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SHALLOW GROUND WATERS AND THE FORMATION OF CARBONATE SOILS IN SOUTHEAST BULGARIA – A STUDY IN PROGRESS

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Abstract: Carbonate soils and indurate calcrete horizons are common in southeast Bulgaria. The carbonate accumulations are of variety of micro-structural and textural types. The calcrete usually forms lens or disk-like bodies on flat hills. The carbonate soils are observed on top of porous sediments but not on crystalline rocks. In the study area, where calcrete is common, the pH value of the agricultural land is usually above 7.5 and the surface, shallow ground and deep ground water is saturated with respect to calcium carbonate. Chemical analyses of indurate calcrete horizons, carbonate soils, rain water and ground water from southeast Bulgaria are commented in the text. It appears that competing processes of leaching and re-precipitation from waters oversaturated with respect to $CaCO_3$ are responsible for formation of transitional compounds - calcrete precursors, which further are transformed to calcrete. Because, the rain water's acidity and ground water's degree of over-saturation with respect to $CaCO_3$ vary with the season, it appears that seasonal variations in the water composition and the temperature control the net balance of soil carbonates.

Keywords: calcrete, soil, water, calcite, Thrace plane

1. Introduction

Carbonate soil or indurate carbonate layer, rich in re-precipitated calcite, is widespread in the Thrace Plane. Layers of carbonate minerals are usually formed around geo-chemical barriers in regions with hot and dry climate, immediately under the organic soil or near the water table. The carbonate crusts grow displacing and replacing the organic soil layer. Because of its dependence on temperature, alkalinity and abundance of water, the carbonate layer, referred to as "calcrete" or "caliche" in the international literature, is an indicator for climate conditions. An increase in the rate of calclete growth is expected, due to the global tendency of temperature raise and aridization. Undersoil, soil and atmospheric precipitation are the main sources of calcium and carbon that form the calcite. Surface and ground water is the transporting agent that facilitates the mobilization and immobilization of calcium and carbonate ions.

The calcrete is formed by displacement or replacement of the other compounds of the soil in areas, where surface and ground waters are saturated with respect to calcite (e.g. Wright, 2007). Two distinct types of calcrete can be recognized. The first type called pedogenic calcrete is formed above the groundwater table immediately below the plant roots. The second type named groundwater calcrete is formed around the ground water table (Alonso-Zarza, 2003; Wright, 2007). In the Thrace plane both calcrete types are common, as the thickest accumulations are exposed in the quaternary and neogene sediments from the Tundja depression. The depression is formed by the valleys of river Tundja and several smaller rivers, such as Popovitca, Kalnitca and Iavuz dere (Fig. 1). This region occupies the eastern part of the upper Thrace plane. It is shallow continental basin filled with mollasic sediments. The main aquifer is located in the low terrace of river Tundja.

In order to effectively manage the agricultural lands affected by calcretization, it is necessary to study the process of calcrete formation. Interactions of different natural and anthropogenic factors leading to formation of the calcrete crust, its growth and negative impact on the soil diversity and fertility are the subject of a multidisciplinary project, lead by the University of Mining and Geology, Sofia. Early data from studies on the geomorphology, geochemistry, hydrochemistry, hydrology and physical chemistry of carbonate precipitates in the studied region are presented in the paper.

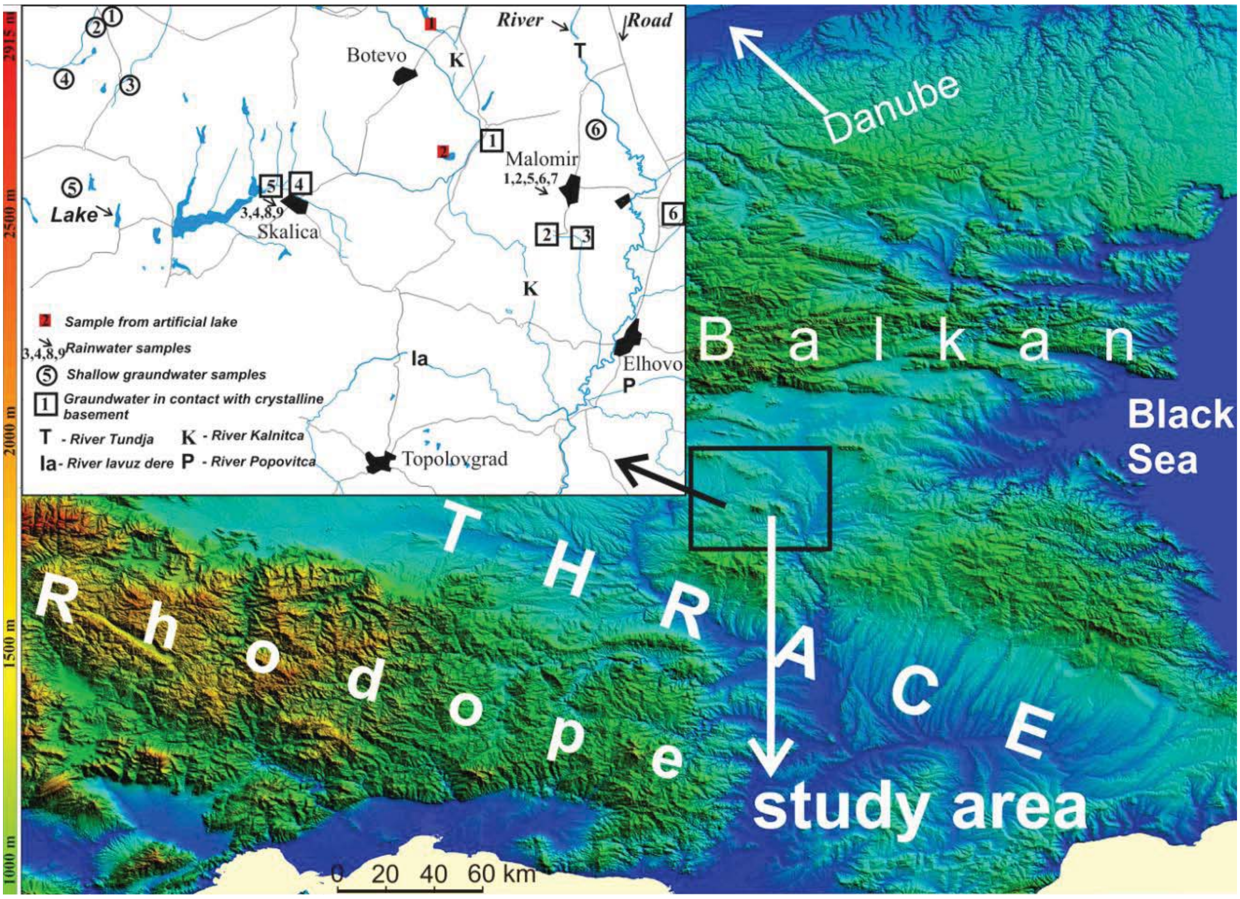

Fig. 1. Orientation map of the study area. Areas of sampling for the data presented in the tables are shown in the inset.

2. Geomorphologic setting

Preliminary mapping of an area of about 1900 km^2 (Fig. 1) have shown that the calcrete is widespread in Thrace. This region is an intramountain continental basin, which has subsided since the late Oligocene. The basement of the basin comprises a variety of low and high-grade Mesozoic, Paleozoic and possibly Precambrian metamorphic rocks, as well as Upper Cretaceous intrusions of intermediate composition, and the associated volcanic rocks. Volumetrically most significant are the Paleozoic granites, the Triassic dolomitic marbles and the Cretaceous rocks of dioritic composition. Since the marbles are magnesium rich, enrichment with this element can be expected in the ground waters. The infill of the basin comprises mostly sands and sandy clays, intercalated with conglomerates.

The thickness and density of the calcrete horizons are irregular. The shape of the carbonated bodies also varies significantly depending on the local geomorphology. In most cases the calcrete forms disk–like bodies located on slightly elevated topographic forms. In the water saturated lowland the carbonate layer is missing (Dimitrov et. al. 2009). Usually the calcrete exposures have areas of several hundred square meters. They are light grey or pinkish in colour. The light colours are due to earthy carbonate aggregates or nodules. In the sand quarries from the study area mature, thick to 3 m calcrete horizons can be observed. In some localities, where buried paleosoils are exposed, carbonate accumulations related to these soils are also common.

The age of the calcrete accumulation is not known yet. Dating based on geomorphologic and archaeological criteria is in progress. The isotope dating, which can be applied in this case is subject to criticism, because of the constant remobilization and re-precipitation of carbonate material in the calcrete crust (e.g. Budd et. al., 2002). One common observation in Thrace is that after its first occurrence, the calcrete crust persisted in time, until at least 20-30 m deep valleys in the Pliocene sediments were formed. Comparison of the average rates of erosion (e.g. Stock et. al., 2005) with the current topographic position of the calcrete might help in dating of some of the horizons.

It was found that the calcrete is developed above sandy strata with clay interbeds. It was never observed above crystalline rocks, even though Jurassic and Trissic marbles are common in this area. The last observation suggests that for calcrete deposition the porosity and permeability of the undersoil is more significant than the chemistry of the rock basement.

3. Fabric and texture of carbonate soils

The calcite is the dominant mineral in the calcrete. The crystals sizes correspond mainly to micrite, which occupies 20% to 60% of the thin sections. Usually the micrite is dark grey. It can be easily distinguished from the microsparite, which is light grey and occupies about 20% of the thin section's area. The sizes of the microsparite crystals vary between 0.004 and 0.02 mm. In the domains occupied by microsparite, dark grey or black spots of organic matter or Fe-hydroxides are common.

In the indurate calcrete usually 10-20% clastic matter is present. It is mainly quartz but in some cases feldspars are also common. More rarely biotite flakes, lithoclasts, epidote, amphibole and zircon grains can be observed. The detrital grain sizes are various. Mostly silt-sized grains are present (under 0.063 mm) but locally larger grains (0.063-0.125 and 0.125-0.25 mm) can be found. In the micritic domains the clastic grains usually have sparitic rims, while in the microsparitic domain such rims are not present, which most likely suggest that they were destroyed by re-crystallization. Frequently, the detrital grains are corroded or they are overgrown with secondary chalcedony. In the calcrete profiles the clastic component usually decreases upwards.

Risolites formed by fossilization of root plants are rare. Only isolated sections were observed cemented by microsparite. Cellular fabric of resolites is even rarer. The porosity of the indurate calcrete is in the range 10-15%. Usually the domains cemented by sparite are less porous. Selective leaching with organic dies shows, that the carbonate mineral is predominantly calcite. Chemical analyses of calcrete from different exposures show, that the MgO varies between 1% and 15%. Although dolomitic marbles are abundant in the study region direct relationships, between the Mg-rich basement and the magnesium content in the calcrete are not yet found.

Based on the micro-structural studies the evolution of the calcrete may be summarized as follows: Solutions rich in carbonate ions percolate through the pores of the shallow undersoil. First crystallizes micrite and around the clastic grains crystallizes sparitic cement. The sparite may form multiple coatings, because two or three rims are observed locally. Later the micrite recrystallized to microsparite. The intensity of re-crystallization increases from bottom to top of the calcrete layers, as it is most intense in the uppermost 20 - 40 cm of the calcrete layer. Corrosion of the detrital grains most likely accompanies the re-crystallization. It is likely, that as the processes of leaching and precipitation are competing, the calcrete layer is constantly rejuvenating.

Different textural types of calcrete can be observed in the study region (Fig. 2). Most common are the massive, vein – like and nodular varieties. In the black organic layer calcrete appears as ephemeral earthy masses, which are abundant in the late summer but decompose during the winter and spring rain periods. Unstable carbonate masses are usually found in soils developed above massive calcrete horizons.

4. Waters in the study region

Chemistry of precipitation, surface and ground water is one of the most important factors influencing the calcrete formation. That is why the general hydro-chemical background and changes in water chemistry, related to the specific geological conditions are to be studied. The integral hydrochemical parameters of waters, such as temperature, pH, ΔpH and specific conductivity - χ, were determined "in situ" with the aid of HI 99121 pH-meter, HI 993310 conductivity meter and HI 98204 combined tester. Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) was used to determine concentrations of Ca^{2+}, Mg^{2+}, $Na^{+}+K^{+}$, HCO_3^{-}, CO_3^{2-}, Cl^{-}, and SO_4^{2-}

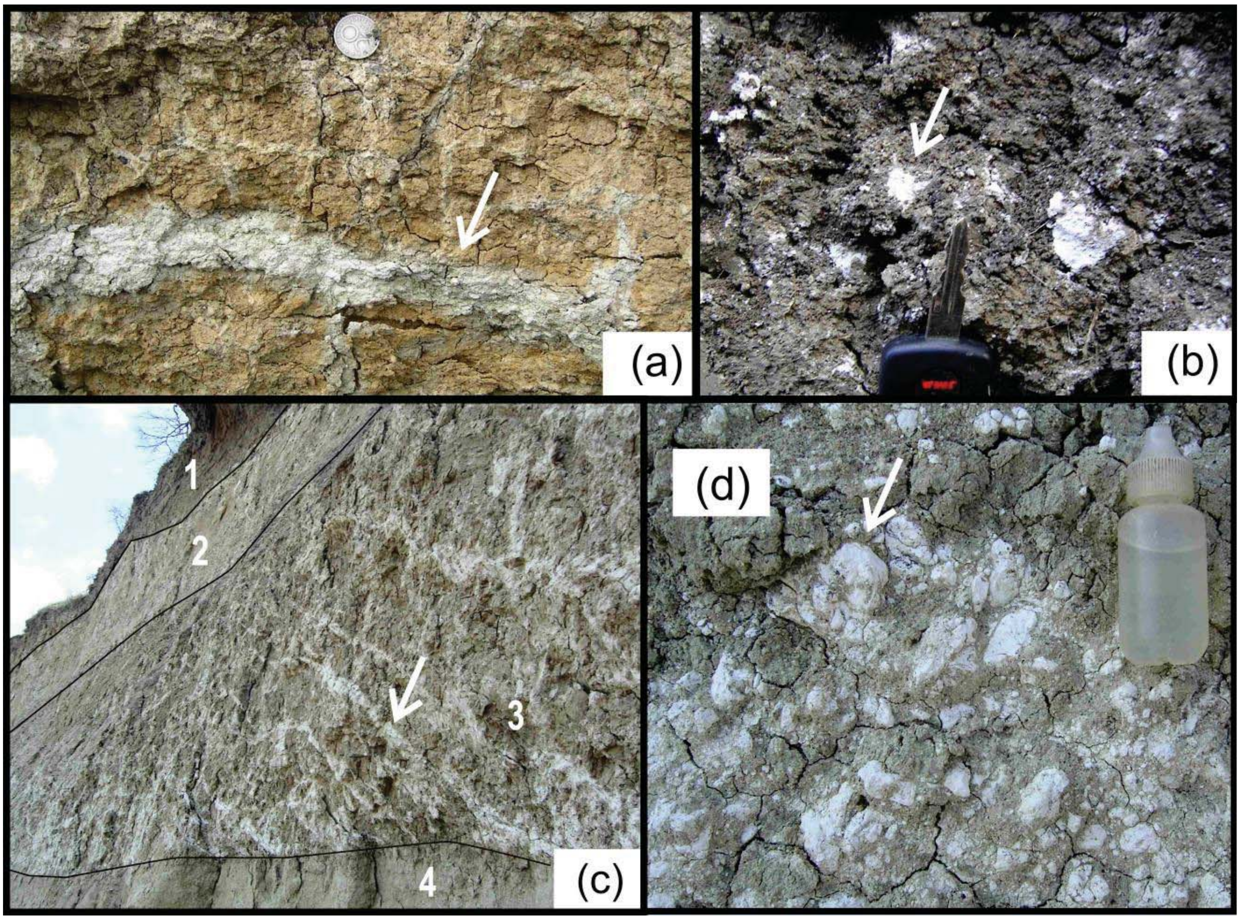

Fig. 2. Textural types of calcrete from Tundja depression. a) Carbonate veins in Pliocene clays. b) Earthy carbonate aggregates in black organic soil. c) Vein-like calcrete located under massive calcrete layer – 1. organic layer; 2. massive calcrete; 3. carbonate veins; 4. sandy clays of Pliocene age. d) Semi- compacted nodules in black organic soil.

in water samples’ from the studied region, as well as in soil leachates from carbonate soils.

4.1. Rain water

Well pronounced seasonal changes can be seen in the rain water pH values. PH values measured “in situ” in March and April in our study sites were in the range of pH=7.3-8.0.

Rain water pH values measured in our stations in the period May - September were in the range of pH = 5.8 - 7.20 (Tab. 1). It has been found, that during a single rainfall the acidity varies, as at the beginning of the rain the water is more acid (samples 6, 7 and 9), while at the end of heavy rains the water is neutral (samples 1 and 2). Only the most acidic rain water, which as a whole possesses higher mineralization (M), bears small amounts of sulphur and chlorine (samples 6 and 7). The data show, that the water is polluted to a certain level

Table 1. Rain water characteristics in the studied region

Study location Parameter	1	2	3	4	5	6	7	8	9
t,°C	17	16	16	14.5	18.5	17.0	18.0	16.5	15.5
pH $_{20oC}$	7.20	7.07	6.3	6.7	6.20	5.86	5.97	6.50	6.14
χ_{20oC} µS/cm	23	17	18	19	33	24	30	23	16
HCO_3^- mg/L	-	-	-	-	15.3	12.2	12.2	5.5	2.7
SO_4^{2-}mg/L	-	-	-	-	14	11	13	-	-
Cl^- mg/L	-	-	-	-	5.5	9.1	5.5	-	-
Ca^{2+} mg/L	-	-	-	-	8.2	8.2	6.0	3.7	2.0
Mg^{2+} mg/L	-	-	-	-	3.0	2.2	4.0	3.7	2.0
Na^++K^+ mg/L	-	-	-	-	<0.2	<0.2	<0.2	<0.2	<0.2

and can not be classifies as de-ionized water. Similar facts (measured averaged water conductivity in the range of 72 – 99 μS/cm) were found by one-year monitoring (2001 – 2002) of rain water in “Chirpan” synoptic station (Machkova et al. 2008) – located close to our study sites. The above mentioned fact justified calculation (based on thermodynamic equilibria) of the coefficient of water saturation with respect to calcite (K^K) and dolomite (K^D). Results showed that the rain water will easily dissolve these minerals at a contact with them.

4.2. Shallow ground water

Such waters (Tab. 2, samples 1-5) were collected from 1-3 m deep channels excavated during local gasification works. In all cases the waters appeared in local topographic depressions. A Piper diagram for these samples is presented in figure 3. On the Piper diagram the samples are clustered in two domains according to their geological origin. The domain containing samples 1, 2 and 5 represents shallow ground waters percolating through calcrete layers. Calcrete crust (with thickness of 0.5-1.0 m) was found in positive topographic forms in proximity to the sampling sites.

The domain containing samples 3 and 4 represents waters in contact with basement clays from the Pleocene. The sulphur enrichment might be due to accumulation of gypsum produced by the nearby power plants. Sample No 6 (Tab. 2) represents shallow ground water collected over thin horizon of pedogenic calcrete.

Experimentally found values of water saturation index with respect to calcite (ΔpH), as well as thermodynamically calculated values of the saturation coefficients with respect to calcite (K^C), point at waters over saturation with respect to this mineral. Most probably water composition is formed as result of leaching of soil and immediate undersoil layer by rain waters percolating though those layers. The very high concentrations of sulphate and calcium ions (samples 1, 2 and 5) are indicative for the increased salt content in the soil as a result of anthropogenic salinization. Alternatively, these high concentrations could be explained by rain water leaching, while it infiltrated the calcrete layer in the area. Three samples of solid calcrete material taken from the region were very rich in sulphur – total S content of 13.1%, 11.7% and 11.09%.

In our opinion, high pH values in sample 6, together with increased Al concentrations could be due to the following mechanism: relatively acid and aggressive with respect of $CaCO_3$ rain water dissolves carbonates from the soil and undersoil, thus increasing pH value of the infiltrated water. In sites with clayish undersoil layer aluminium is mobilized due to local alkalization, which causes re-structuring of the clay minerals. The high concentrations of mobilized calcium and carbonate lead to over saturation with respect to $CaCO_3$, which may result in a secondary precipitation of calcite–a process that is accelerated by the temperature increase.

4.3. Ground water in contact with the crystalline basement

The composition of the deep ground water in the

Table 2. Characteristics of shallow ground waters in the studied region

Sampling point; Parameter	1	2	3	4	5	6
t,^{o}C	23	21	22	23	19.5	28.2
pH $_{20oC}$	7.5	7.8	7.6	7.8	7.65	8.63
ΔpH $_{20oC}$	+0.28	+0.46	+0.19	+0.16	+0.31	+0.20
χ_{20oC} μS/cm	-	2648	1710	1545	4142	382
HCO_3^- mg/L	363	336	448	427	592	163
SO_4^{2-} mg/L	1440	1400	420	350	2400	25
Cl^- mg/L	35	74	29	24	33	<4
Ca^{2+} mg/L	527	559	220	191	598	74
Mg^{2+} mg/L	62	80	40	40	358	6
Na^++K^+ mg/L	102	44	49	37	21	14
CO_3^{2-} mg/L	-	-	-	-	-	18
K^C	3.26	6.29	2.81	5.29	5.43	55.38
K^G	0.07	0.74	0.02	0.012	K^D61.93	-

Saturation coefficients with respect to gypsum (K^G) and dolomite (K^D); Hydro-chemical type of waters (based on the major ions in amounts higher than 20 eq.%): 1 and 2 – Sulphate – hydro - carbonate – calcium - magnesium; 3 and 4 - Sulphate — calcium; 5 – Sulphate – calcium - magnesium; 6 Hydrocarbonate – calcium type, polluted with nitrates (84.64 mg/L) and aluminium (total Al - 27.94 mg/L).

Table 3. Ground water in contact with the crystalline basement.

Study locations, Date, Remarks	Parameter	1	2	3	4	5	6
№№ 1-4	t,°C	14.5	16	14.6	14	23.2	23.9
15-17.04.2009	pH $_{20oC}$	7.50	7.56	7.45	7.30	7.03	7.32
№№ 5,6	χ_{20oC} μS/cm	2504	895	389	2272	2090	1002
04.07.2009	HCO_3^- mg/L	366	400	397	389	512	476
	SO_4^{2-} mg/L	1200	116	41	286	275	60
	Cl^- mg/L	42	58	6	100	195	52
	Ca^{2+} mg/L	324	198	122	304	382	122
	Mg^{2+} mg/L	74	5	12	25	60	62
	Na^++K^+ mg/L	235	5	10	51	49	18
	TDS mg/L	2279	782	588	1499	1941	890
	K^C	2.38	3.39	2.00	2.46	1.72	1.50
10.07.2009	t,°C	16.6	-	-	18.2	17.7	17.6
№1after heavy rains	pH $_{20oC}$	7.44	-	-	7.28	7.09	7.36
	χ_{20oC} μS/cm	2432	-	-	1522	2230	1064
	HCO_3^- mg/L	400	-	-	373	419	514
	SO_4^{2-} mg/L	949	-	-	175	264	61
	Cl^- mg/L	159	-	-	159	210	73
	Ca^{2+} mg/L	244	-	-	230	368	124
	Mg^{2+} mg/L	93.6	-	-	60	73	61
	Na^++K^+ mg/L	245	-	-	48	52	45
	TDS mg/L	2091	-	-	1269	1888	983
	K^C	2.11	-		1.499	1.31	1.67
03,04.08.2009	t,°C	20.1	19.8	20.0	17.6	18.5	17.6
	pH $_{20oC}$	7.63	7.33	7.55	7.25	7.07	7.40
	χ_{20oC} μS/cm	1804	906	607	1532	2150	1067
	HCO_3^- mg/L	370	410	370	339	394	479
	SO_4^{2-} mg/L	949	84	44	154	242	43
	Cl^- mg/L	145	73	6	169	214	57
	Ca^{2+} mg/L	243	168	120	239	352	77
	Mg^{2+} mg/L	95.7	1.2	12	37	69	86
	Na^++K^+ mg/L	262	45.5	11	63	58	43
	TDS mg/L	2189	860	586	1273	1875	946
	K^C	3.50	2.46	2.56	1.80	2.42	1.35

Hydro-chemical type of the waters (based on the major ions in amounts higher than 20 eq.%): No. 1: (a) 16.04.2009: Sulphate-calcium-sodium; (b) 10.07.2009: Sulphate-hydro-carbonate-calcium-sodium-magnesium; (c) 04.08.2009: Sulphate-calcium-sodium-magnesium, with increased nitrates content (120 mg/L). No. 2: (a) 17.04.2009: Hydro-carbonate-sulphate-calcium, $K^D \cong 1$; (b) 04.08.2009: Hydro-carbonate-calcium, with increased nitrates content (54 mg/L); $K^D = 1.24$. No. 3: (a) 17.04.2009: Hydro-carbonate-calcium, $K^D = 1.37$; (b) 04.08.2009: Hydro-carbonate-calcium, $K^D = 2.20$. No. 4: (a) 15.04.2009: Hydro-carbonate-sulphate-calcium, polluted with nitrates (298 mg/L); (b) 10.07.2009: Hydro-carbonate-chloride-sulphate-calcium-magnesium, polluted with nitrates (224 mg/L); (c) 03.08.2009: Hydro-carbonate-chloride-calcium, polluted with nitrates (238 mg/L). No. 5: (a) 04.07.2009: Hydro-carbonate-sulphate-chloride-calcium-magnesium, polluted with nitrates (468 mg/L); (b) 10.07.2009: Hydro-carbonate-chloride-sulphate-calcium-magnesium, polluted with nitrates (502 mg/L); (c) 03.08.2009: Hydro-carbonate-chloride - calcium, polluted with nitrates (510 mg/L). No. 6: (a) 04.07.2009: Hydro-carbonate-calcium-magnesium, with increased nitrates content (98 mg/L); (b) 10.07.2009: Hydro-carbonate-calcium-magnesium, with increased nitrates content (105 mg/L); (c) 04.08.2009: Hydro-carbonate-magnesium-calcium, with increased nitrates content (135 mg/L).

studied region is controlled by its interaction with clayish-sandy Pliocene sediments and crystalline Mesozoic and Palaeozoic rocks of the basement.

Water chemistry, studied by sampling springs, is presented in tab. 3 and fig. 3. The chemical interactions of the waters described in tab. 3 are as follow:

1. Water percolating through Paleozoic granite;
2. Water coming from Triassic dolomites injected with Upper Cretaceous dioritic dykes;
3. Water coming from Triassic dolomites;
4. Water infiltrated through calcrete horizon and discharged through Pliocene sands and clays;
5. Water percolating through ploicene sands and upper cretaceous diorites;

6. Water discharged through thick horizon of indurate calcrete.

The Piper diagram showed the different geological origin of the samples 1a and 1b from one side and samples 2 and 3 from the other side. Samples 1c, 2b, 4, 5 and 6 are not plotted on the Piper diagram, because of their high content of nitrates. The nitrate is believed to be of anthropogenic origin, mainly derived from fertilisation of the soils in the area. Recalculating the eq. % of the major water ions using their ratios in order to exclude nitrates is not justifiable from the geochemical point of view.

The calculated coefficients of water saturation with respect to calcite for water taken from different sampling points indicate for over saturation with respect to this mineral. Most probably, the high calcium and carbonate/hydro-carbonate concentrations are result of combined soil, undersoil and rock basement leaching.

The increase in the saturation coefficient K^C, considered together with the increase in the relative amounts of magnesium ions with respect to calcium ions, can be explained with calcite precipitation (study location No 1). Small decrease in concentrations of calcium and sulphate ions and increase in concentrations of sodium and chloride ions was observed in water sampled in summers, compared to water sampled in the spring (study location No 2). The observed change in the water hydro chemical type and the decrease in the saturation coefficient K^C could be related to (even very low) precipitation of calcium carbonate. The slight increase in K^C and K^D summer values, compared to spring ones, points at eventual possibility for future precipitation of these compounds (study location No 3). However, the data available up to now do not allow drawing of reliable conclusions. The decrease in the calcium concentrations, conductivity and mineralization, considered together with (even slight) decrease in K^C could be assumed as an indicator for immobilization of calcium ions in warmer weather (study location No 4). Chloride replaces sulphate as a second major ion in summer samples (study location No 5). The slight increase in K^C is likely to indicate for a slight tendency for calcium immobilization. The decrease in K^C values, considered together with the decrease in calcium concentrations imply that $CaCaO_3$ was precipitated to a certain level (study location No 6).

4.4. Water from artificial lakes

Hydrochemical parameters of water from two artificial lakes in the study region give an idea on the composition of water that flows on the surface of calcrete layers. Lake No 1 was sampled in April 2009 and Lake No 2 – in August 2009 (Tab. 4). As it can be expected, the water is oversaturated with respect to $CaCaO_3$. Lake No. 1 was totally dried in summer and the precipitated material was very rich in calcium, magnesium and sodium carbonates and sulphates.

4.5. Seasonal variation of the carbonate content in the soils

Interactions of rain/snow water with soils are other important factor which contributes to calcrete formation. Changes in soil chemistry due to calcrete

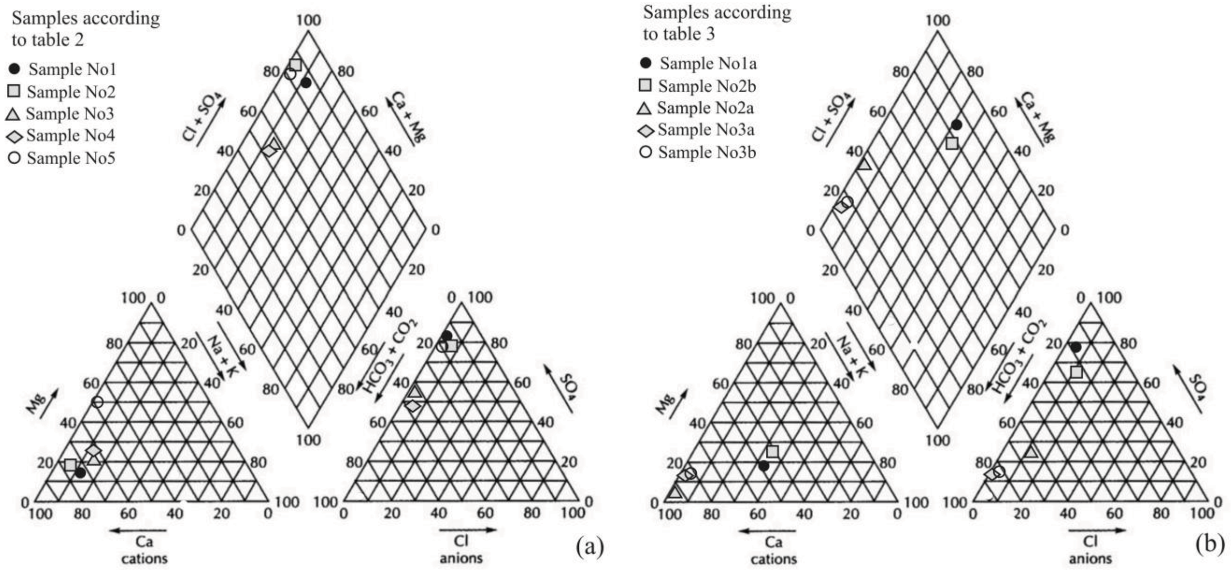

Fig. 3 A Piper diagram for the samples shown in tables 2 and 3.

Table 4. Hydrochemical parameters of water from two artificial lakes in the study region

Lake No	T, °C	pH	ΔpH	χ_{20oC}, μS/cm	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+}+K^{+} mg/L	SO_4^{2-} mg/L	Cl^{-} mg/L	HCO_3^{-} mg/L	CO_3^{2-} mg/L	TDS mg/L
1	11.7	9.5	+0.40	1107	94	35	74	265	51	145	56	722
2	29.5	8.84	+0.07	563	41	28	70	46	48	259	16	528

No. 1: Sulphate-hydro-carbonate-calcium-sodium type, K^C = 158; No 2 Hydro-carbonate-sodium-magnesium-calcium type, K^C = 26.14.

formation usually affect soil fertility. That is why the soil chemistry has to be studied. Sampling, sample preparation and analyses were made following standard procedures, described for the specific parameters in table 5.

The main studies on the variation of soil chemistry are planned for the future, however some important conclusions can already be drawn. The soils from topographic depressions, where tick organic soil layer is present have lower pH values. In calcretized soils the acidity decreases from the organic top towards the calctete rich undersoil. Where the calcrete appears on the soil surface, the soil is slightly alkaline. Alkaline and acidic soils are distributed spot-wise and the reasons for this distribution are to be studied in the future.

The light increase in the quantity of water soluble hydro-carbonates and the specific conductivity in summer samples, compared to spring samples, in all studied horizons (Tab.5) implies for a possibility for initial formation of transitional compounds, that are pre-cursors of calcrete. This statement is supported by the increased pH values of soil water leachates. The most significant changes were observed in the transitional layer, where increased concentrations of water-soluble calcium, magnesium, sulphate and of inorganic carbon also support the statement about formation of transitional compounds - calcrete precursors.

5. Conclusions

The geomorphological forms correspond to geochemical zonation. The calcrete is present in the well-drained elevated topographic forms, where the soil acidity is low. In the topographic depressions the content of sulfur, chloride and magnesium in the shallow ground waters increases but calcrete is missing. Apparently, the waters immobilize these elements depositing them in the well drained elevated parts of the topography. From the upper, towards the lower part of the relief the geochemical conditions favor deposition of calcite, dolomite and gypsum. All waters in the study region are oversaturated with respect to carbonates, which is the most important condition for deposition of carbonate minerals in the soil. The acidity of the soil varies seasonally and the same applies for the calcrete formation.

Based on the results obtained up to now, the mechanism of pedogenic calcrete formation is as follow: Aggressive with respect to $CaCO_3$ rain water dissolves carbonates from soil and immediate undersoil. Solutions oversaturated with respect to $CaCO_3$ percolate through the pores of the shallow undersoil. It is likely, that because the processes of leaching and precipitation are competing, the calcrete layer is constantly rejuvenating. As the rain water acidity and ground water degree of oversaturation with respect to $CaCO_3$ depends on the

Table 5. Soil analysis in a study site (near Skalitsa village) located close to the water sources described in table 3 under №4

Sampling level, cm; Parameter	0 -20 cm (organic soil)		20-40 cm (transitional layer)		60–80 cm (calcretized layer)	
	Spring	Summer	Spring	Summer	Spring	Summer
$pH(H_2O)$[1]	8,41	8,58	8,69	8,83	8,85	9,03
Specific conductivity[2], mS/cm	0,137	0,149	0,113	0,135	0,102	0,130
Water soluble hydro-carbonates[3], mgeq/100g	0,70	0,84	0,56	0,77	0,42	0,58
Water soluble sulphates[4], mgeq/100g	0,39	0,38	0,48	0,94	0,51	0,54
Water soluble calcium[5], mgeq/100g	0,84	0,82	0,55	0,73	0,58	0,53
Water soluble magnesium[6], mgeq/100g	<0,04	0,23	0,11	0,36	<0,04	0,28
Inorganic carbon, g/kg -calculated as difference between total C and organic C[7]	56.2	51.9	58.3	64.1	82.9	74.2

Analytical standards: [1]BNS ISO 10390; [2] BNS ISO 11265; [3] BNS ISO 11048 and BNS EN ISO 9963-1; [4] BNS ISO 11048 and BNS 17.1.4.03; [5] BNS ISO 11048 and BNS ISO 6058; [6] BNS ISO 11048 and BNS ISO 6059; [7] BNS ISO 14235; ISO 10694.

season, it appears that formation of transitional compounds - calcrete precursors and probably their transformation to calcrete also depends on the season.

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References

Alonso-Zarza A. M., 2003. Palaeo-environmental significance of palustrine carbonates and calcretes in the geological record. Earth-Science Reviews, 60, 261–298.

Budd D. A., Pack S. M. and Fogel M. L. 2002. The destruction of paleo-climatic isotopic signals in Pleistocene carbonate soil nodules of Western Australia. Paleogeography, Palaeoclimatology, Palaeoecology, 188, 249–273.

Dimitrov I., Panayotova M., Koleva-Rekalova E., Anastasova E., 2009. Initial geochemical and physicochemical studies of regions affected by calcretization in East Thrace Plane. Annual of UMG, Vol. 52, part I, Geology and geophysics, 55-60 (in Bulgarian with English abstract).

Machkova M., Velikov B., Dimitrov D., Neykov N. and Neytchev P., 2008. Quality Status of the Upper Thrace Plio-Quaternary Aquifer, South Bulgaria. Natural Groundwater Quality, 391-403.

Monger H.C. & Gallegos R.A., 2000. Biotic and abiotic processes and rates of pedogenic carbonate accumulation in the southwestern United States – relationship to atmospheric CO_2 sequestration. In: Lal, R., Kimble, J.M., Eswaran, H. & Stewart, B.A. (Eds) *Global Climate Change and Pedogenic Carbonates*. Boca Raton: CRC Press/Lewis Publishers, pp. 273–289.

Stock J. D., Montgomery D. R., Collins B. D., Dietrich W. E., Sklar L., 2005. Field measurements of incision rates following bedrock exposure: Implications for process controls on the long profiles of valleys cut by rivers and debris flows. GSA Bulletin; 117, 174–194.

Wright V. P., 2007. Calcrete. In: Geochemical Sediments and Landscapes, Nash D. J. and McLaren S. J. (eds), RGS-IBG Book Series, Blackwell Publishing.