Doctoral School of Geosciences

Characterizing Small-Scale Heterogeneity in Quaternary Freshwater Carbonates of Hungary Using CT Scan Data

Ph.D. Thesis booklet

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2023

Szeged

I : General background:

The Danube-Tisza Interfluve (DTI) is the area between the Danube River and the Tisza River over the Southern Great Hungarian Plain (GHP) which is composed of wind-blown sand and loess deposits that contain up to 10% carbonate minerals, mainly dolomite (Molnár et al., 1995). During the end of the Pleistocene and the beginning of the Holocene period, hypersaline lakes formed through interdunes due to high groundwater levels or surface runoff (Jenei et al., 2007; Lóczy, 2015).

Two types of carbonate strata are presented in the area, with loose carbonate mud restricted to the north-western part, while solid carbonate rock (dolomitic limestone) overlain by unlithified carbonate mud is present in the southeast. The type of carbonate mineral formed is controlled by temperature, evaporation rate, pH, CO_2 absorption by aquatic plants, and ions concentration, with the Mg/Ca ratio playing a crucial role (Molnár et al., 1980).

The lakes dry up during summers, and secondary carbonates occur when the salinity fluctuates greatly during the year. Rainfall during autumn supplies freshwater to the DTI alkaline lakes, decreasing Na and K concentrations and increasing the Mg/Ca ratio from 7–12, creating favourable conditions for the precipitation of high-magnesium calcite. The high-magnesium calcite precipitates seasonally based on climatic conditions and groundwater table fluctuations (Müller et al., 1972). Proto-dolomite forms in mud deposited over a lakebed via a transformation of Mg-bearing calcite during periods when pore waters are rich in Mg. (Molnár et al., 1980). Sedimentary rocks provide valuable records of past environmental and climatic changes. By analysing the composition and proportion of rock-forming components (RFCs), we can reconstruct these changes at high resolution.

Computer tomography techniques have found applications beyond medical imaging. Researchers have utilized these techniques in various non-medical fields, such as specialized cross-sectional imaging for non-destructive testing, determining celestial sphere brightness distribution, and three-dimensional imaging with electron microscopy. Tomographic imaging involves recreating a picture from its projections, where a projection represents the integral of the picture in a specific direction. Projections can be derived from transmitted energies or diffracted sources like ultrasound and microwaves. The advancements in reconstruction algorithms played a crucial role in the rapid improvement of X-ray computed tomography, making it capable of producing high-quality and anatomically accurate images (Kak & Slaney, 1999). X-ray computed tomography (CT) can be used in sedimentology and geology to produce cross-sectional tomographic images of sedimentary rocks and assess the nature of their formation and diagenetic history. Furthermore, CT is used in materials science and engineering to investigate the internal structure and properties of materials, as well as in archaeology, art conservation, and palaeontology.

II : Research Objectives and Hypothesis

The main objective of this study is to quantitatively distinguish the rock-forming components of freshwater carbonates based on their density differences and make inferences about heterogeneity. Therefore, the minor goals were researched as follows.

1. Understanding the small-scale heterogeneity in Quaternary freshwater carbonates found in Central Hungary.
2. Defining the rock-forming components (RFCs) by applying univariate statistical and EM mixture analysis on the Holocene freshwater carbonate rocks.
3. Discussing how X-ray CT scans can be used to draw paleoenvironmental and paleoclimatic inferences from alkaline lake deposits in Hungary.
4. Exploring how CT data analysis can help reveal structural heterogeneity and potential flow paths in freshwater carbonates used as decorative and building stones.

III : Sampling, methods, and workflow

Three major choices were followed in picking samples in this research: RFCs, mixture analysis algorithm, and watershed algorithm.

III.1 : Sampling

The samples used in this study are the same ones collected and analysed by Mucsi (1963) from a now protected outcrop near Csólyospálos. The outcrop is approximately one meter deep. The four carbonate samples are currently housed in the sedimentary rock collection of the

Department of Geology and Palaeontology at the University of Szeged. Each sample was initially cut in half and had their surfaces polished.

Four samples, namely Cs-1, Cs-2, Cs-3, and Cs-4, were selected to represent all members of the Csólyospálos carbonate sequence. Cs-1 and Cs-2 are represented by a single sample (referred to as sample I) taken from a depth ranging between 65 to 90 cm in the section. Cs-3 is represented by two adjacent samples (referred to as samples II and III) obtained from a depth of 65-60 cm. Lastly, Cs-4 is represented by a single sample (referred to as sample IV) collected from a depth of 55-25 cm (Molnar et al., 1976).

III.2 : CT scan parameters

At the University of Pécs in Hungary, the Institute of Diagnostic Imaging and Radiation Oncology conducted high-resolution X-ray CT scans. The scanning process utilized an instrument operating at a peak kilovoltage (kVp) of 140, with a current of 189 milliampere seconds (mAs) and a sampling interval of 1.5 seconds. The lateral resolution of the scan was 0.234 mm x 0.234 mm, and each scan slice had a thickness of 1.5 mm. The image reconstruction matrix comprised 512 x 512 pixels. CT images were saved in a DICOM (Digital and Imaging Communications in Medicine) format.

The metadata of a DICOM file includes important scanning parameters such as Pixel Spacing and Slice Thickness attributes. These metadata hold crucial information for geoscientific applications as they document the dimensions (in millimetres) of each voxel in the x, y, and z directions. DICOM is a widely used image format in medical applications and can be easily interpreted by conventional 3D volume rendering software like VOXLER.

In this study, CT data analysis is shown to provide a more objective and comprehensive understanding of the heterogeneity and textural properties of freshwater carbonates of the GHP compared to traditional thin-section analysis. The thin-section analysis is limited to selected areas of the sample, making estimations subjective. CT data analysis provides quantitative 3D data at different scales, allowing for more accurate characterization of the rock-forming components (RFCs) and their textural heterogeneity. The density information obtained from CT data correlates with the composition of RFCs. Mixture analysis is used to segment RFCs based on CT data, considering the complexity and overlap of distribution curves. The study suggests reevaluating the nomenclature of rocks based on the more accurate estimations provided by CT.

III.3 : *Rock-Forming Components and Mixture analysis algorithms*

The identification of the rock-forming components (RFCs) was accomplished through mixture analysis. In this approach, a non-hierarchical clustering technique based on maximum likelihood was employed to estimate the parameters (Mean and Standard Deviation) of multiple univariate normal distributions. These distributions represent groups that overlap and correspond to the RFCs. The algorithm used for this purpose was the EM algorithm introduced by Dempster et al. in 1977. Since our research primarily focuses on the spatial distribution, orientation, and connectivity of voids in brick samples, it was sufficient to determine the void spaces and the main minerals of the rock-forming components. A histogram provides a graphical representation of the distribution of pixel intensity values in an image, where the x-axis denotes the intensity values, and the y-axis denotes the frequency of occurrence.

III.4 : *Watershed algorithms*

The term "watershed transformation" refers to a geographical boundary or dividing line between adjacent drainage basins. In simple terms, when a drop of water falls on a terrain, it naturally flows towards the nearest lowest point. This lowest point is identified as the endpoint of the steepest descent path. In the context of topography, this occurs if the point lies within the catchment basin of that lowest point (Beucher & Meyer, 1993).

A watershed map takes data from a grid file and divides the grid into separate basins or catchment areas. The number of basins depends on the sizes of the individual areas and is determined by the number of upstream cells that flow into the grid cells. Increasing the threshold value reduces the number of identified basins. The calculation of flow lines or flow paths is based on the amount of flow into a grid node from surrounding nodes. These lines connect the lowest points on the map. Various algorithms exist for watershed transformation, such as the ones proposed by Beucher & Meyer (1993) and Wang & Liu (2006). In our research, we applied a specific topological algorithm called the accurate eight-direction four-point algorithm, which utilized the Laplace operator. This algorithm was used to identify potential areas of dissipation and confluence. By assigning potential non-real flow paths (PWP) to the grid at each grid node of the CT slices obtained from the SURFER system, we were able to calculate the flow direction at each grid node. (Quick start guide - Surfer Software 2023).

IV : Main results

The study of quaternary freshwater carbonate from the Great Hungarian Plain has produced important new results concerning the freshwater carbonate in the hypersaline lake in GHP, the rock-forming components, the palaeoclimatic and palaeohydrological conditions during the late Pleistocene and Holocene, in addition to petrophysical properties such as void space larger than 200 microns, and the freshwater carbonate controlling factors:

IV.1 : Defining rock-forming components of Holocene freshwater carbonates via univariate statistical and mixture analysis of computer tomography data.

1- The research conducted on four carbonate samples from Csólyospálos utilized computed tomography (CT) scanning to investigate and record the heterogeneity and textural characteristics of the carbonates. The study found that CT analysis offers a more objective and direct approach compared to traditional thin-section analysis. The quantitative data obtained through CT analysis in three dimensions enables a comprehensive evaluation of the entire sample, including detailed micro-scale resolution. In contrast, thin sections provide limited information as they rely on selectively chosen subsamples of small (couple of square mms) parts and being also subjective estimations.

2- By using CT data we investigated lithified and unlithified freshwater carbonate samples. We applied an EM-mixture analysis algorithm to determine the HU range of each rock forming component known from the textural analysis of previous studies. For the lithified samples the following intervals were defined for each RFC: empty pores < 850 HU, filled or partially filled pores between 600 - 2500 HU, calcium carbonate matrix between 2000 – 3100 HU, high magnesium carbonate matrix between 2500 – 3200 HU, high-density matrix components and limonite between 2800 – 3400 HU. On the other hand, RFCs of the non-lithified samples had somewhat different ranges: the empty pores < 550 HU, filled or partially filled pores between 300 - 1900 HU, calcium carbonate matrix between 1300 –

2300 HU, high magnesium carbonate matrix between 1600 – 3100 HU, high-density matrix components 2500 – 3200 HU.

3- We calculated the relative percentage of each component, and the average percentage of the lithified samples were as follows: empty pores ~ 0.13%, filled or partially filled pores 18.37%, calcium carbonate matrix 62.0 %, high magnesium carbonate matrix 14.3%, high-density matrix components and limonite 5.2%. For non-lithified samples the following values were received: empty pores ~ 1.65 %, filled or partially filled pores 40.5%, calcium carbonate matrix ~55.35%, high magnesium carbonate matrix 1.25%, high-density matrix components 1.25%. To provide an example, the characteristics of the minerals that make up rocks were matched with descriptions of samples given by Molnár (1991).

IV.2 : ***Palaeoenvironmental and palaeoclimatic inferences based on X-ray computer tomography: a case study of alkaline lake deposits in Hungary.***

1- X-ray computer tomography (CT) allows for quantitative data based on density differences of RFCs, providing insights into sediment formation and environmental properties through time at high resolution. Density changes in the matrix, as captured by medical CT, correspond to climatic oscillations and precipitation patterns in carbonate formations at high resolution. Changes in evaporation rates, temperature, and rainfall influence the type of carbonate minerals precipitated, leading to variations in densities. The CT method, combined with statistical analysis, proves effective in revealing millennial and centennial sedimentary cycles and past paleoenvironmental changes.

2- Analysing computer tomography data, colder conditions in the North Atlantic from 10.3 to 9.3 thousand years before the present (kilo-years Cal BP) had a notable impact on freshwater carbonate formation in the GHP. These conditions led to increased humidity, resulting in a rise in the groundwater table and the precipitation of dominantly calcite from pore waters instead of high-magnesium calcite. The negative shifts in CT density values in the dated rock samples depicted these changes clearly and showed a good correlation with isotope geochemical and paleoecological data of previous studies (Molnár 1996).

IV.3 : The use of CT analysis in revealing structural heterogeneity of freshwater carbonate decoration and construction stone.

1- Zones are defined based on the major trend changes in the percentage of void space and the mean value; therefore, some directions could contain only two zones such as (ZYX sample I), and others involved seven zones like (XZY sample II).

2- Macro-CT scanned data revealed voids which are greater than voxel size. Major trending was vertical with horizontal connected from the front and back sides once the water reaches the interior parts, the good connectivity and vertically oriented pores facilitate upward by capillary action and downward flow by gravity.

3- The analysis of Sample I revealed that the front and back of the brick had higher porosity and greater susceptibility to water absorption compared to the left and right sides of the central part. This indicates the need for effective insulation in the front and back positions to prevent water ingress into the central areas.

4- The lateral areas of the brick displayed negligible lengths and proportions of potential water pathways (PWPs), making them less prone to water uptake. Consequently, minimal insulation can be deemed acceptable for these regions, reducing the risk of water infiltration.

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List of publications used in the dissertation.

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Alzoubi, N., Geiger J., Gulyas S, 2023: The use of CT analysis in revealing structural heterogeneity of freshwater carbonate decoration and construction stones. *Archeometriai muhely*. (In press). (Impact factor: 0.45).

Alzoubi, N., Geiger J., Gulyas S, 2023: Palaeoenvironmental and palaeoclimatic inferences based on X-ray computer tomography: a case study of alkaline lake deposits in Hungary. *Geologos*. 39: 2 pp. 113-128. 16 p. Doi: 10.24425/sq.2022.140887. (Impact factor: 1.000).

Alzoubi, N., Geiger J., Gulyas S, 2022: Defining rock-forming components of Holocene freshwater carbonates via univariate statistical and mixture analysis of computer tomography data. *Studia Quaternaria* 39: 2 pp. 113-128. 16 p. Doi: 10.24425/sq.2022.140887. (Impact factor: 0.964).

Conferences Abstracts

Alzoubi, N., Gulyas, S., Geiger, J. 2021: Defining rock-forming components of Holocene freshwater carbonates via univariate statistical and mixture analysis of CT data" ORAL, webGeoMATES, Hungary.

Alzoubi, N., Gulyas, S., Geiger, J. 2021: Measuring the significant cyclicity and variability of non-water carbonates – interfluve Hungary, using CT data"- POSTER, IAS Prage_21.

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Alzoubi, N., Gulyas, S., Geiger, J. 2021: Heterogeneity of Holocene freshwater dolomites from central Hungary based on a statistical analysis of rock-forming component properties derived from CT data. – ORAL, EGU.

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Alzoubi, N., Gulyas, Sandor; Geiger, J. 2020: Analysing small cyclicity and heterogeneity of non-marine carbonates from Danube-Tisza interfluve, by using CT data" – TALK, DOSZ – Hungary.

Alzoubi, N., Gulyas, S., Geiger, J. 2020. "Analysing statistical properties and heterogeneity of Holocene freshwater dolomites from Hungary using CT data" – ORAL, Carbonate Forum, May

Co-authors' declaration

We as co-author of the publication entitled **"Defining Rock-Forming Components of Holocene Freshwater Carbonates Via Univariate Statistical and Mixture Analysis of Computer Tomography Data"** officially declare that the jointly published results in the thesis and the publication are greatly contributed by the candidate and was not or will not be used in the past or in the future, respectively, for the purpose of acquiring an academic degree or title.

Date: 24 – 05 – 2023

Name and signature of co-authors

János Geiger ....

Sándor Gulyás ....

Co-authors' declaration

We as co-author of the publication entitled **"Palaeoenvironmental and palaeoclimatic inferences based on X-ray computer tomography: a case study of alkaline lake deposits in Hungary."** officially declare that the jointly published results in the thesis and the publication are greatly contributed by the candidate and was not or will not be used in the past or in the future, respectively, for the purpose of acquiring an academic degree or title.

Date: 24 – 05 – 2023

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János Geiger ....

Sándor Gulyás ....

Co-authors' declaration

We as co-author of the publication entitled **"The use of CT analysis in revealing structural heterogeneity of freshwater carbonate decoration and construction stones: implications for conservation"** officially declare that the jointly published results in the thesis and the publication are greatly contributed by the candidate and was not or will not be used in the past or in the future, respectively, for the purpose of acquiring an academic degree or title.

Date: 24 – 05 – 2023

Name and signature of co-authors

János Geiger ....

Sándor Gulyás ....

Statement of the supervisor

I, **Dr. Sándor Gulyás,** as supervisor, declare that the thesis written by ***Nour Nayef Hassan Alzoubi*** titled ***Characterizing Small-Scale Heterogeneity in Quaternary Freshwater Carbonates of Hungary Using CT Scan Data*** is her own writing prepared under my supervision; the candidate's contribution to the results used in the discussion of the thesis is approved. I also declare that the thesis meets the formal and professional requirements of the Doctoral School of Geosciences of the University of Szeged and the Faculty of Science and Informatics/ Department of Geology and Paleontology; thus, I support its submission.

Szeged, 14/07/2023

(supervisor)

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Statement of Acceptance

To Nour Alzoubi
University of Szeged, Department of Geology and Palaeontology
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Dear Nour Alzoubi,

Hereby, I confirm that your manuscript *'Nour Alzoubi – Sándor Gulyás – János Geiger: The use of CT analysis in revealing structural heterogeneity of freshwater carbonate decoration and construction stones'* submitted to the Archeometriai Műhely / Archaeometry Workshop, electronic open access journal (www.ace.hu/am) published by the Hungarian National Museum, has undergone a double blind peer-review process and has been accepted for publication (*In Press* status). Your article is going to be published in the issue No.2023/XX./2 of the journal (Autumn 2023).

Best regards,

Budapest, 2023-07-13

Szilágyi Veronika
editor
Archeometriai Műhely / Archaeometry Workshop