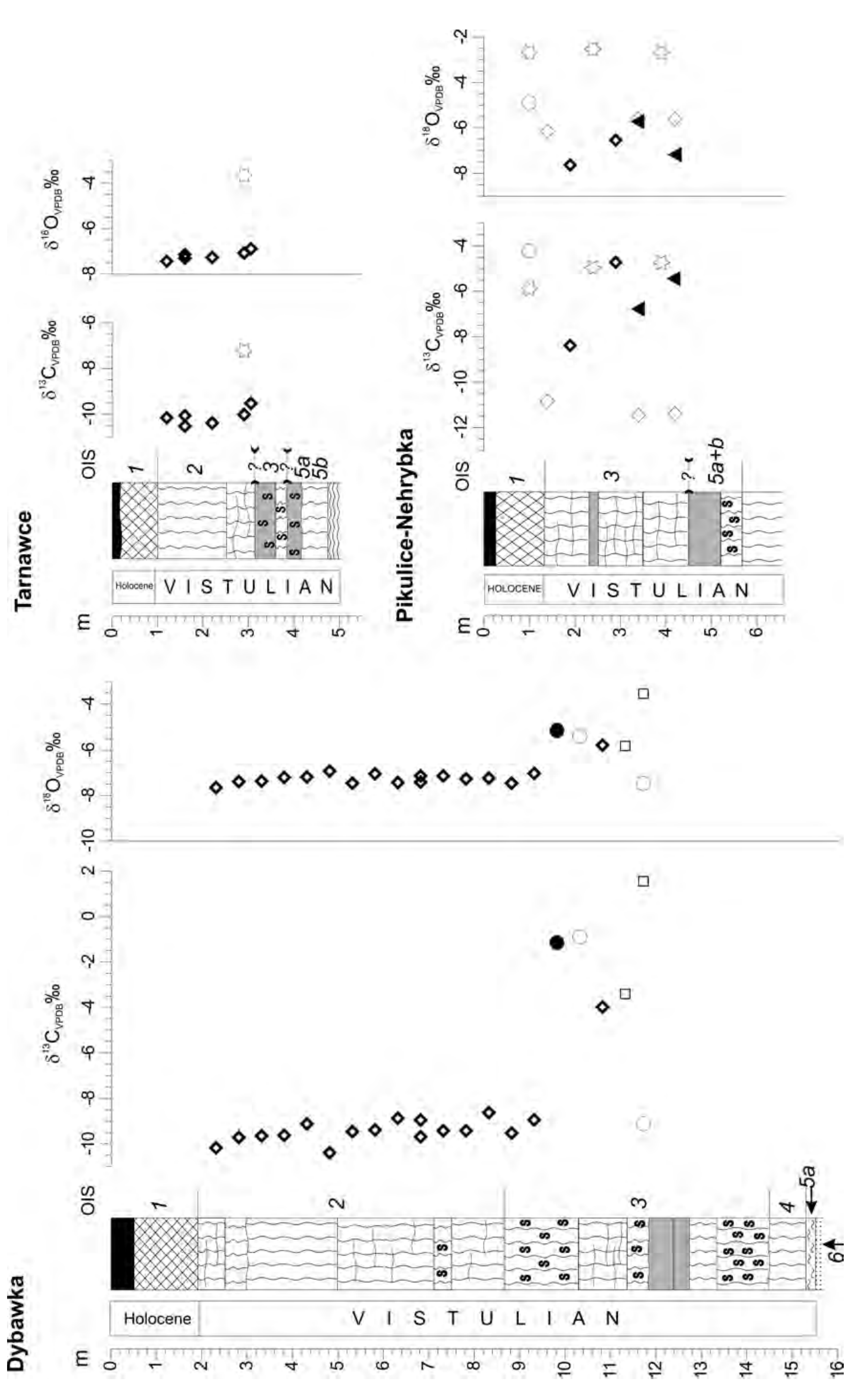

Fig. 3. Geological sections of Vistulian from Dybawka, Tarnawce and Pikulice-Nehrybka and the variation of $\delta^{13}C$ and $\delta^{18}O$ values along these profiles. Explanation on Fig. 2.

Pollen assemblages in carbonate loess (the uppermost part of the profile 1–3.2 m deep from the surface) reflect the flora of open landscapes of mosaic type with changing proportions of tundra and steppe vegetation, and with rare clumps of trees, mainly birch, which indicate humidity fluctuations of cold climate. In the first stage of loess accumulation, contribution of pioneer and steppe plants increased, which probably indicates occurrence of erosion-denudation processes. Then situation has slightly stabilized, tundra and steppe communities developed, as well as pine, birch trees, fir, alder and shrubs. The last stage was characterized by the minimum proportion of trees and shrubs in the vegetation cover, which probably points to arctic climate.

The profile at Tarnawce was TL dated by Fedorowicz (Fedorowicz & Łanczont 2004, Fedorowicz 2006). Two samples of this carbonate loess from the depths of 1.6 m and 2.8 m were TL dated at 12.8±1.4 and 16.8±1.5 ka BP, respectively. These TL ages resemble those obtained for carbonate loess in the nearby profile at Dybawka. The TL ages obtained for the deposits occurring between this loess and the Eemian soil are not fully consistent with pollen interpretation of the profile. The upper palaeosol was TL dated at 31.5±3.8 ka BP, the lower palaeosol – 43.1±4.7, and the underlying loess – 52.8±6.0 and 69.6±7.6 ka BP. These results indicate that both interstadial soils represent Inter-Plenivistiulian. However, the pollen data suggest that only the palaeosol situated at the depth of 3.6–3.2 m can be correlated with Inter-Plenivistiulian. The older palaeosol on account of the occurrence of thermophilous plants, can be regarded as a final (?) soil of the Early Vistulian. It could be pointed that in an outline, the vegetation characteristic of milder climate periods show similarities with former investigation in the Carpathians (e.g. Mamakowa, Starkel 1974, Środoń 1987). But probably continuous presence of trees even in the coldest periods of the Vistulian is new in comparison with previous data (Starkel 1980). The problem of the Vistulian history of vegetation requires further studies because of exceptional situation of the site in the vicinity of the Carpathian refuges. The planned pollen analysis of the Dybawka loess profile is expected to put a light on this problem.

Pikulice-Nehrybka

The Pikulice-Nehrybka profile is situated in the Wiar River valley (Fig. 1), 4 km to the south of the San River valley and the Przemyśl town. The section occurs in an old brickyard cutting a loess slope exposed southward, at an altitude of 225 m a.s.l. (49°45’10’’N, 22°49’00’’E). The loess sediments are 8.4 m thick, but only the upper part, to the depth of 4.6 m, contains carbonates (Fig. 3).

Malicki (1961, 1972a) was the first who described the profile, and then Laskowska-Wysoczańska (1971) included it into her study of the Carpathian Foreland loess. Maruszczak (1991a) placed the profile in the list of main loess sections in Poland. For sampling an old outcrop was used, newly cleaned.

0.00 – 1.30	Holocene brown soil (after Maruszczak), chernozem (after Malicki).
1.30 – 2.40	Typical pale loess, slightly laminated.
2.40 – 2.60	Weakly developed gley soil.
2.60 – 3.50	Pale loess, slightly laminated.
3.50 – 4.50	Laminated clayey silt.
4.50 – 5.20	Interstadial gley soil.
5.20 – 5.70	Stratified clayey silt.

Carbonate loess, which occurs between the Holocene soil and interstadial soil found at the depth of about 5 m, can be correlated with Inter-Pleniglacial (OIS 3). After Alexandrowicz *et al.* (1989) it is the so-called middle younger loess, and its age in this profile falls into the period between 34±5 and 72±11 ka BP.

The malacofauna of this profile was studied by Alexandrowicz (Alexandrowicz *et al.* 1989). Poor assemblage of *Succinea oblonga elongata* accompanied by *Pupilla loessica* was found at the depth of 2.3–2.5 m. This poor fauna suggests rather unfavorable conditions for molluscs and “indicates an open, quite humid habitat and cold, subpolar climate”.

PROBLEMS OF THE LOESS CHRONOLOGY AND THE ORIGIN OF CARBONATES

The examined profiles differ in lithology, number and type of palaeosols, and the occurrence of frost deformation structures. In stratigraphic interpretation, the original studies concerning individual sites were used, especially those published by M. Łanczont (1995). They are based on the results of examination of many profiles from this region, on observation of loess and soil sequences, on dating by TL, OSL, and ^{14}C methods, and on the results of different basic and specialized analyses. In the paper, in order to standardize and simplify the results of analysis of stable isotope composition of carbonates in loess, stratigraphic interpretation of the profiles was related to the oxygen isotopic stages – OIS, and based on a general insight into the sequence of climatic changes. However, the stage limits are outlined arbitrarily, mostly due to the fact that in the analysed profiles, well-developed soils, especially interglacial ones, transformed underlying loess. Some illuvial horizons, formed in warm periods, reach to a depth of about 2 metres from the contemporary ground surface. On the other hand, the pedogenesis, especially the development of interstadial soils, did not completely stop loess accumulation or local redeposition of sediments. The results of pollen analysis of intraloess palaeosols evidence silt accumulation during soil development, as plant succession is distinctly visible in the composition of spectra. Of course, accumulation was not continuous.

The second important problem in the interpretation of the results of isotope analysis is estimation of time when different carbonate forms were formed in comparison with time of silt accumulation. And so, snail shells occur on old ground surfaces, they were not much redeposited during aeolian sedimentation. Ostracod valves found in muds of small water bodies, without traces of water flow, can be also considered as occurring *in situ*.

Rhizoliths and rhizocretions formed around roots, mostly of grasses and herbaceous plants, which grew on ground surface not only when soils developed but also during loess accumulation. Therefore, they occur at a depth of sev-

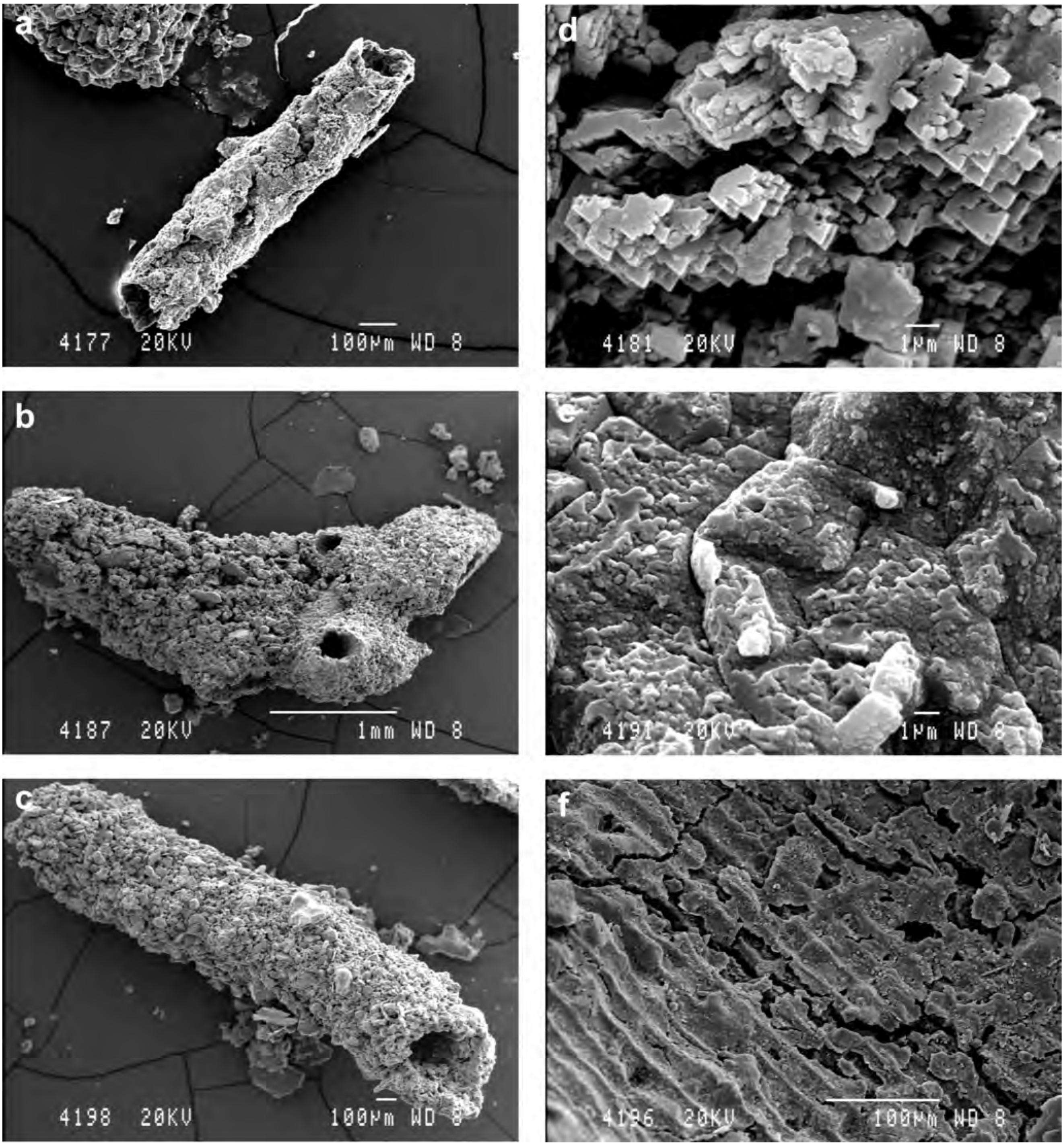

Fig. 4. SEM microphotographs. **a–c** – rhizolith forms; **d** – general view of platy calcite crystals with signs of etching on surfaces; **e** – uneven external faces of blocky calcite crystals; **f** – the internal surface of rhizocretion tube with well preserved root structure.

eral to several dozen centimetres from contemporary land surface. Thus, we can consider them to be practically of the same age as loess deposits, except when longer sedimentation gaps occurred, which are visible mainly as discontinuity surfaces. On the contrary, carbonate concretions (loess dolls) are always secondary in comparison with the time of deposit accumulation, and are mostly connected with pedogenesis. Carbonates precipitated as concretions usually at a depth of several dozen centimetres to several metres from the ground surface, which depends on local water conditions.

MATERIAL AND METHODS

The loess-palaeosol sequences under study contain common authigenic carbonates. The samples of carbonates were collected at 50 cm intervals in the Dybawka section and at 30 to 10 cm intervals in loess sequences with more differentiated lithology (Pikulice, Zarzecze, Tarnawce and Radymno sections). The carbonate fraction was separated under a binocular microscope from residuum (> 0.09 mm fraction) after wet sieving of the bulk samples. The microfabric analysis of the selected samples was performed on fractured surfaces coated with platinum, using a JEOL JSM-840A scanning electron microscope (SEM) equipped with a THERMO NORAN VANTAGE EDS system.

Carbonate cemented bodies dispersed throughout the loess take a form of nodule, rhizolith and rhizocretion. The rhizoliths are bio-sedimentary structures that have been formed around roots, frequently living ones. They occur as thin and dense tubes of carbonate cemented sediments (similar to that described by Klappa 1980, Jones & Ng 1988, Alonso-Zarza 1999) up to 2 mm wide and 15 mm long, usually without any infilling (Fig. 4). The internal surface of rhizoliths is exceptionally lined by micrite. Rhizocretions are slightly larger and irregular in shape concretions that originated due to the carbonate cementation of loess close to rhizoliths. In addition to rhizoliths and rhizocretions, the upper horizons of Radymno sequence contain composite nodules of about 2–5 cm in diameters (Fig. 5), which have been developed as a result of coalescence of several smaller ones (up to 0.5 cm in diameter).

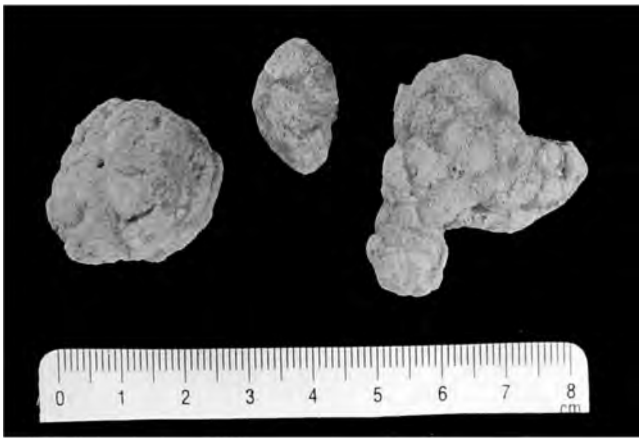

Fig. 5. Photograph of the composite nodules from Radymno section.

Ostracod valves, snail shells, and sparse other molluscs shells are common components of bioclasts. Because of the scarcity of shells and difficulties in identification of taxonomic species from shell detritus, the isotopic composition of these biogenic carbonates was determined for all snail shells or ostracod valves found in one sample.

Broken snail shells were found within some horizons of the Vistulian (Radymno, Pikulice and Tarnawce) sequence. Moreover, within and below the interstadial soil horizon of Radymno sequence there are numerous ostracod valves as well (Fig. 6). The relatively good preservation of poorly calcified ostracod valves (very thin valves with unchanged pore structure and without infilling of the shell) indicates that they appear to retain primary isotopic signals.

The deposits from Pikulice succession corresponding to OIS 3 contain very many small, purely calcitic globules, from

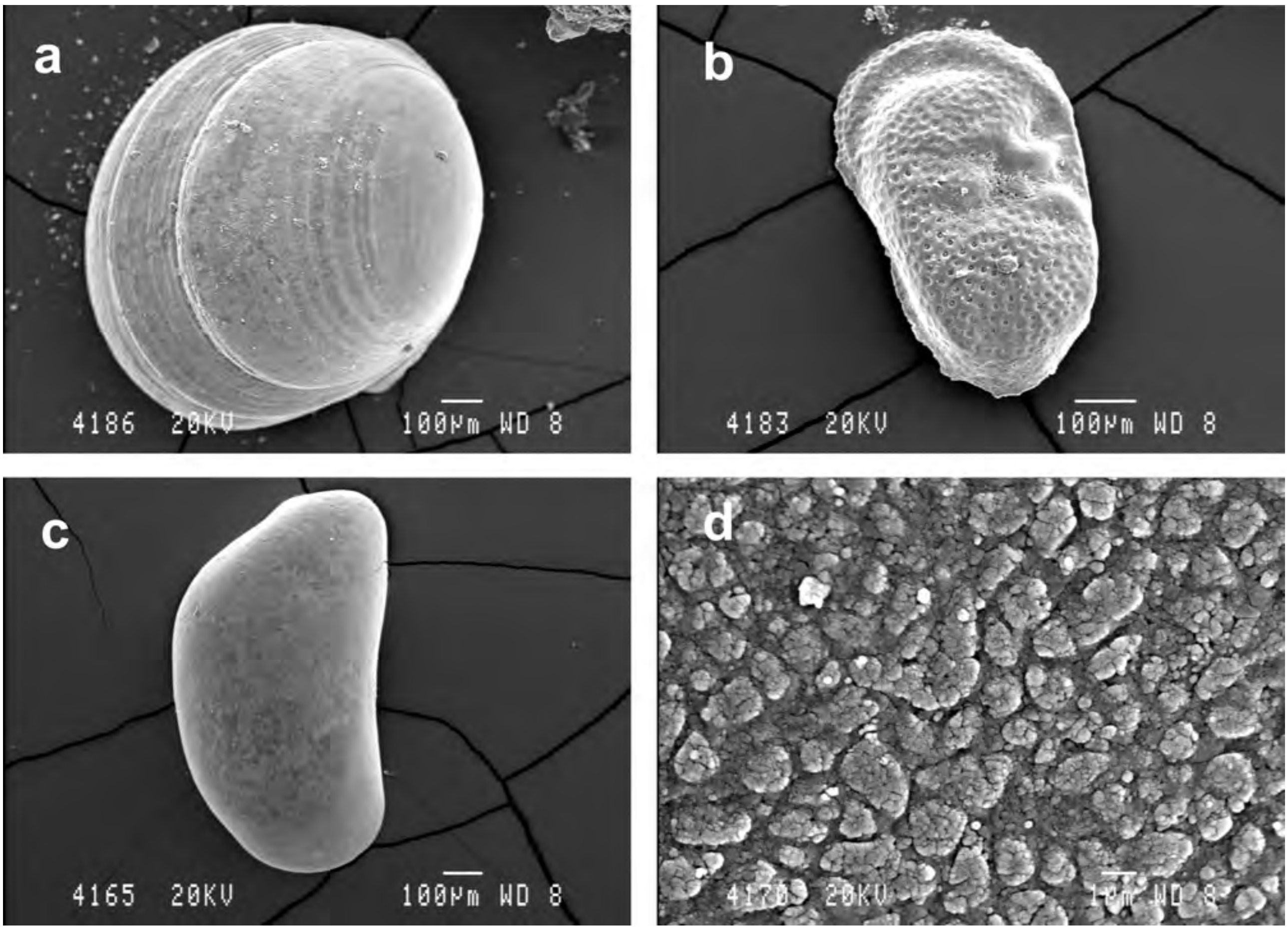

Fig. 6. SEM microphotographs. **a** – small pelecypod shell; **b**, **c** – ostracod valves; **d** – structure of the ostracod valve.

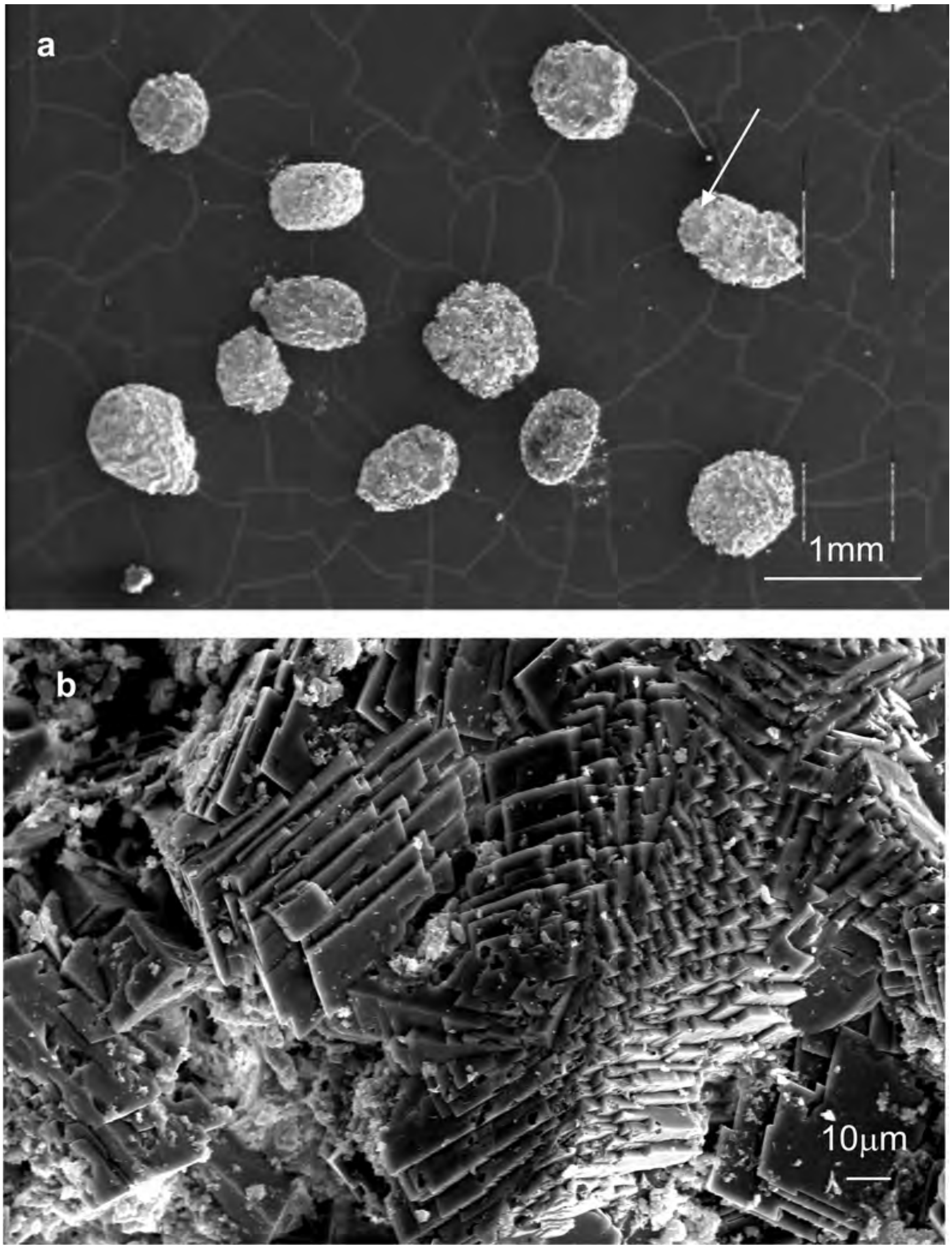

Fig. 7. SEM microphotographs. **a** – calcite globules; **b** – magnification of platy calcite crystals aggregates from the globule shown in microphotograph a (arrow).

0.5 to 0.7 mm in diameter, which consist of aggregates of small platy crystals, composed of numerous paper-thin subcrystals (Fig. 7). Unfortunately, the origin of such globules is unknown. In the analysed sequences they were only found in sediments with the land snail shells, but not in the sediments containing land snail shells and ostracod valves together. There is no evidence that such calcite morphologies have originated due to inorganic precipitation within loess or soil. Taking into account the association of calcitic globules with land snail shells we suggest that calcitic globules may be considered as the internal shell of the naked snails (*Arionidae?*).

The detrital grains in rhizoliths and rhizocretions are cemented by two, differing in morphology, types of calcite crystals (Figs 4 and 8). The most common cement displays clusters of loosely packed calcite crystals. At high magnification they appear to consist of rhombic platelets with distinct evidence of etching (Fig. 4d). Besides, the similar calcite cements are developed within the outermost zone of rhizocretion (Fig. 8a, b) within pores between detrital grains surrounded by a numerous root hairs. The second type of calcite cement that was found in rhizocretions forms the patches of tightly packed blocky crystals (Fig. 4e). The surfaces of the constituent crystals are irregular with ridges and groves,

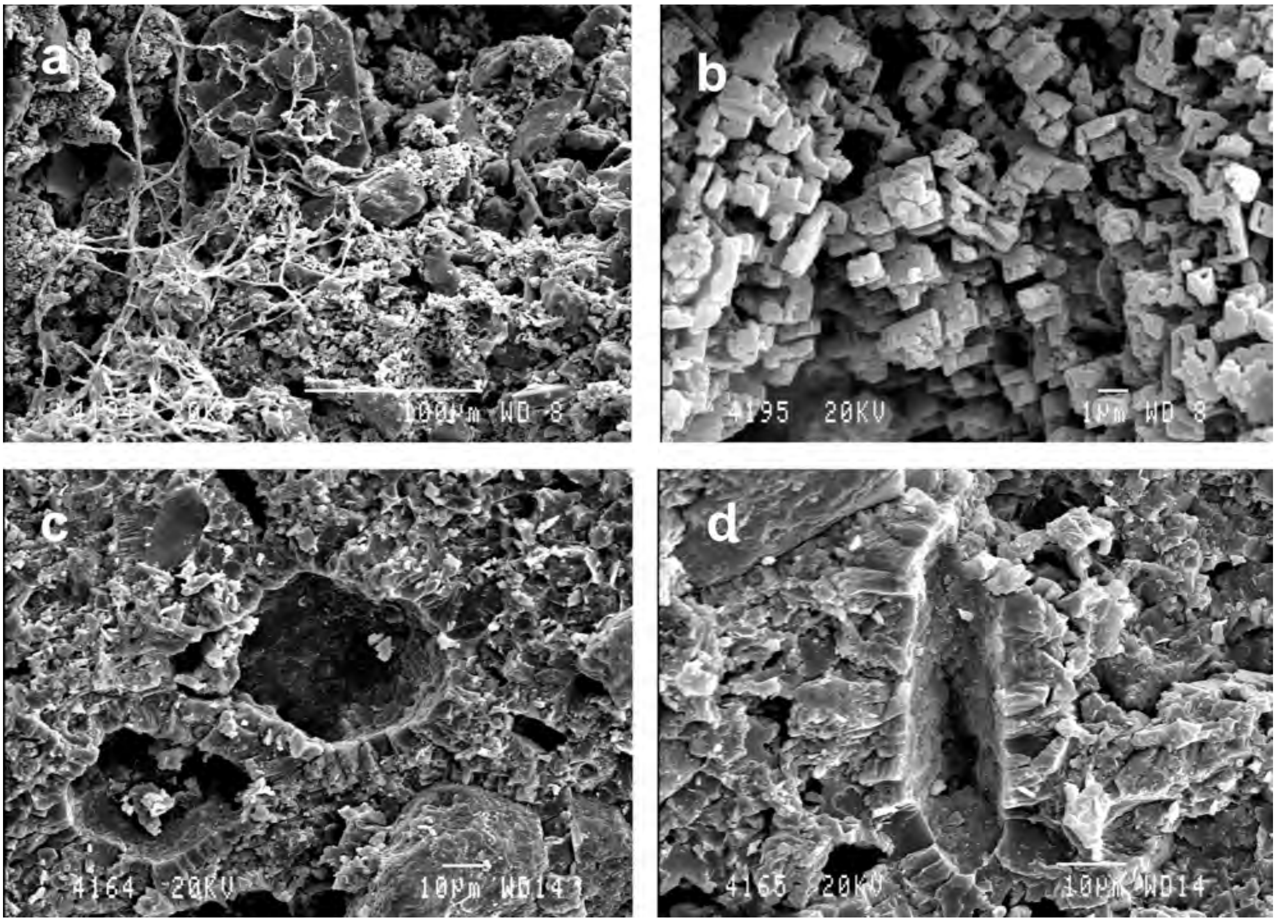

Fig. 8. SEM microphotographs. **a** – morphology of calcite cement in rhizocretions; **b** – magnification of rhombic platelets of calcite crystals formed between root hairs seen on the microphotograph a; **c**, **d** – the rim of calcite crystals oriented perpendicularly to the surface of coarse detrital grain in the composite nodule.

which usually have rounded outlines. However, the edges of surface unevenness are parallel to the faces of host crystal. Loess nodules are poorly cemented. In most cases, calcite crystals are oriented perpendicularly to the substrate such as a surface of coarse detrital grain (Fig. 8c, d).

The morphology of pedogenic carbonates is considered to be a valuable indicator of properties of soil environment (Becze-Deák *et al.* 1997, Kovada *et al.* 2003), which permit reconstruction of global and local climatic changes based on carbonate isotopic composition. The most important petrological criterion that is used for this purpose is related to the occurrence of inorganically precipitated calcite in the micrite to microspar grain size or rhombic calcite crystals, both without diagenetic alteration e.g. recrystallization (Dworkin *et al.* 2005). Micromorphological analysis of pedogenic carbonates under study showed that calcite cements of rhizoliths have resulted from the direct precipitation from the soil solution near the soil surface. Therefore, the isotopic composition of calcite cements from rhizoliths and rhizocretions may be used to determine some climatic features during loess deposition and soil formation.

Prior to the isotopic analysis, all separated samples containing carbonate were dried at 105°C and ground to <70 mm fraction using an agate mortar and pestle. CO_2 for the isotopic analysis was extracted from samples by reaction with anhydrous phosphoric acid (d = 1.90 g cm^{-3}) for 20 hours at 25°C under vacuum. The resulting CO_2 was analysed on a Finnigan Mat Delta^{plus} spectrometer working in dual inlet mode with universal triple collector at Stable Isotope Laboratory of Institute of Geological Sciences and Institute of Paleobiology in Warsaw. The δ values were calculated relative to isotopic ratios of the international standard sample NBS 19. The results are expressed as $\delta^{13}C$ and $\delta^{18}O$ notations with respect to VPDB (Vienna Peedee Belemnite). The reproducibility of results based on analyses of our internal working standard (N = 44) was better than ± 0.05‰ and ± 0.1‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively.

RESULTS

48 samples of rhizolith and rhizocretion from all studied sequences, and also 4 of composite nodules from the Radymno sequence were analysed. Moreover, isotopic composition of 9 broken snail shells, 3 ostracod valves and 3 calcitic globules samples from Pikulice and Radymno successions were determined (Tab. 1). When available, carbonate lithoclasts as well as authigenic concretion enriched with Fe and Mn oxides were analysed for reference (12 samples from Dybawka and Radymno sections).

Rhizoliths are unequally scattered throughout the Vistulian deposits. They are numerous within loess horizons just below the Holocene soil, but they become sparse in soil horizons and in loess showing the evidence of the gley formation. The $\delta^{13}C$ values for calcite cement of rhizoliths in loess fall in a range between –10.6 and –8.5‰ (Figs 2, 3). Nevertheless, in the Zarzecze and Radymno sections the values are rather constant, fluctuating close to –10‰. The $\delta^{13}C$ values for rhizoliths from the interstadial soils as well as from lower loess horizons overlaying them (Dybawka, Tarnawce, Radymno) shift to less negative values, falling between –9 to –8‰. Composite nodules along the Vistulian sequence (OIS 2) of Radymno have nearly constant $\delta^{13}C$ values that fall in a narrow range between –10.6 and –10.4‰ (Fig. 2). Unlike the data from previously described sequences, the variation of $\delta^{13}C$ values for Pikulice rhizolith and rhizocretion samples span from –8.4 to –4.7‰ (Fig. 3). However, these sediments deposited in OIS 3 contain numerous snail shells and calcitic globules, but rhizoliths are rare and poorly developed.

Three of nine analysed snail shell samples were separated from loess horizons above the interstadial soil of Pikulice, one sample from Tarnawce section, and five others represent loess horizons with cryogenic structures below the interstadial soil of Radymno. Shell carbonates are ^{13}C enriched by about 2‰ with respect to calcite cement in rhizoliths and rhizocretions (Figs 2, 3). The $\delta^{13}C$ values for snail shells from Pikulice section decrease upward the profile from –4.7 to –5.9‰, whereas in Radymno section these values stepwise increase within deposits formed during OIS 5 (from –7.3 to –6‰) and then, within the sediments of the OIS 3, they are nearly constant (–5.3‰). In sediments of OIS 3, $\delta^{13}C$ values of ostracod valves range from –3 to –5.8‰.

The $\delta^{13}C$ values for calcitic globules from Pikulice fall between –11.6 and –10.8‰, so they show distinct shift towards more negative values compared with the values for other bioclasts as well as for all types of pedogenic carbonates (Fig. 3).

Carbonate lithoclasts and rock fragments coated by iron and/or manganese oxides were found in loess horizon just above the interstadial soil of Dybawka sequence and also within loess with cryogenic structures underlying interstadial soil horizon in Radymno profile (Fig. 2). The carbon isotope values for lithoclasts display considerably broader range than the $\delta^{13}C$ values for other studied calcite forms. The lithoclastic $\delta^{13}C$ values ranges from –8 to 1‰ in Radymno, and from –8 to 2‰ in Dybawka, but more frequently they are enclosed in a range –4 and –1‰ for both sequences.

The $\delta^{18}O$ record of calcite cements in rhizoliths from all investigated loess-palaeosol sequences displays slightly narrower ranges than $\delta^{13}C$ values (Figs 2 and 3). The $\delta^{18}O$ values for rhizoliths from Dybawka and Tarnawce loess sections exhibit negligible inter-sample variability and the values fluctuate in the range from –6.9 to –7.4‰. The variability range of the $\delta^{18}O$ values for rhizoliths from Radymno loess section is slightly wider and it is shifted towards less negative values (from –6.9 to –6‰). The $\delta^{18}O$ record along the Zarzecze section shows clearly marked two parts, which differ in the trend of the $\delta^{18}O$ values variability. The $\delta^{18}O$ values for rhizoliths from the interstadial soil and loess with the evidence of gley processes (OIS 3 + 4) steadily decrease up the profile from –5.5 to –6.4‰. This is followed by an increase in the $\delta^{18}O$ values of almost 1.3‰ (from –7.3 to –6‰) upward the loess horizon (OIS 2). Likewise the distribution of $\delta^{13}C$ values, the $\delta^{18}O$ values for rhizoliths and rhizocretions from Pikulice section do not exhibit any distinct trend. The data are scattered between –5.7 and –7.6‰.

Composite nodules from Radymno section (Fig. 2) have nearly constant $\delta^{18}O$ values that fall in a very narrow range between –6.4 and –6.1‰, with the one exception of the nodule from the Holocene soil for which the $\delta^{18}O$ value decreases to –6.9‰.

Land snail shell carbonates are ^{18}O enriched up to 5‰ with respect to calcite cement in rhizoliths and rhizocretions. $\delta^{18}O$ values for snail shells from Pikulice (Fig. 3) section are nearly constant and the values range from –2.7 to –2.5‰, whereas in Radymno section (Fig. 2) these values for OIS 3 and OIS 5, display greater variability –1.3 to –3.7‰. Likewise the trend of lighter carbon isotope depletion upward the Radymno profile, the $\delta^{18}O$ values for ostracod valves slightly decrease in OIS 3, from –3.1 to –3.2‰. The only one recorded shift of $\delta^{18}O$ values towards the significantly less negative values for both land snail and ostracod bioclasts is recorded in deposits of OIS 5.

The $\delta^{18}O$ values for calcitic globules from Pikulice fall between –5.6 and –6.2‰ so they show a shift towards slightly less negative values compared with the values for calcite cements. Moreover, these values display distinct depletion of heavier oxygen isotope (^{18}O) in comparison with that for land snail and ostracod shells.

The oxygen isotope values for carbonate lithoclasts from the Radymno section display considerably narrower range than the $\delta^{13}C$ values. The $\delta^{18}O$ values range from –5 to –4.1‰, whereas in the lower part of the Dybawka profile the range of $\delta^{18}O$ is somewhat broader (from –5.8 to –3.5‰).

The data for calcite from rhizoliths and rhizocretions are plotted on a graph of $\delta^{13}C$ against $\delta^{18}O$ in Fig 9. There is no apparent correlation between the results. However, the values for Radymno, Tarnawce and Zarzecze are grouped within narrow range of $\delta^{13}C$ values (from –9.8 to –10.3, –9.5 to –10.5, and from –9,7 to –10.3‰, respectively), though within broader range of $\delta^{18}O$ values (from –5.7 to –6.9, from –6.9 to 7.3, and from –5.5 to –7.3‰, respectively). Opposite to this trend, the values for Dybawka profile are grouped within broad range of $\delta^{13}C$ values (from –8.4 to –10.4‰), and in narrow range of $\delta^{18}O$ value (from –6.9 to –7.7‰).

DISCUSSION

Carbonate cemented bodies in the analysed loess-palaeosol sequences have most frequently the form of rhizoliths. The chemical, physical and biological properties of soil close to the roots (rhizosphere) are considerably different from those within the bulk soil. Processes occurring at the root/soil interface create environment favourable for the bacterial and fungal colonisation and the root induced variation of chemical properties such as pH, redox potential and ionic concentration (Lynch 1990, Hinsinger 1998, Gregory & Hinsinger 1999). The pH changes (up to 2 pH at different points along the root of an individual plant) are mainly a consequence of the form of nitrogen uptake by root. Uptake of nitrate results in production of HCO_3^- and pH increase and, on the contrary, the ammonium uptake by root results in H^+ production and pH decrease. These processes of acidifica-

Table 1

Isotopic composition of authigenic carbonate from calcite cements, and calcitic land snails, ostracod valves and globules. The δ values are expressed with respect to VPDB

Depth m	Rhizoliths		Nodules		Land snail shells		Ostracod valves		Calcitic globules		Limestone fragments with Mn oxides		Limestone fragments		Nodules containing Fe oxides	
	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
	‰		‰		‰		‰		‰		‰		‰		‰	
Dybawka																
2.3	-10.18	-7.66														
2.8	-9.72	-7.39														
3.3	-9.65	-7.37														
3.8	-9.63	-7.21														
4.3	-9.13	-7.19														
4.8	-10.04	-6.93														
5.3	-9.47	-7.46														
5.8	-9.39	-7.05														
6.3	-8.88	-7.43														
6.8	-8.96	-7.14														
6.8	-9.69	-7.41														
7.3	-9.43	-7.14														
7.8	-9.43	-7.27														
8.3	-8.63	-7.24														
8.8	-9.53	-7.46														
9.3	-8.95	-7.03														
9.8											-1.15	-5.15				
10.3															-0.9	-5.38
10.8	-3.98	-5.79														
11.3	-3.41	-5.82														
16													1.55	-3.54	-9.12	-7.47
Pikulice																
1					-5.89	-2.68									-4.22	-4.89
1.4									-10.84	-6.15						
1.9	-8.39	-7.63														
2.4					-4.97	-2.53										
2.9	-4.73	-6.54														
3.4			-6.77	-5.72					-11.45	-5.60						
3.9					-4.74	-2.69										
4.2			-5.45	-7.17					-11.38	-5.60						
Radymno																
0.15	-9.76	-5.74	-10.58	-6.91												
0.5	-10.27	-6.90														
0.5	-10.57	-6.65														
1	-10.14	-6.61														
1.5	-10.28	-6.29	-10.51	-6.42												
2.15	-10.22	-6.73														
2.5	-10.30	-6.92	-10.51	-6.51												
3	-10.32	-5.95														
3.5	-10.40	-6.44														
5.8	-8.50	-6.14			-5.25	-3.70	-3.88	-3.24								
6.2							-3.03	-3.07			0.66	-3.37				
6.6											-0.92	-4.98	-3.43	-4.26		
6.9			-10.44	-6.59							-1.71	-4.12	-7.97	-5.07		

Table 1 continued

Isotopic composition of authigenic carbonate from calcite cements, and calcitic land snails, ostracod valves and globules. The δ values are expressed with respect to VPDB

Depth m	Rhizoliths		Nodules		Land snail shells		Ostracod valves		Calcitic globules		Limestone fragments with Mn oxides		Limestone fragments		Nodules containing Fe oxides	
	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
	‰		‰		‰		‰		‰		‰		‰		‰	
Radymno																
7.2					-5.31	-2.74										
8.5					-6.78	-3.10										
9					-6.99	-1.32	-5.81	-1.59								
9.5					-7.27	-3.09							-3.73	-4.73		
Tarnawce																
1.2	-10.17	-7.44														
1.6	-10.08	-7.30														
1.6	-10.54	-7.14														
2.2			-10.40	-7.27												
2.9			-10.03	-7.08	-7.22	-3.65										
3.05			-9.54	-6.89												
Zarzecze																
0.7	-10.25	-6.72														
1	-10.20	-6.04														
1.3	-9.94	-6.39														
1.5	-9.92	-6.61														
1.75	-10.04	-6.34														
1.9	-10.03	-6.74														
2.1	-9.93	-7.33														
2.5	-10.02	-6.70														
3.3	-9.71	-6.13														
3.5	-10.32	-6.04														
3.85	-9.85	-5.51														

tion and alkalisation are recorded up to a few centimetres from the root plane. Soil carbonate precipitation is the result of calcite supersaturation due to the changes in activities of the calcium and/or bicarbonate ions, and/or the partial pressure of CO_2 according to the equilibrium constant of the reaction: $Ca^{2+} + 2HCO_3^-{}_{(aq)} = CaCO_3 + CO_2 + H_2O$. The source of carbon in pedogenic calcite is CO_2 dissolved in soil solution. Calcite precipitated within soil in isotopic equilibrium with gaseous CO_2, because the soil system can not be regarded as close one mainly on the account of soil respiration which cause the continuous CO_2 flux (Cerling 1984). Isotope study of recent soil CO_2 revealed that $\delta^{13}C$ variation is for the most part controlled by biomineralization of organic matter (Cerling 1984, Quade *et al.* 1989, Cerling & Wang 1996, Nordt *et al.* 1996, Pustovoytov 2002, Alonso-Zarza 2003). Thus, it is controlled by the ratio of C_3 to C_4 plants in a local ecosystem (Cerling 1984, Cerling & Wang 1996, Fox & Koch 2004) since C_3 and C_4 plants fractionate carbon isotopes through different metabolic pathways. The C_3 photosynthetic pathway discriminates more strongly against ^{13}C than C_4 pathway resulting in origin of organic matter with lower $\delta^{13}C$ values (mean $\delta^{13}C$ values –27‰ and –13‰, respectively). Other significant environmental factors that affect carbon isotope values in soil system are (1) molecular diffusion of atmospheric CO_2 (mean $\delta^{13}C$ values –7‰) to deposits near their surface and (2) local climatic parameters, such as the ratio of evaporation to rainfalls, surface temperature, humidity and altitude, (3) biological activity. Long periods of dry weather, when evaporation exceeds precipitation, result in ^{13}C enrichment of CO_2 dissolved in soil water. On the other hand, when precipitation exceeds evaporation only negligible change of $\delta^{13}C$ values of soil CO_2 occur. The $\delta^{13}C$ values of carbonates that precipitate in soils are distinctly higher (nearly 15‰) than these of organic matter due to differences in diffusion coefficients for $^{12}CO_2$ and $^{13}CO_2$ (~ 4‰) and the fractionation factor of carbon between CO_2 and $CaCO_3$ (~ 10‰).

The isotopic composition of carbonate oxygen depends on a wide range of inter-linked environmental parameters, among which temperature and oxygen isotopic composition of soil water are the most significant (Cerling 1984, Cerling & Wang 1996, Liu *et al.* 1996, Nordt *et al.* 1996, Hsieh *et al.* 1998, Wang & Anderson 1998, Mack & Cole 2005, Stevenson *et al.* 2005). One of these parameters, isotopic composition of soil H_2O is largely controlled by the composition of meteoric water which, in turn depends on the oxygen

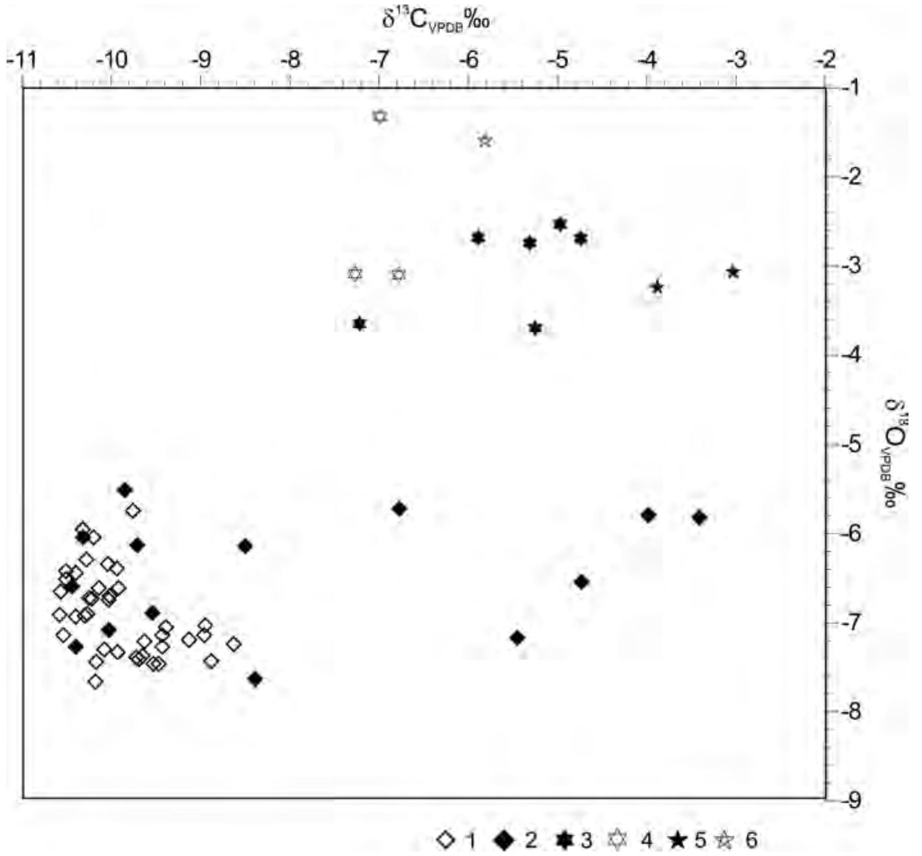

Fig. 9. Diagram of $\delta^{13}C$ versus $\delta^{18}O$ variability for rhizoliths, rhizocretions, nodules and bioclasts: ostracod valves and land snail shells. *1* – calcite cement in rhizoliths and rhizocretions from sediments corresponding to OIS 2; *2* – calcite cement in rhizoliths and rhizocretions from sediments corresponding to OIS 3; *3* – shells of land snail from sediments corresponding to OIS 3; *4* – shells of land snail from sediments corresponding to OIS 5; *5* – ostracod valves from sediments corresponding to OIS 3; *6* – ostracod valves from sediments corresponding to OIS 5.

isotopic composition of precipitation. In the middle latitude environments, the latter is closely tied to the mean annual temperature (Różański et al 1992, Różański 1993). Thus, $\delta^{18}O$ values of meteoric water reflect air temperature and also the amount, source, and seasonal distribution of rainfall. In general, $\delta^{18}O$ values for soil water and simultaneously $\delta^{18}O$ values for precipitated carbonates increase with increased temperature and decrease with higher rainfall. Intense evaporation near the soil surface during dry seasons would produce isotopic changes, which lead to enrichment of near-surface water in ^{18}O, as the evaporation preferentially removes the lighter isotope. In the absence of soil water evaporation, the $\delta^{18}O$ of soil water should be roughly equivalent to $\delta^{18}O$ values of meteoric water. It is assumed that at the depth greater than 30 cm, soil temperature approaches mean annual temperatures (Quade *et al.* 1989). Decrease of temperature with depth along soil profile causes the decrease in $\delta^{18}O$ values of soil water. However, the decrease in $\delta^{18}O$ values downward the soil profile may be also attributed to the preferential infiltration of isotopically lighter rainfall (Quade *et al.* 1989).

Most of the analysed carbonate cemented bodies occur within loess sequences that were deposited in the coldest stage of the Vistulian (OIS 2). The $\delta^{13}C$ values for authigenic carbonate cements (rhizoliths, rhizocretions and nodules) vary in a narrow range from –10.6 to –8.5‰. However, mean $\delta^{13}C$ values along three from five analysed sections are rather constant and they fall close to –10‰. The $\delta^{13}C$ values for carbonate-cemented rhizoliths from Dybawka section are more differentiated, up to 2‰. In this section, variations of $\delta^{13}C$ values are probably connected with preservation of micrite lining on the rhizolith internal surface. Micrite lining is usually related to biogenic precipitation of calcite arising from bacterial or fungal colonisation for which $\delta^{13}C$ values are distinctly lower (Boguckyj *et al.* 2006). Basing on the discussion concerning the factors having influence on the isotopic composition of pedogenic carbonates, the obtained data may suggest that rhizoliths, rhizocretions and small composite nodules were formed under roughly similar conditions, with considerable supply of CO_2 derived from mineralization of organic matter to soil water. The $\delta^{13}C$ values, approximately –10‰, may indicate the C_3 plants predominance in the vegetation (Nordt *et al.* 1996, Pustovoytov 2002, Fox & Koch 2004). Moreover, ^{13}C depletion points to insignificant influence of atmospheric CO_2 on isotopic composition of soil water, although carbonate cementation on nearby roots took place close to the surface of deposits. In the loess-palaeosol sequences corresponding to OIS 3, OIS 4, and OIS 5, there are clearly marked shifts of $\delta^{13}C$ towards less negative values. During warmer periods of Vistulian, OIS 3, OIS 5a and OIS 5c, the seasonal wetlands have arisen, followed by land snails colonisation and even ostracods in pools. Therefore, the isotopic composition of numerous carbonate lithoclasts and bioclasts occurring in these deposits may have an effect on the isotopic composition of rhizoliths from sediments corresponding to the OIS 3.

The $\delta^{18}O$ record of calcite cements in rhizoliths from all investigated loess-palaeosol sequences is generally less differentiated than that of $\delta^{13}C$ values. The mean $\delta^{18}O$ values along the Dybawka and Tarnawce loess sections from OIS 2, fluctuate close to –7‰. The $\delta^{18}O$ values for rhizoliths and composite nodules from the Radymno loess of OIS 2 change as well, however, they are more dispersed and slightly shifted towards less negative values (from –7 to –6‰). The distribution of $\delta^{18}O$ values for carbonate cements in sediments from Zarzecze section shows more complex pattern. The $\delta^{18}O$ values for deposits corresponding to OIS 3+4 and OIS 5a, stepwise decrease upwards by 1‰, and then they increase towards the Holocene soil horizon by 1.3‰ in deposits correlated with OIS 2.

The distribution pattern of $\delta^{18}O$ values for carbonate cements along the sequence of OIS 2 exhibits relatively little variability suggesting homogeneity in $\delta^{18}O$ values of soil water. The exception to this pattern is the Zarzecze section. The $\delta^{18}O$ pattern displays upward decrease of $\delta^{18}O$ values in rhizoliths of OIS 3+4 followed by their stepwise increase in OIS 2. Such variation of oxygen isotopic composition may reflect environmental changes caused by climatic conditions, mainly surface temperature. Taking into account the theoretical consideration based on empirical data, the shift of $\delta^{18}O$ values for carbonate cements indicate probably warmer temperature during calcite precipitation in the OIS 3+ 4 than in OIS 2. However, quantitative interpretation of the $\delta^{18}O$ record as temperature effect is difficult without additional data with respect to the environment of these sediments deposition.

For comparison, the isotopic analysis was also performed on bioclasts by reason of distinctly different isotopic composition of shells of the organisms living on the surface of deposit and pedogenic carbonates precipitated in sediments. However, isotopic signature of calcite from bioclasts has the advantage of climatic reconstruction only if it is determined for individuals of one species coming from the same, non-bioturbated horizon (Magaritz & Heller 1980). Isotopic composition of biogenic carbonates depends on the superficial conditions and also it is influenced by "vital effect" different for different species. The "vital effect" includes a variety of changes induced by organisms that make the isotopic composition of biogenic carbonate different from that inorganically precipitated (Chivas *et al.* 2002, Holmes *et al.* 1996).

The $\delta^{18}O$ values of land snail shell carbonates are very strongly correlated with the estimated $\delta^{18}O$ values of precipitation (Magaritz & Heller 1980, 1983, Goodfriend 1991, 1999, Leone *et al.* 2000). But frequently observed 5‰ enrichment of snail shell carbonate in ^{18}O relative to equilibrium with precipitation probably relates to input of metabolic CO_2 ("vital effect") and not to environmental effects (Goodfriend 1999). In the Radymno section, the $\delta^{18}O$ values for snail shells from OIS 3 are similar to those from OIS 5 with the exception of one sample in sediments corresponding to OIS 5, where $\delta^{18}O$ value increases by 1.5‰. Very narrow range of $\delta^{18}O$ fluctuation for OIS 5 and OIS 3 in Pikulice, and also for OIS 5 and 3 in the Radymno sections may indicate nearly the same isotopic composition of rainfall during these two stages. However, climatic changes of a lower order (a rise of temperature) during OIS 5 are also recorded. The $\delta^{13}C$ values of snail shells for OIS 3 from Radymno are nearly constant. The observed >1.5‰ shift of $\delta^{13}C$ to more negative values for snail shell (Fig. 9) in OIS 5 in comparison with OIS 3 from Radymno and OIS 3 from the Pikulice section may be account for climatic or seasonal difference in the microenvironmental conditions (Magaritz & Heller 1983).

Wetlands, the habitat frequently colonised by ostracods, are more likely to be affected by seasonal changes in both the temperature and chemical composition of meteoric waters. The isotopic composition of water from wetlands can vary considerably in response to changes in the composition of precipitation, drainage basin hydrology, the precipitation/evaporation ratio and residence time of water (Holmes *et al.* 1997, Holmes *et al.* 1996). Thus, $\delta^{13}C$ values of ostracod shells depend on the changes in the isotopic ratio of total dissolved inorganic carbon, which is, in turn, controlled by the rate of exchange of CO_2 with atmosphere, the rate of photosynthesis and bacterial decomposition of organic matter. The variations of $\delta^{18}O$ record for different ostracod species from the same place are attributed to their habitat or seasonal preferences and also to "vital effect". Experiments have led to conclusion that carbonate from ostracod shells precipitated in nearly isotopic equilibrium with the host water but its isotopic signatures provide only a local and temporal information about the environment (Chivas *et al.* 2002).

In the profiles under study, the $\delta^{13}C$ values of ostracod valves display the same pattern as that of snail shells but they are usually enriched in ^{13}C by > 1.2‰. Moreover, the $\delta^{18}O$ values fluctuate in similar range and, likewise for snail shells, there is clearly evidenced shift of ostracod $\delta^{18}O$ to distinctly less negative value in the one sample from the deposits of OIS 5 in the Radymno profile (Figs 2 and 9).

CONCLUSIONS

Isotopic analysis of authigenic carbonates from Vistulian loess-palaeosol sequences was carried out on the various carbonate-containing components: rhizoliths, rhizocretions, nodules as well as land snail and ostracod shells debris. The studied successions may be divided into two distinct sections basing on the type of the carbonate occurrence: (1) the upper Vistulian loess deposited in environment with poor vegetation, where authigenic carbonates are represented solely by cements in rhizoliths and rhizocretions and (2) the middle and lower Vistulian loess with well developed soil as well as gley horizons, where carbonate cemented bodies are rare and poorly developed but remains of land snails and ostracod valves are present. These two main forms of carbonates differ from each other markedly in isotopic composition. These differences seem to be more important than those between samples of one form of carbonates found in different sections.

Because of numerous factors affecting fractionation of carbon and, in particular, oxygen isotopes, stable isotopic composition of authigenic calcite is hard to apply as a paleoclimatic indicator. The interpretation of isotope data requires detailed knowledge of processes that control and modify $\delta^{18}O$ and $\delta^{13}C$ values in the environment. However, basing on this study we can conclude that some $\delta^{18}O$ and $\delta^{13}C$ variation in the analysed sequences resulted from paleoclimatic changes.

The enrichment with lighter carbon and, in particular, lighter oxygen isotopes of carbonate cements from loess of the Younger Plenivistulian, as well as the slight shift of $\delta^{18}O$ and $\delta^{13}C$ towards the less negative values nearby the top of OIS 3 deposits may evidence cooling down during OIS 2 in comparison with OIS 3.

Both, the land snail shells and ostracod valves from OIS 3 and OIS 5 are depleted of ^{16}O and ^{12}C. The isotopic composition of carbonate cements can not be directly compared with that of bioclasts because the isotopic composition of ostracod valves provides only information about the isotopic composition of local surface water, and the isotopic signature of snail shell depends on $\delta^{18}O$ values of precipitation and metabolic CO_2. The $\delta^{18}O$ values of both, land snails and ostracods, fluctuate around 1‰, close to –3‰ in deposits of OIS 3 and OIS 5. The only one shift of $\delta^{18}O$ values towards the significantly less negative values (Figs 2, 3), recorded in deposits of OIS 5, probably corresponds to the short-lasting environmental change (warming and/or more intense evaporation).

The $\delta^{13}C$ values for bioclasts vary in broad range and usually the snail shell carbonate is more enriched with heavier carbon isotope than this from ostracod valves resulting from the isotopic equilibrium with precipitation and surface waters, respectively. The shift of $\delta^{13}C$ towards more negative values for bioclasts from soil formed in OIS 5a may arise from the greater rate of photosynthesis and bacterial decomposition of organic matter. Therefore, this shift of $\delta^{13}C$ may be the evidence of the warmer and more humid climate during OIS 5 than in OIS 3.

The carbon isotopic composition of calcitic globules from the Pikulice deposits of OIS 3 distinctly departs from that for all other components of carbonate fraction. The lowest and nearly constant $\delta^{13}C$ values may arise from the greater contribution of metabolic CO_2 and also from the crystallization of calcite in quite different environment, probably inside a body of living snails.

Despite different origin of carbonates, the general trend of $\delta^{18}O$ variation in the analysed carbonate fractions from loess-palaeosol sequences displays some connections with climatic fluctuation. However, the number of carbonate samples in particular profiles is not sufficient for investigation of short lasting and minor climatic fluctuations.

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