ANALYSIS OF SECONDARY CARBONATES FROM THE YOUNG LOESS-PALEOSOL SEQUENCES OF THE CARPATHIAN BASIN – ESPECIALLY REGARDING THEIR PALEOENVIRONMENTAL ROLE

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1. **Introduction**

My dissertation set the following goals:

1) to introduce the different secondary carbonates in a detailed way and provide the clarification of their nomenclature – the update of the terminology was crucial, since the appellations and definitions of the certain types are commonly confusing;

2) to collect secondary carbonate and bulk samples in high vertical resolution and analyse their stable carbon and oxygen isotope composition;

3) to draw conclusions from the stable isotope values and use them for paleoenvironmental reconstruction.

2. **Sampling sites**

Sampling sites were chosen along a North-(North-Eastern) – South-(South-Western) transect, and contained the loess-paleosol sequences of Verőce, Paks and Villánykövesd. The main aim was to examine the stable carbon and oxygen isotope composition of the studied sequences and discover the stable isotope patterns among the different sedimentary units.

3. **Methods of sampling and analysis**

Secondary carbonate samples were collected in 10 cm vertical resolution in bulk form. Wet sieving method was carried out on these samples by using a 500 µm sieve. Remaining material was dried for an hour between 80-100°C and secondary carbonate types were selected under a binocular microscope. Bulk samples were taken in 2 cm vertical resolution. Stable isotope measurements were carried out by using a Thermo Finnigan Gasbench II for CO₂ processing and for the measurement a Thermo Finnigan Delta XP isotope ratio mass spectrometer was used in continuous flow mode. Sample preparation method was crushing the material with an agate pestle and mortar and react the remaining material with anhydrous phosphoric acid in Exetainer® vials after flushing headspace gas with helium. Aliquots of 1 mg were used from bulk samples, whereas different quantities were needed from secondary carbonates, as 250 µg from CRC and 400-450 µm from HC, HC+CC, CC, CC2 and EBS. Isotope values were given in per mil (‰) and expressed against V-PDB (Vienna Peedee Belemnite).

4. **Thesis**

**Thesis 1. Clarification of the nomenclature concerning the different secondary carbonate types.**

The appearance of secondary carbonates is commonly documented during the field investigations, but in many cases they are not correctly determined due to disorder in the nomenclature (BARTA, G. 2011). As guiding principle the paper of BECZE-DEÁK, J. et al.
(1997) was used in my dissertation, since the introduced terms and concepts in the mentioned paper are exact on the one hand, and on the other hand their paleoenvironmental role is also well expressed. In many cases different concepts are used for the same features, which make the literature of secondary carbonates ambiguous: some concepts are used as collective nouns, even though they determine exact subtypes with exact genetics. In my dissertation I used the nomenclature of Becze-Deák, J. et al. (1997) as a guideline to create a classification system which defines the different and in many cases wrongly determined concepts and orders them to the clearly determined ones. Since the analysis of secondary carbonates requires a consistent nomenclature to make possible the comparison of research works in the topic, therefore a clarified nomenclature was needed.

**Thesis 2.** The importance of different paleotopographic positions connected to local paleosol variations can be highlighted by the comparison of stable carbon and oxygen isotope compositions of hypocoatings (HC) at the Verőce site.

Paleosols may have locally different appearances due to their paleotopographic position. Such case was discovered for the Verőce sequence (Bradák, B. et al. 2014), where the paleosol variations developed in valley bottom, local top and paleoslope positions. These variations of the so-called P4 paleosol contained HC, which was characterized by different stable carbon and oxygen isotope values.

In my dissertation I determined the stable carbon and oxygen isotope composition of hypocoatings for each paleosol type at the Verőce site and determined the following patterns:

1) the valley bottom paleosol showed $\delta^{18}O$ and $\delta^{13}C$ values, which were shifted towards the more positive direction (indicating enrichment in $^{18}O$ and $^{13}C$);

2) the local top paleosol showed $\delta^{18}O$ and $\delta^{13}C$ values, which were shifted towards the more negative direction (indicating depletion in $^{18}O$ and $^{13}C$);

3) the paleosol situated in the paleoslope position showed both tendencies. These patterns were important, because they denoted different local characteristics of the vegetation densities and evaporative effects, which were characteristic of the paleotopographic position – but could only be extrapolated to the development of the whole sequence with caution.

**Thesis 3.** The appearance of soil-like hypocoatings (HC) strengthens the theory of pedosedimentary sequence evolution at the Verőce site.

HC are CaCO$_3$ impregnations around the pores of the soil/sediment matrix and around plant biogalleries, their formation is thought to be synsedimentary (Wieder, M. – Yaalon,
D.H. 1982; Bullock, P. et al. 1985; Becze-Deák, J. et al. 1997; Durand, N. et al. 2010). Their appearance reflects the colour and mineral composition of the soil/sediment matrix, therefore HC was divided into sediment-like and soil-like appearances (own observations in the common work of Bradák, B. et al. 2014). The latter one was observed at the Verőce site not just in paleosols, but in loesses as well and denoted the higher availability of organic matter in the surrounding matrix.

I recognized that the reworked layers of the Verőce sequence contained whole, non-detrital soil-like HC, and I defined ways of their formation:

1) formation after the translocation process ended (and thus impregnation of the reworked material); or
2) the translocation process was slow enough and the formation of HC was simultaneous with the process.

I discovered that the L5-C loess unit (under the paleosol of local top position at Verőce site) contained soil-like HC besides the sediment-like ones, and was guided by the presence of high amount of earthworm biospheroids (EBS) and calcified root cells (CRC), which together strengthened the theory of the pedosedimentary evolution towards the paleosol. High amounts of EBS and CRC denote the former stability of the surface, which is also connected by the decrease or pause of dust accumulation towards the interglacial phase and lead to the presence of enhanced organic matter accumulation – and thus indicated pedogenetic marks during sedimentation (Catt, J.A. 1990; Becze-Deák, J. et al. 1997).

Depletion in $^{13}$C in secondary carbonates causes that $\delta^{13}$C values shift towards the negative direction (e.g. Rao, Z. et al. 2006). I recognized that $\delta^{13}$C values of hypocoatings were shifted towards the more negative direction, which indicated that the vegetation cover became more dense towards the end of the sedimentation phase until the soil developmental phase begun.

Thesis 4. Paleoenvironmental comparison of different paleosols in the same sequence is possible by the help of bulk stable carbon and oxygen isotope compositions.

Stable carbon and oxygen isotope values of bulk samples were applicable to show different characteristics in value range and tendencies among the paleosol - as it was observed at the Villánykövesd Brickyard sequence. Three paleosols were recognized, as Unit 19, Unit 16 and Unit 11. The latter one is referred as the ‘Basaharc Double I’ paleosol of the Hungarian loess stratigraphy, based on unpublished AAR data of Oches, E.A. – McCoy, W.D. – Kaufman, D. Malacological investigations by Újvári, G. (2004) concerning the
‘Basaharc Double’ pedocomplex were available for the Villánykövesd site and I used it for comparison, which helped to refine the stable isotope data for Unit 11.

I determined the paleoenvironmental signals of the three paleosols of the Villánykövesd sequence based on the bulk δ13C and δ18O values in the following way: 1) development of Unit 19 and Unit 11 indicated moderate humidity and less enhanced/more opened vegetation cover compared to Unit 16; 2) the paleosol Unit 16 developed under more humid conditions and was characterized by higher vegetation densities.

**Thesis 5.** Comparison of the stable isotope signals of the ‘Basaharc Double 1’ paleosol is possible between the Paks and Villánykövesd site from the paleoenvironmental point of view.

As a connecting link, the ‘Basaharc Double 1’ (BD1) paleosol was recognized in the Paks and Villánykövesd sequences. I determined that ‘Basaharc Double 1’ paleosol at Paks was characterized by decreasing δ13C and δ18O values of bulk samples towards the more negative values upwards in the paleosol, whereas the same paleosol in the Villánykövesd sequence showed gradually increasing values towards the more positive direction.

In my dissertation I determined that the development of both paleosols were characterized by moderately humid conditions based on the δ18O values, but the tendency of the δ18O curves showed differences (possibly due to regionality). I discovered that the δ13C values indicated opened vegetation cover for both BD1 variations, but the difference in the tendencies suggested that BD1 variation at Villánykövesd tended to develop under even more opened vegetation coverage, whereas the BD1 variation at Paks showed the opposite and tended to develop under slightly more closed vegetation cover.

**Thesis 6.** Stable carbon and oxygen isotope values of bulk and HC samples show different patterns in over- and underlying transition zones of paleosols.

Transition zones were present in two different positions within the sequences: 1) above the paleosols (as sediment/soil transition), where the influence of sedimentation had an important role; and 2) below the paleosols (as soil/sediment transition), which were mainly caused by bioturbation effects.

I determined the following pattern of overlying transition zones of paleosols at the Verőce site: stable δ13C and δ18O values of HC showed increasing tendency upwards in the transition zone towards the more positive direction (towards enrichment in 13C and 18O). I interpreted the patterns in the following way: 1) tendencies of δ13C values suggested that during the transition from the paleosol towards the sediment, the characteristics of the vegetation cover changed and became less dense; 2) according to the tendencies of δ18O values, the moisture conditions showed transition from humidity towards moderate
humidity or aridity. These similarities suggested that the transition from the paleosol towards dust accretion happened gradually (e.g. BECZE-DEÁK, J. et al. 1997).

I recognized that the overlying transition zone of the ‘Basaharc Double 1’ paleosol at the Paks site (Unit 8) showed similar tendencies of bulk and HC δ^{13}C and δ^{18}O values, which showed upwards increasing habit towards enrichment in ^{13}C and ^{18}O - with large fluctuations. Both tendencies of bulk and HC stable isotope values suggested a larger amplitude climatic shift during the transition.

I recognized that the underlying transition zone of P3-C (C-9) at the Verőce site showed different pattern, as both δ^{13}C and δ^{18}O values of HC shifted towards the more negative direction and showed similarities to the stable isotope composition of the paleosol. These tendencies of the synsedimentary HC feature were possibly the first signs of the climatic change towards the interglacial phase (e.g. RAO, Z. et al. 2006), since dust accretion rates were probably lowered, vegetation cover became more enhanced and more available organic matter were present in the strata as a forerunner of soil development (e.g. BECZE-DEÁK, J. et al. 1997).

The bulk samples of the Villánykövesd transition zones showed gradual, continuous tendencies towards the overlying paleosols and loesses – as I defined it in my dissertation. Transitions, which were overlavings of paleosols showed different patterns: Unit 14 (overlying of Unit 15-16 paleosol) referred to a transition towards moderately humid conditions and more opened vegetation cover, whereas Unit 10 (the overlying of Unit 11 paleosol, ‘Basaharc Double 1’) represented possibly a transition towards more humid conditions and more closed vegetation cover. It has to be considered, that bulk stable isotope compositions of those transitions, which are underlyings of paleosols (as Unit 20 and Unit 12) can be influenced by bioturbation effects and thus reflect partly connections to the stable isotope composition of the paleosols.

**Thesis 7.** Possible hiatuses in the loess-paleosol sequences are traceable on the basis of bulk stable carbon and oxygen isotope values.

Larger amplitude shifts of δ^{13}C and δ^{18}O bulk values were characteristic of Unit 1 at the Paks sequence. Based on the curves and fluctuations of δ^{13}C and δ^{18}O values, Unit 1 was ordered into certain cycles. The boundary of cycles indicated the large amplitude shifts, where the stable isotope values altered significantly on both sides of the boundary. No signs of erosion or missing horizons were recognizable on the field and this loess unit seemed to be macroscopically homogeneous and continuous, however, the larger shifts indicated possibly missing horizons. **The presented shifts were large, but gradual, which led me to the**
following theory: after a possible erosion event dust accumulation and the built-up of the sequence continued and was contributed by the continuous effects of bioturbation. Bioturbation mixed and homogenized the freshly accreted dust and freshly produced organic matter with the buried horizon and thus seemed to hide the signs of the former erosion. Hiatuses were recognized in Unit 1 by the luminescence dating results of Thiel, C. et al. (2014).

The tendencies of bulk $\delta^{13}C$ and $\delta^{18}O$ values showed differences in Unit 2 of the Villánykővesd sequence. Gradual, but large shifts towards the negative direction were characteristic of $\delta^{13}C$ values upwards from 1.80 m, whereas $\delta^{18}O$ values showed the opposite tendency (shift towards the more positive direction) upwards from 1.42 m. I explained this observation in the same way, as in the former paragraph for Paks: bioturbation mixed possibly the freshly accumulated material and produced organic matter with the buried horizon and thus hide the signs of former hiatus. Enhanced bioturbation was visible along whole Unit 2 on the field. The Villánykővesd sequence contains possibly more hiatuses, since not all paleosols were present in the site suggested in the Hungarian loess stratigraphy (based on own investigation and former studies as Újvári, G. 2004 and Hum, L. et al. 2006).

This observation could be helpful, since thin sections are not always available from the sections or maybe they are not taken from these horizons. 

**Thesis 8.** The applicability of HC+CC was proven for the Paks and Verőce sites, whereas it was denied for the Villánykővesd section due to regional differences.

HC+CC is a combined secondary carbonate type, which consists of the synsedimentary HC feature and contains a thin calcite tube (type of carbonate coating, CC) on its inner channel wall, which is of postsedimentary origin (Barta, G. 2011a; Barta, G. 2014).

The $\delta^{13}C$ and $\delta^{18}O$ values and tendencies of HC and HC+CC features were compared to each other and different observations were made. I made calculations for the Verőce site and determined the difference of $\delta^{13}C$ and $\delta^{18}O$ values for HC and HC+CC, which showed only slight differences, the values showed almost the same. I recognized that the tendency of HC+CC curves followed the same tendency as of HC along the Verőce sequence. Although the calculated differences for the Paks site were slightly larger, I recognized that the tendencies of HC+CC were similar to those of HC, also concerning the amplitude of fluctuations.

In the case of the Villánykővesd sequence the comparison of $\delta^{13}C$ curves of HC+CC and HC showed similarities, which is due to the general fact that HC components of both features were formed in the same soil/sediment matrix and reflected synsedimentary effects. I
determined that the comparison of $\delta^{18}$O curves at the Villánykövesd site showed two different characteristics: 1) tendencies were similar between HC and HC+CC, which indicated contemporaneous and/or repeated infiltration or leaching during the sedimentation phase; and 2) tendencies were different, which reflected the postsedimentary formation effect of the CC component. In the latter case the infiltration or leaching processes happened after the sedimentation phase and derived from meteoric water of other stable isotope composition.

I draw the following conclusions based on the observations: it is seems that the analysis of the relationship between HC and HC+CC is not functioning well in the Southern regions of Hungary, since this area was under the influence of submediterranean effects (as it was presented for Villánykövesd by Hum, L. 2001 and Hum, L. et al. 2006). This submediterranean effect had local influence on the composition of meteoric water and on the amount of infiltrating water – and thus effected isotopically the infiltrating solutions and the formation of the CC lining on the inner channel wall of HC. The stable carbon isotope composition of the HC component of HC+CC remained mainly unaltered, since it formed below the same surface and under the same circumstances as the synsedimentary HC.

**Thesis 9.** Stable carbon and oxygen isotope compositions of bulk and secondary carbonate samples are applicable for the description of relative environmental changes – but the results are complicated to compare with other sequences without other proxies or absolute dating results.

I highlighted the importance of different paleotopographic positions as an important influencing factor, as it was shown in the case of the three paleosol variations at the Verőce site. Each of the paleosol variations of P4 were located in another position, as local top, paleoslope and valley bottom situations. These variations were characterized by different stable isotope patterns and tendencies according to the composition of analysed secondary carbonate types.

I determined certain similarities and fluctuations of the $\delta^{13}$C and $\delta^{18}$O curves of bulk and secondary carbonate samples and ordered them into cycles. I recognized that for a deeper understanding on the habit of these cycles and their paleoenvironmental role other proxies would be useful – as the examination of magnetic susceptibility or further malacological studies.

The method in itself is not advised to use for the correlation of loess-paleosol sequences from different localities. **However, I concluded that it is seems to be applicable for the comparison of paleoenvironmental signals of such horizons, which were correlated**
formerly by using luminescence dating or AAR methods – or when specific marker horizons are present. It is always important to take paleotopographic positions into account during the application of the method.

I suggested two possibilities in order to improve the applicability of the stable isotope analysis method for bulk samples and secondary: during the interpretation of signals other proxies should be used as well, especially regarding the analysis of different amplitude fluctuations in the $\delta^{13}C$ and $\delta^{18}O$ curves; and several profiles should be excavated and analysed at the same location, which makes possible the recognition of paleotopography and help the understanding of different stable isotope patterns.

5. Summary

The stable carbon and oxygen isotope composition of bulk and secondary carbonate samples seemed to be applicable for the analysis of individual sequence development as a descriptive proxy. This proxy is different from other ones (e.g. from magnetic susceptibility), since the results reflect local paleoenvironmental changes and cannot be effectively expanded on a regional basis – at least in the case of the studied loess-paleosol sequences of the Carpathian Basin.

References


**Research papers of Gabriella Barta connected to the topic**


