

Article

Applicability of Magnetic Susceptibility Measurements on Cave Sediments in Karst Areas: Insight from Dinaric Karst (Velebit Mt., Croatia)

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Abstract: Magnetism in Croatian caves has been significantly underexplored, despite the well-documented preservation of cave sediments. This study investigates whether magnetic susceptibility can be effectively recorded in Croatian caves and, if so, whether there are differences between in situ and laboratory measurements, as well as the extent of these differences. The focus is on two prominent sites within the Velebit Mountain range of the Dinaric Karst: the deep Slovačka Cave and the extensive Crnopac Cave System (ex. Kita Gačešina Cave). Magnetic susceptibility was measured in soft sediments using the Kappameter KM-7 for in situ assessments and the Bartington MS2B System for laboratory analyses. The comparison of the two devices aimed to evaluate the feasibility of detecting magnetic susceptibility variations within carbonate sediments. Sampling locations were selected based on preliminary assessments of magnetic susceptibility variations and accessibility for sampling. Characteristic samples from each profile underwent X-ray powder diffraction analysis. Results revealed significant variations in magnetic susceptibility across each profile under both in situ and laboratory conditions. In situ measurements ranged from -45×10^{-5} SI to 120×10^{-5} SI, while laboratory measurements ranged from 4.00×10^{-5} SI to 99.40×10^{-5} SI. The portable Kappameter KM-7 provided satisfactory results for preliminary investigations, while the Bartington MS2B System demonstrated high precision in analyzing these variations in detail. These findings support the potential for further investigations into magnetic susceptibility in karst cave environments, with an emphasis on understanding depositional history and the timeline of climate and tectonic changes.

Keywords: magnetic susceptibility; Dinaric Karst; caves; sediment analysis; Bartington MS2B



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1. Introduction

Cave sediments are one of the best archives of geological, paleoenvironmental, and speleogenetic processes [1,2]. Climate conditions within caves are much more stable than those on the Earth's surface, making them intriguing areas for field research. These environments provide valuable insight from geological [3,4], physical [5], and biological, particularly paleontological [6,7] perspectives.

The Dinaric Karst is known for its well-developed profiles of allocthenic cave sediments [8]. However, these deposits in the Croatian part of the Dinaric Karst are poorly investigated. Most previous research has focused on paleontological excavations [9]. Recently, there has been an increased focus on sedimentological and mineralogical research and establishing a chronostratigraphic framework for depositional processes [10].

In the northwestern part of the Dinaric Karst, there is a well-developed magnetostratigraphy of cave deposits [11]. However, research on magnetism and magnetic susceptibility in caves within the Republic of Croatia is significantly lacking.

Magnetic susceptibility serves as a valuable metric of a material's magnetism, offering diverse analytical advantages. It aids in identifying minerals rich in magnetism within samples, enabling high-resolution determination of their concentration or total volume. Furthermore, it assists in classifying different rock types and understanding their formation or transport processes, while also facilitating the creation of an “environmental fingerprint” [12]. It is most commonly used in studies of igneous rocks [13]. Magnetic susceptibility represents the aggregate magnetic behavior of rocks, known as rock magnetism, from various components including ferromagnetic, ferrimagnetic, canted antiferromagnetic, paramagnetic, and diamagnetic groups. Measuring magnetic susceptibility is straightforward, convenient, and versatile [14]. It can be carried out on all types of rocks, both in the laboratory and in the field, with minimal preparation. These measurements are quick, non-destructive, and complement a wide range of studies. Moreover, a large number of samples can be economically measured without restricting subsequent research. In situ measurements expedite the integration of measured data and field observations, proving particularly beneficial for individuals in remote areas lacking laboratory access.

Given that Croatian allogenic cave sediments originate from various provenance areas, their mineral detritus often exhibits diverse mineral composition, and, therefore, diverse magnetic properties. In the area of Velebit Mountain, particularly near the former Kita Gaćešina Cave, which is today a part of the Crnopac Cave System, there are documented occurrences of opaque mineral fractions, as well as pyroxene, chromite and biotite [10]. Additionally, calcium carbonate is expected, given that the speleogenesis of the area is primarily connected to the thick sequence of Mesozoic carbonate host rock of the Adria Microplate [15–18]. The presence of allogenic sediments in Velebit caves that contain both carbonate clasts and heavier mineral fractions suggests that both paramagnetic and diamagnetic materials are likely present in these caves.

The research area is located within Dinaric Karst which is *locus typicus* for global karst evolution and geomorphology [19]. This study aimed to investigate the possibility of precise measurement of magnetic susceptibility in caves in Velebit Mountain. This study also aimed to establish whether significant changes in magnetic susceptibility were accompanied by variations in mineral composition. Furthermore, a statistical analysis was conducted between in situ and laboratory results to evaluate the compatibility of the two devices. In situ measurements utilized the Kappameter KM-7 device from SatisGeo s.r.o. (Brno, Czech Republic), while laboratory measurements employed the Bartington MS2B System (Bartington Instruments, Oxford, UK). Sampling exclusively targeted soft sediment, with profile locations selected based on accessibility.

In cases where the measurement of magnetic susceptibility in Croatian caves within the Dinaric Karst can be performed satisfactorily, systematic investigations could enable the observation of changes in magnetic materials over time. This, in turn, could unravel timelines of climatic and tectonic changes, as well as provide critical information on the depositional history of caves associated with karst development.

2. Geological Setting

The Dinaric Mountains originated with the convergence of the Adriatic Microplate and the Eurasian Plate from the Late Jurassic until the present day [15–18]. Folded and overthrust Upper Palaeozoic, Mesozoic and Cenozoic carbonate deposits predominate in the External (Karst) Dinarides, including Velebit Mountain. Velebit Mountain (145 km long, with the highest peak of 1757 m asl) is declared as a Nature Park, with two strictly protected areas: National Parks Northern Velebit and Paklenica. The geology of Velebit Mountain is well described in [20–32], as well as the geology of the two Nature Parks in [33,34].

The investigated caves are located in the Northern Velebit National Park (Slovačka Cave—see SL in Figure 1), and in southern Velebit, within the Crnopac Cave System (former Kita Gaćešina Cave—see KG in Figure 1). The geology of the Northern Velebit National Park, with heavily tectonized Upper Triassic, Jurassic and Cretaceous carbonate limestones and dolomites, as well as prevailing Eocene–Oligocene carbonate breccias, is well described

in [32]. The geology of the southern part of Velebit and the surrounding area, with Upper Palaeozoic clastics and carbonates, Triassic and Jurassic limestones and dolomites, as well as with Eocene–Oligocene carbonate breccias, are well described in [34–38], among others.

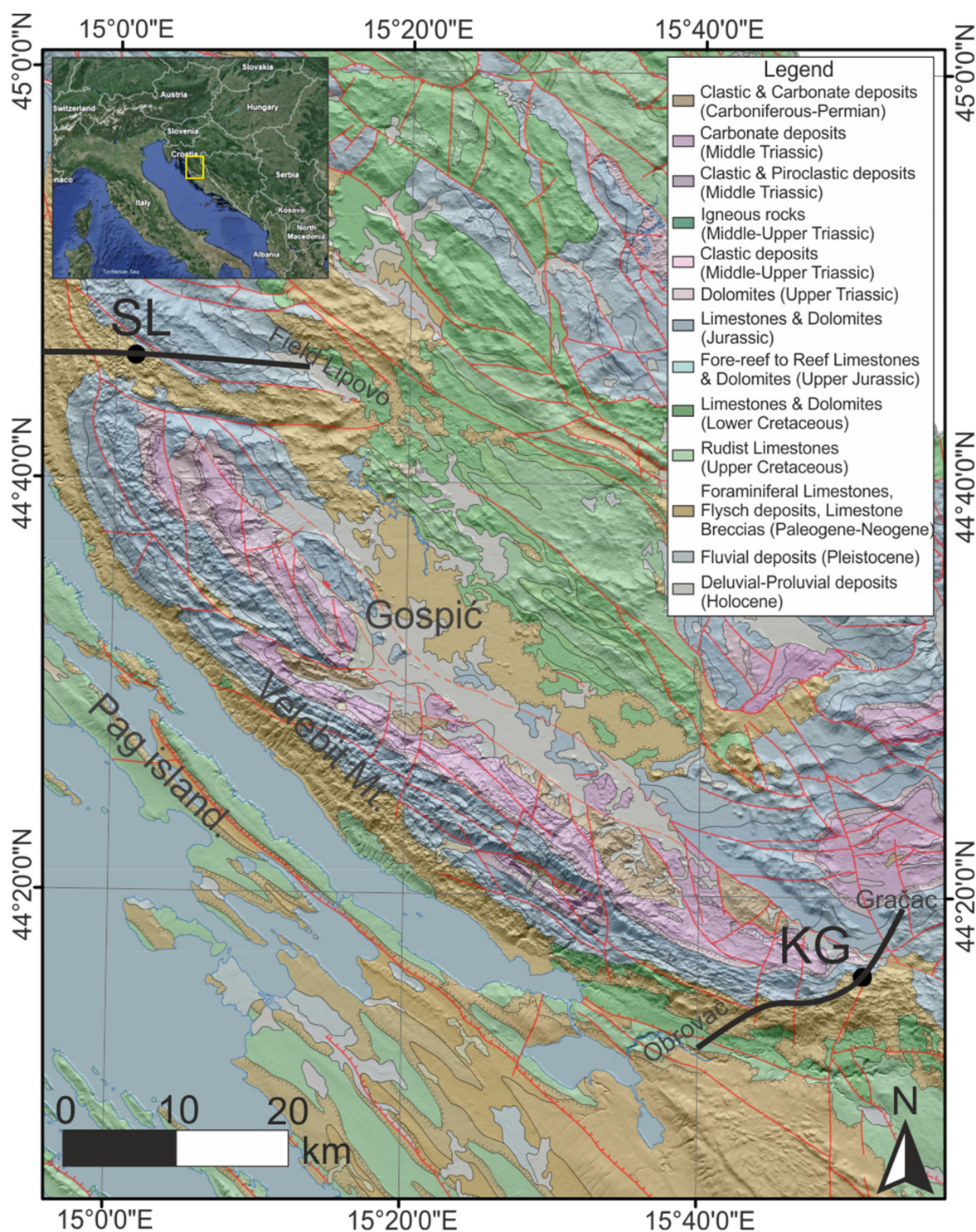


Figure 1. The inset shows the location of the research area on a regional scale. The two investigated caves are marked with black circles: “SL” represents the Slovačka Cave and “KG” represents the former Kita Gačešina Cave (today part of the Crnopac Cave System). Black lines indicate locations of the profiles presented in Figure 2. The top right corner contains a legend indicating the geological units present in the area, adapted and modified from [39,40].

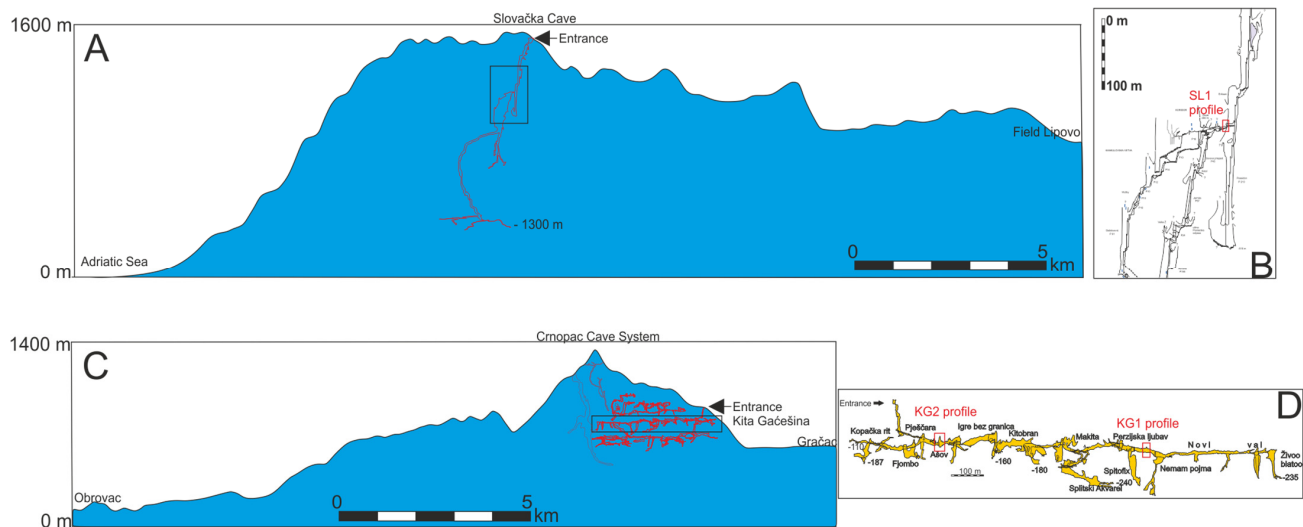


Figure 2. (A) The elevation graph highlights the entrance and profile of Slovačka Cave. (B) An enlarged section of the Slovačka Cave profile with the investigated area highlighted in red. (C) The elevation graph shows the complexity of the Crnopac Cave System, with the former Kita Gačešina Cave part highlighted in red and the entrance location indicated. (D) An enlarged section of the former Kita Gačešina Cave profile, highlighting the sampled locations. The profiles of Slovačka Cave and the Crnopac Cave System are schematically illustrated with an exaggerated vertical scale.

3. Materials and Methods

The study commenced by measuring magnetic susceptibility using the Kappameter KM-7 device on one profile in Slovačka Cave and two profiles within the Crnopac Cave System (see Figure 2). Subsequently, another round of magnetic susceptibility measurements on the same samples were conducted in the laboratory using the Bartington MS2B System. Additionally, for three selected samples, each from a different profile, the X-ray powder diffraction (XRD) method was applied. The research methods are delineated in chronological order as they were utilized in the preparation of this study.

Sampling locations were selected based on accessibility and the presence of suitable vertical profiles within soft sediments. The chosen sites represented two distinct cave systems in the Dinaric Karst, with varying material sources (northern and southern Velebit Mountain). Sampling intervals were set to minimize errors from sediment layer variations: 0.5 m for KG1 and 0.2 m for KG2. For the SL1 profile, intervals were denser in the upper section (0.05 m), intermediate in the middle (0.1 m), and wider in the lower section (0.2 m). The varying intervals account for the significant variation in readings, with denser spacing in areas with greater variability.

3.1. Magnetic Susceptibility Measurement

3.1.1. Field Magnetic Susceptibility Measurement

The values obtained from in situ measurements in caves were acquired using the handheld Kappameter KM-7 device [41]. This device finds widespread use in mineral deposit research, borehole cores, and archaeology. Its specifications include a sensitivity of 1×10^{-6} SI units and an operating frequency of 10 kHz. It can withstand temperatures ranging from $-20\text{ }^{\circ}\text{C}$ to $+60\text{ }^{\circ}\text{C}$, which makes the Kappameter KM-7 a versatile tool for field measurements. It is calibrated for the idealized case in which the needle is attached to an absolutely smooth plane confining a half-space filled with a magnetically homogeneous and isotropic medium. Then the displayed value of the susceptibility is the true value. The true value of susceptibility is computed in the microprocessor from the measured, so called apparent, susceptibility.

The Kappameter KM-7 offers three measurement modes for magnetic susceptibility: individual, scanning, and remote. During field research, the individual measurement mode

was employed to capture individual readings, with the measuring needle acting as the sensor. This measurement process involves three steps. Firstly, the device was positioned at least 30 cm away from the rock (AIR1). Then, the measuring needle was aligned parallel to the rock surface to obtain the sample value. Finally, a measurement was taken again at least 30 cm away from the rock (AIR2), and the obtained sample value was recorded as the measured magnetic susceptibility.

3.1.2. Laboratory Magnetic Susceptibility Measurement

During magnetic susceptibility measurement, the Bartington sensor (Whitney, UK) generates a subtle magnetic field through alternating electric current and detects the material's magnetization within it [12]. The MS2B sensor was employed, providing magnetic susceptibility values in SI units. The sensor measures samples prepared according to specific protocols. Plastic utensils and bags were utilized for sampling to prevent contamination with metallic materials. Samples were dried for three days in a dryer, crushed, and then filled into 10 cm³ plastic vials. The MS2B sensor, a portable laboratory device, conducts measurements at two different frequencies, enabling the detection of superparamagnetic minerals, crucial for soil and rock analysis. Its calibration is continuous with the electronic standard based on diamagnetism of water. This was performed using a cylindrical 10 mL sample of distilled, de-ionised water.

The procedure on the MS2B sensor is more intricate than that on the KM-7 device. It is configured to display magnetic susceptibility in dimensionless SI units (10^{-5}). Before sample measurement, a plastic calibration vial provided by the manufacturer was used to verify the MS2B device's calibration. Samples were first measured at a low frequency (LF) of 0.46 kHz and a 0.1 range multiplier, with air and sample measurements taken sequentially. Ideal measurements exhibit a zero difference between the first and third readings; otherwise, the measurements were repeated. The device calculates volume susceptibility, indicating the ratio of sample magnetization to magnetic field (80 Am^{-1}). These values on the MS2B device are typically in the order of 10^{-5} . After low-frequency measurements, samples were measured at a high frequency (HF) of 4.65 kHz. The plastic vials were consistently oriented to minimize measurement errors [12].

The MS2B sensor finds extensive application across various fields. In geology and soil analysis, it is instrumental for individual sample assessments. In archaeology, it aids in former settlement location, stratigraphic analysis, and magnetic material identification. Additionally, it supports environmental pollution research by analyzing rock, soil, and vegetation samples. Furthermore, it is utilized in construction material testing, facilitating the determination of geological origin and assessment of overall material permeability [12].

3.2. X-ray Powder Diffraction Analysis (XRD)

Three samples were subjected to X-ray powder diffraction to ascertain their mineral composition. Samples SL1-3, KG1-14 and KG2-8 were chosen based on their magnetic susceptibility values in the respective profiles. Data processing was carried out using the X'PertHighScore program version 1.0d. The diffraction patterns of the powder were captured using a Philips diffractometer with a counter (Philips, Amsterdam, The Netherlands), employing $\text{CuK}\alpha$ radiation ($U = 40 \text{ kV}$, $I = 35 \text{ mA}$). Original sample diffraction patterns were recorded for comparison.

4. Results

4.1. Field Measurements of the Magnetic Susceptibility

Field measurements comprised magnetic susceptibility values recorded using the Kappameter KM-7 device on one profile in the Slovačka Cave in northern Velebit and two profiles in the Crnopac Cave System (former Kita Gaćešina Cave) in southern Velebit.

4.1.1. Slovačka Cave In Situ Magnetic Susceptibility Measurement

Magnetic susceptibility was measured using the Kappameter KM-7 device along with the profiles in the vicinity of the speleologist's rest stop (in Croatian, "bivak"), located 360 m from the cave entrance (see Figure 2A,B). All profiles were recorded vertically from top to bottom (Figure 3). Profile SL1 was selected because, in addition to its interesting morphology and extensive spread compared to other vertical parts of the cave, it was possible to temporarily anchor a research person above it, making sampling both safe and feasible.

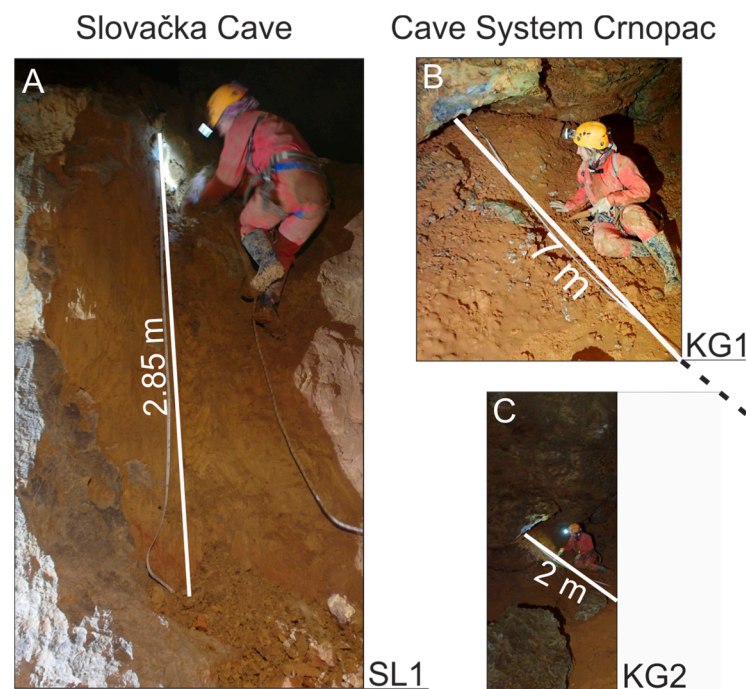


Figure 3. Measurement process of magnetic susceptibility from (A) profile SL1, (B) KG1 and (C) KG2 profiles.

At 27 locations along the profile with a total length of 2.85 m, magnetic susceptibility values were obtained and are shown in Table S1 in the Supplementary Materials. From the 27 measurement points on the profile, samples were taken, and their magnetic susceptibility was later measured again in the laboratory using the Bartington device.

On the SL1 profile, from zero meters to 0.45 m, 10 locations were measured and sampled with a spacing of 0.05 m. Their magnetic susceptibility ranged from 65.00×10^{-5} SI to 120.00×10^{-5} SI. From 0.45 m to 1.45 m, 10 measurement points were also determined, with a range of 7.00 – 88.00×10^{-5} SI. From 1.45 m to the end of the profile, seven measurement points were placed at 20-cm intervals. The lowest magnetic susceptibility in this part of the profile was -45.00×10^{-5} SI, and the highest was 21.00×10^{-5} SI, resulting in a range of measured values of up to 66×10^{-5} SI. Measurement points SL1-21, SL1-23, and SL1-26 have negative values (see Table S1 in the Supplementary Materials).

4.1.2. Crnopac Cave System (former Kita Gaćešina Cave) In Situ Magnetic Susceptibility Measurement

Two profiles were recorded and measured (Tables S2 and S3), also from top to bottom, from which soft sediments were sampled for further laboratory analysis. Both profiles are located on the first level of the Crnopac Cave System, consisting of the former Kita Gaćešina Cave, and Figure 2C shows its schematic profile, while Figure 2D represents an enlarged part of the map showing measurement locations KG1 and KG2.

Profile KG1, seven meters long, is located at the end of the “Perzijska ljubav” channel (see Figure 2D). Throughout the KG1 profile, measurement points are half a meter apart. All magnetic susceptibility values range between 36.00×10^{-5} SI and 95.00×10^{-5} SI. Measurement point KG1-6 has the lowest value and is located at 2.50 m on the profile. The lowest measurement point on the profile, KG1-15, has the highest magnetic susceptibility value.

Profile KG2 is located directly next to the “Ašov” resting point (see Figure 2D). The profile has length of two meters, and the measurement points are spaced 20 cm apart. The highest recorded magnetic susceptibility value is 34.00×10^{-5} SI, and the lowest is -14.00×10^{-5} SI. Measurement points KG2-6 and KG2-9 have negative values.

4.2. Laboratory Measurements Results

In the laboratory, magnetic susceptibility measurements were conducted using the Bartington MS2B System on the samples on which magnetic susceptibility was measured in situ using the KM-7 device (Tables S4–S6). Based on the obtained values, one sample was extracted from each profile for XRD analysis.

4.2.1. Laboratory Measurements of Magnetic Susceptibility

After magnetic susceptibility was recorded for all measurement points on profiles SL1, KG1, and KG2 using the Kappameter KM-7 device, soft sediment samples were collected. These samples were dried and then crushed in the laboratory (detailed procedure described in Section 3). Subsequently, their magnetic susceptibility was measured using the Bartington MS2B device. Magnetic susceptibility was measured at two frequencies, lower (0.465 kHz) and higher (4.65 kHz).

On the first profile from the Slovačka Cave (SL1), no negative values of magnetic susceptibility were recorded (see Table S4). At the lower frequency, values ranged from 6.60 to 99.40×10^{-5} SI. The lowest value was recorded on sample SL1-27, at the lowest point on the profile. The highest value of magnetic susceptibility corresponds to sample SL1-7. At the higher frequency, values increase from 6.50×10^{-5} SI on sample SL1-27 to 86.40×10^{-5} SI on sample SL1-7 (see Figure 4A).

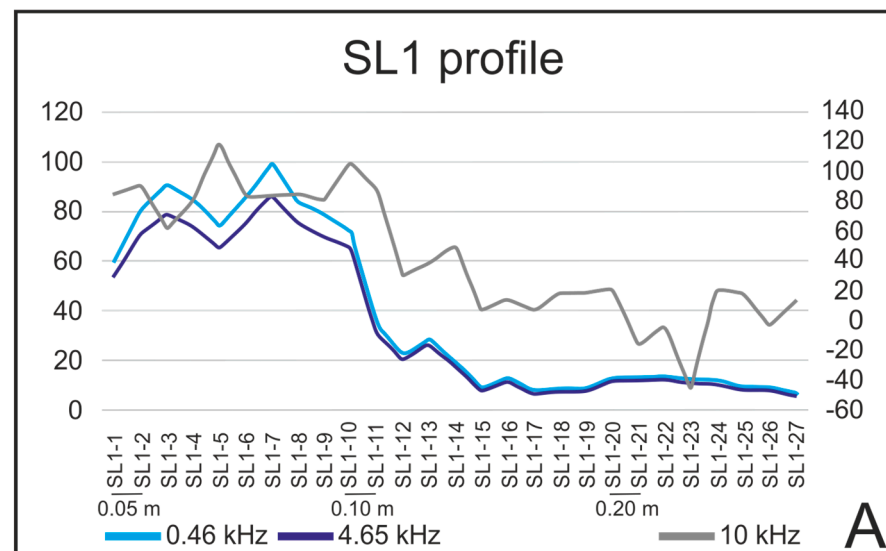


Figure 4. Cont.

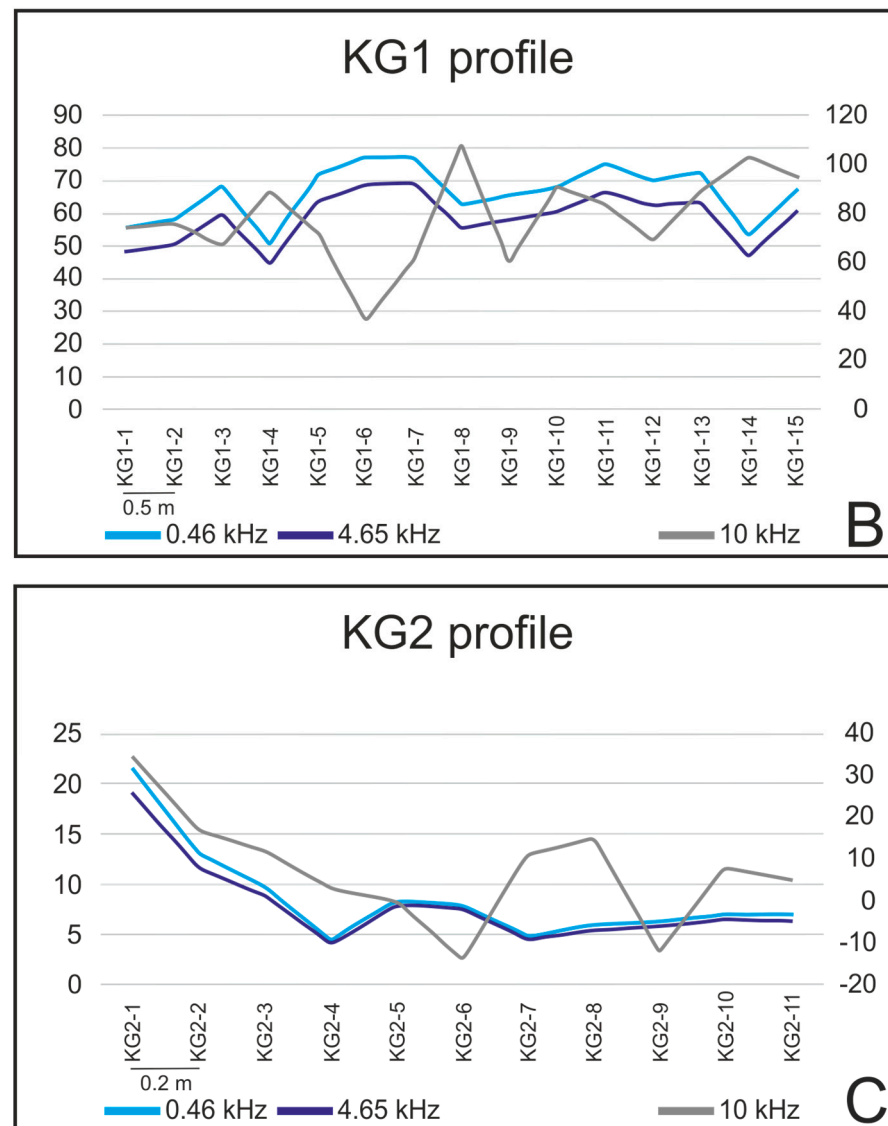


Figure 4. Magnetic susceptibility values obtained along the profiles (A) SL1, (B) KG1 and (C) KG2 using the Bartington device in the laboratory (light and dark blue), and in the field (grey). Left *y*-axis refers to laboratory measurements at 0.46 and 4.65 kHz frequencies, and the right *y*-axis refers to values measured in situ at 10 kHz. In the SL-1 profile samples SL1-1–SL1-10 have distance of 0.05 m, SL1-11–SL1-20 have 0.1 m, and SL1-21–SL1-27 have 0.2 m. Profile KG1 has samples with 0.5 m distance, while KG2 profile 0.2 m.

The measured values of magnetic susceptibility at two different frequencies on profile KG1 in the Crnopac Cave System are shown in Table S5 (see the Supplementary Materials). At a frequency of 0.46 kHz, a range of values from 51.00 to 77.20×10^{-5} SI was obtained. The lowest value was recorded in sample KG1-4, and the highest in samples KG1-6 and KG1-7 (see Figure 4B). At the higher frequency, values ranged from 44.80×10^{-5} SI to 69.30×10^{-5} SI. The lowest value of magnetic susceptibility was recorded on sample KG1-4, and the highest on sample KG1-7.

The values of magnetic susceptibility obtained at double frequency on samples from profile KG2 are shown in Table S6. Registered values at the lower frequency ranged from 4.50 to 21.40×10^{-5} SI, while at the higher frequency from 4.00 to 19.00×10^{-5} SI (see Figure 4C). At both frequencies, sample KG2-4 has the lowest value, and sample KG2-1 has the highest value.

4.2.2. XRD Analysis

The qualitative mineral composition of samples SL1-3, KG1-14, and KG2-8 was determined by analyzing the powder diffraction patterns (XRD), as shown in Table 1. The mineral abundance was determined semi-quantitatively. In sample SL1-3 taken from the Slovačka Cave profile, the most abundant minerals are 14 angstrom (Å) phyllosilicates. Additionally, kaolinite, quartz, calcite, goethite, and opaque minerals are present in significant amounts. Gibbsite and an amorphous component are minimally represented in the sample. It is assumed that hematite, anatase, chlorite, potassium feldspars, and irregular mixed-layer minerals are also present. Their proportions are very small, and their presence cannot be reliably confirmed.

Table 1. List of minerals and their representation in samples SL1-3, KG1-14, and KG2-8 determined by XRD. Mineral abbreviations after [42].

	SL1-3	KG1-14	KG2-8
calcite (Cal)	presence/high	high/very high	absence
siderite (Sd)	absence	possible	absence
quartz (Qz)	high	presence/high	very high
plagioclase (Pl)	absence	absence	possible
K-feldspar (Kfs)	possible	possible	possible
goethite (Gth)	presence/high	presence	Gth and/or Hem presence
hematite (Hem)	possible	possible	
gibbsite (Gbs)	presence	presence	absence
anatase (Ant)	possible	possible	absence
magnetite (Mag)	absence	possible	absence
unidentified mineral (X1)	absence	absence	presence
unidentified mineral (X2)	absence	presence	absence
mica (Mca)	presence/high	high	possible
mixed layer/irregular minerals (MM/IM)	IM possible	IM possible	possible
kaolinite (Kln)	high	Kln and/or Chl high	possible
chlorite (Chl)	possible		possible
14 Å minerals (14 Å)	high/very high	Vrm, Sme, MM high	absence
amorphous component (AC)	presence	presence	possible

From the first profile measured in the Crnopac Cave System, sample KG1-14 was selected for X-ray powder diffraction analysis. Calcite predominates in composition (see Table 1). Significant amounts of 14 Å phyllosilicates (vermiculite, smectite, mixed-layer minerals), kaolinite and/or chlorite, opaque minerals, and quartz were observed. Additionally, minor amounts of goethite, gibbsite, an amorphous component, and an unidentified mineral X2 are present in this sample. Some minerals (siderite, potassium feldspars, hematite, anatase, magnetite, and irregular minerals) are also considered as potentially present, but they cannot be certainly identified.

On the second profile in the Crnopac Cave System, sample KG2-8 was chosen due to its suitable texture for analysis using this method. Quartz is predominant in the composition of this sample. Goethite and/or hematite, along with an unidentified mineral X1, are less abundant minerals in this sample (see Table 1). Plagioclases, potassium feldspars, opaque minerals, kaolinite and/or chlorite, and the amorphous component were presumed to be present in the mineral composition of sample KG2-8, but without additional analyses, their presence cannot be reliably asserted.

5. Discussion

Magnetic characteristics are rarely explored in cave environments with a carbonate origin. Since allogenic cave sediments in the Dinaric Karst have shown the presence of heavier mineral compositions [10], as in caves of similar origin around the world [43], this research aimed to determine whether magnetism can be effectively measured in a cave environment and to compare a portable measuring device with a commonly used laboratory device.

Magnetic susceptibility values measured in Slovačka Cave and the Crnopac Cave System using the Kappameter KM-7 device differ significantly from those obtained in

the laboratory with the Bartington MS2B device (see Figure 4, and Tables S1–S6). This discrepancy is further supported by the statistical analysis (see Table 2), with the KG1 profile showing the largest differences. However, the correlation coefficient and r-squared indicate low to moderate correlation with the laboratory values. Furthermore, evidenced errors (RMSE and MAE) from 16 to 30×10^{-5} SI for SL1 and KG1 profiles, while for KG2 errors are lower than 10×10^{-5} SI. Therefore, the KG2 profile has the closest distribution of magnetic susceptibility values compared to the values measured in the laboratory (see Table 2). A comparison of low and high laboratory frequencies indicates that there are no superparamagnetic minerals present.

Table 2. Pearson’s correlation coefficient (Cc), root mean square error (RMSE), mean absolute error (MAE) and r-squared (RSQ) calculated between values obtained at three different frequencies: 10 kHz from in situ measurements, and 0.46 and 4.65 kHz from the laboratory analysis.

	Profile	10 kHz/0.46 kHz	10 kHz/4.64 kHz	0.46 kHz/4.64 kHz
Cc	SL1	0.8415	0.8461	0.9997
	KG1	−0.4951	−0.4829	0.9973
	KG2	0.6726	0.6528	0.9988
RMSE	SL1	22.9418	24.4087	5.8791
	KG1	26.1759	30.0549	7.6723
	KG2	10.4041	0.4909	0.9723
MAE	SL1	16.6370	18.0074	3.8444
	KG1	20.7800	25.1400	7.6267
	KG2	7.9091	8.2545	0.7455
RSQ	SL1	0.7082	0.7159	0.9994
	KG1	0.2452	0.2332	0.9946
	KG2	0.4524	0.4262	0.9976

Discrepancies between the values recorded by the two devices are anticipated, given that each device operates at different frequencies. However, even the statistical parameters reveal distinct patterns within the values. These findings suggest that the KM-7 device is highly sensitive to cave environments. Nevertheless, this in situ device proves to be sufficiently precise and accurate for preliminary investigations, allowing for the examination of profiles with measurable changes in magnetic susceptibility values on site.

Profile SL1, located near the entrance of the Slovačka Cave (see Figure 2) is densely measured and significant variations in magnetic susceptibility values are determined. The highest values were obtained within the first 0.5 m of the profile, up to 99.4×10^{-5} SI units. In the interval from 0.5–1.0 m of the profile, values constantly decrease to 20×10^{-5} SI units, and further are constant. Sample SL1-3 has one of the highest measured magnetic susceptibility values and comprise the following minerals: goethite, gibbsite, kaolinite, as well as various phyllosilicates, including micas. Due to metallic ions in their composition, these minerals are paramagnetic, even ferrimagnetic to anti-ferrimagnetic. Below sample SL1-10, having the highest measured value along the profile, mainly carbonate sediment appeared toward the end of profile (see samples SL1-11 and further in Figure 4A). Consequently, these sediments are diamagnetic and non-magnetic.

Along the seven-meter long KG1 profile measured in the Crnopac Cave System (former Kita Gačešina Cave), magnetic susceptibility values are between 50.0 – 80.0×10^{-5} SI units (see Figure 4B). In sample KG1-14, the following minerals have been determined by XRD: calcite, quartz, goethite, gibbsite, kaolinite, chlorite, and micas. In sample KG1-14 the lowest magnetic susceptibility value has been measured: 53.3×10^{-5} SI units, still indicating minerals with metal ions in its mineral composition.

The second profile (KG2) measured in the Crnopac Cave System is two meters long, and it is located closer to the cave entrance, compared to profile KG1 (see Figure 2). Measurements were taken with 20 cm distance between sampling points. Except for the first measuring point, the measured magnetic susceptibility values are very low (10×10^{-5} SI

units) and persistent along the profile. Diamagnetic minerals are confirmed by XRD in sample KG2-8, showing sediment composition of almost completely quartz.

According to the data obtained at the SL1 profile, sediment with predominantly paramagnetic, even ferrimagnetic to anti-ferrimagnetic minerals in its composition can be distinguished at the upper third of the profile. This sediment was probably accumulated during cave development, as the residue of intensive karstification and weathering, as well as pedological processes [44,45]. In the rest of the profile, diamagnetic minerals prevail (carbonates and some quartz), developed from the underlying karst carbonate rocks. Data obtained from profiles KG1 and KG2 show evidence of re-sedimentation from various rocks and possibly of the changing climate while they were being re-sedimented. Changes in magnetic susceptibility values along the measured profiles can also be considered as a result of sediment composition variations.

The accuracy of the Bartington MS2B device is nearly 100% due to its continuous electronic standard calibration. The measured values align closely with the magnetic susceptibility values documented in similar studies [44]. Therefore, the magnetic susceptibility values recorded in this research demonstrate high stability at both low (0.46 kHz) and high (4.65 kHz) frequencies (see Figure 4, Table 2). The main obstacle for Kappameter KM-7 calibration is weathering of the surface, which affects the results considerably. The weathering effect can hardly be evaluated. Unstable cave environment conditions can influence magnetic susceptibility recordings in situ. Therefore, the results of this study suggest using the portable KM-7 device for preliminary examination of the presence of magnetic susceptibility variations along sediment profiles. However, for precise analysis, especially for climate and dating analysis, samples should be analysed with a laboratory device in an optimal environment with dry conditions.

Original samples taken in the field were analysed by XRD without previous chemical treatment procedures to enhance the visibility of some XRD peaks. Nevertheless, the results are reliable, and some questionable interpretations are successfully solved (i.e., goethite and hematite were distinguished by observing the color of the mineral powder). Finally, the density of the measurement points along the profiles should be planned carefully to obtain reliable results.

This preliminary research suggests that the measurability of magnetic susceptibility in Croatian caves within the Dinaric Karst can be performed at a satisfactory level. Future findings could provide information about the depositional history of the investigated caves. Furthermore, systematic and dense investigations of magnetic susceptibility values, and thus observations of the magnetic material changes through time, could unravel a timeline of climatic and tectonic changes.

6. Conclusions

Magnetic susceptibility measurements in Croatian cave sediments of the Dinaric Karst are possible to detect in situ, and significant changes are likely to be obtained along sediment profiles in such environments.

Magnetic susceptibility measurements along one profile in Slovačka Cave at northern Velebit Mountain, and along two profiles in the Crnopac Cave System (the former Kita Gaćešina Cave, southern Velebit Mt.) showed variations attributed to changes in the mineral composition of the sediment, determined by XRD analysis. A comparison of magnetic susceptibility values and the results obtained by XRD analysis showed that a correlation of sediment composed of metallic ions bearing minerals corresponded well with measured magnetic susceptibility values higher than 50×10^{-5} SI units. Sediments composed mainly of diamagnetic minerals (i.e., calcite and quartz) showed magnetic susceptibility values lower than 40×10^{-5} SI units. Changes in magnetic susceptibility and the presence of minerals with magnetic characteristics in the sediments may be the result of various source material in the sediments, as well as evidence of climate changes during sediment deposition.

Measurements with the Bartington MS2B device obtained precise and accurate results that were reliable for interpretation, while measurements with the Kappameter KM-7 device obtained satisfactory preliminary field results that were partly comparable to MS2B measurements and highly dependent on the design of the measurement along the profiles and especially on the rate of weathering on site.

In the future, extensive investigations, combined with field and laboratory analysis, should be performed on the several-meter long soft sediment profiles, applying dense sampling and measurement design.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14166973/s1>, Table S1: Magnetic susceptibility values recorded in situ by Kappameter KM-7 at SL1 profile in Slovačka Cave; Table S2: Magnetic susceptibility values recorded in situ by Kappameter KM-7 at KG1 profile in Crnopac Cave System; Table S3: Magnetic susceptibility values recorded in situ by Kappameter KM-7 at KG2 profile in Crnopac Cave System; Table S4: Magnetic susceptibility values recorded in laboratory by Bartington MS2B at SL1 profile in Slovačka Cave; Table S5: Magnetic susceptibility values recorded in laboratory by Bartington MS2B at KG1 profile in Crnopac Cave System; Table S6: Magnetic susceptibility values recorded in laboratory by Bartington MS2B at KG2 profile in Crnopac Cave System.

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