LACUSTRINE CARBONATE FORMATION IN THE DANUBE-TISZA INTERFLUVE

Theses of PhD dissertation

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1. Introduction

Geology is the key to geochronological past, as from the results of a process we can infer how things could have happened in the past. By studying sedimentary areas and finding modern analogies, we can guess about the changes which took place in the past. Dolomite can not be artificially produced in lab conditions under the temperature of 100 ^{o}C. In nature, and in the shallow alkaline ponds of the Danube-Tisza Interfluve in Hungary, where according to our present knowledge the maximum temperature of the water is 37 ^{o}C, dolomite formation is rather common. To understand this process is highly important, because internationally, many researchers show great concern about dolomite formation.

If we want to look at carbonate formation in general and dolomite formation in special, there are two possible ways our work can take.

One would be the analysis of the properties of the water, the other method is the study of carbonates which were precipitated from the water.

Previous researches have almost fully described this latter one, concerning the properties of lacustrine carbonates.

The financial support from the Hungarian National Science Research Foundation (OTKA) made now possible, to implement studies dealing with the properties of the water from which these carbonates were precipitated.

Concerning the study of the water, so far there was a lack of experiments which focused on collecting water samples monthly for a period of several years, in order to be track geochemical changes continously. This work can help fill this gap.

As I am experimenting with water with high salt content directly in contact with the soil, I also would like to touch upon the relationship between soil and alkalization of the area as well.

The study area will be mostly that of the Kiskunság National Park (KNP), so I will also give a special overview of this place.

/According to the international research, dolomite formation in nature is determined by the following issues(Morrow, D.W 1992):

1. *Dolomites are thermodynamically stable in the majority of natural solutions their thermodynamical transformation goes through calcite and aragonite to dolomite.*

2. *The precipitation of the dolomites can be hindered by such thermodynamical effects as the orderly crystal lattice, caused by the hydration of the* Ca^{2+} Mg^{2+} *and* $Co_3{}^{2-}$ *ions.*
3. *The coincidence of three critical parameters define the way in which these factors prohibit dolomite formation*
    - a.) *The speed of the crystallization is determined by the crystallographical order of the precipitated Ca-Mg carbonate. The dilution of the too highly saturated solutions reduces the crystallization ratio.*
    - b.) *The Mg/Ca ratio of the solutions defines the quantity of* Mg^{2+} *in the Ca-Mg carbonate, which will be infiltrated in the dolomite. This ratio often rises by the precipitation of gypsum and anhydrite, because calcite is used, and it influences positively the formation of dolomite (such places are e.g.. that part of the Persian-gulf, which is above the flux and reflux zone).*
    - c.) *If the* CO_3/Ca *ratio of the solutions is higher than one, it favors the precipitation of dolomite (This proportion can be increased in the groundwater by the crumbling of igneous rocks, or when sulphate anaerob bacterial reduction takes place).*
4. *The reaction which takes place is the following:*

$$(2-X)\ CaCO_3 + Mg^{2+} + XCO_3^{2-} = CaMg(CO_3)_2 + (1-X)Ca^{2+}$$

where X=0.11 by the dolomite formation of the aragonite, and X=0.25 by the dolomite formation of the calcite./

2. Material and methods, sampling sites

In order to study the properties of the water, I have assigned specific sampling sites in the Kiskunság National Park (KNP). On the other hand as a control area, I have chosen places, where natural resources are used for economic purposes. These are the following:
a) Kelemenszék, which is part of the KNP; **b)** Szappanosszék Pond, being also part of the KNP, where two groundwater monitoring wells were deepened (W,E); **c)** Ródliszék Pond, which is 5 km to the north of Bugac, and is used now for grazing after having been dried up, with also 2 groundwater wells (W,E); **d)** The well from Csólyospálos, which is in the KNP nature reserve; **e)** Csólyospálos 3.which is the pit next to this one; **f)** Csólyospálos 1, the pit

south of Csólyospálos, next to the road; **g)** Csólyospálos 1/1-pit, located next to the previous site.

For comparison, further samples of boreholes were carefully studied from the Danube-Tisza Interfluve .

The groundwater monitoring wells were established on the shores of the alkaline lakes. These were formed by the Agrogeological Department of MÁFI. To make a comparison, I examined the groundwater from the Danube-Tisza Interfluve, and the water from lakes in Anatolia, Tunis, and Switzerland. The geological setting and sedimentary features of the boreholes were depicted on logs. The hydro-dynamical state of the water from the wells, the temperature of the water and the air were also recorded on the spot. When taking water samples, special attention was paid to avoid contamination.

The pH values, redoxpotential and specific conductivity of the water samples were measured using the German WTW pH/Cond 340i/Set instrument. The dissolved salt content was calculated from these parameters. Further geochemical analysis of the water took place in the Hydrogeological Lab of the Geology and Paleontology Department of the University of Kiel. The study of the cations took place by using Vista AX, CCD instrument, optical emission spectrometer, inductance coupling (ICP-OES/ for the study of anions, I used Hersteller DX 500 ionchromatographic method. The HCO_3 content was established in mg/l 4.3 pH hydrochloric titration.

The stable isotope analysis took place in Sehnde not far from Hannover using the MAT 251 mass spectrograph of the Geochemical Research Institute from Finningan. We studied the δ^{13}C PDB and δ^{18}O PDB values, taking the necessary quantities from the carbonate after treating it witch 100% phosphoric acid on 25° C and measuring the evolved CO_2 after 10 minutes and 48 hours, according to McCrea, I.M. (1950) analysis, then the values were established in PDB standard, while the values of the pore waters in $\delta\ ^{18}$O SMOW and δD SMOW.

The hydrogen isotope determination of the water was made by reduction to hydrogen of the water samples. It took place in vacuum, by heating a 6 mm bar of glass with 4 granulated zink and kieselguhr.

After putting 1.0 μl water into the glass tube, the apparatus must be closed immediately. The bottom of the tube must be cooled with fluid nitrogen, and the water has to be frozen slowly. After pumping nitrogen for 5 minutes into the tube, the ice has to be melted by flame in vacuum. The reduction of the hydrogen isotope from the water takes place at 500 °C after 30 minutes. Then, the zinc oxide on the kieselguhr, or on the glass tube shows white deposit, from which I could define the D/H content of the water using a mass spectrograph. The radiographical examinations were made at the University of Kiel using a Philips PW 1710 X-ray outfit Cu Kα radiation 2^o / speed. The organic and inorganic carbon was formed from the CO_2, after liberating the whole carbonate with Ströhleiun 712. The inorganic carbon has been dissolved while the organic one could be measured.

The composition of the organic carbonate was determined using profiles having diameter less than 1 mm, using transmitted light and fluorescent microscope in blue, and oil immersion.

3. Results of the research

1. I have stated, that on the sampling sites, from November 2003, until December 2006, the level of the groundwater was high. The former tendency of sinking was turned displaying a slight increase.

2. The chemical composition of the studied groundwater samples was highly varying spatially. There are major differences observable between the individual sites, and the annual changes are also significant. In case of the groundwater, annual changes in the chemical composition are attributable to evaporation triggered by capillary rise of these waters. The strong difference between the summer and winter composition of surficial waters are also attributed to the strong evaporation in the area.

3. The recorded pH values are between 6.7 – 9.5, and total dissolved salt content of both the collected groundwater samples and surficial water samples is between 500 – 5000 mg/l, due mostly to the local water movement characteristic induced by morphological differences. The maximum pH values were generally recorded in the middle part of the year, meanwhile the recorded total salt content, including Na has a maximum towards the end of the year.

4. Prerequisites for carbonate formation are generally given in the study area as all studied samples contained sufficient amount of Ca. The ratio of Mg/Ca is not the same in all samples. In some places this ratio favours the formation of high-magnesium

calcite, which is syngenetically transformed into dolomite. The CO_3/Ca ratio in all the samples enables the direct precipitation of the mineral dolomite.

5. According to the results of the stable isotopic studies, dolomite formation was characteristic in waters characterized by either the smallest negativity or with positive isotopic values, so samples collected during the hottest part of the year, characterized by most intensive evaporation, while the precipitation of calcite was characteristic in those parts of the year, when either evaporation was the lowest or the CO_2 removal of plants was the most intense.

6. The $\delta\ ^{18}O_{SMOW}$ and $\delta\ D_{SMOW}$ values of the more waters ranging between 3.5 – -10.2 ‰ and 4.6 – -19.0‰ again indicates the role of a strong evaporation factor in carbonate precipitation.

7. Inorganic carbon content of the dolomites is always exceeding the amount of organic carbon which again proves the inorganic origin of carbonates (dolomite).

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