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Magnetic Susceptibility and Heavy Metals in Guano from South Sulawesi Caves

H Rifai[1]*, R Putra[1], M R Fadila[1], E Erni[2], C M Wurster[3]

[1] Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Indonesia
[2] Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Indonesia
[3] School of Earth and Environmental Science and Centre for Tropical Environmental Science and Sustainability, James Cook University, Australia

*rifai.hamdi@gmail.com

Abstract: Measurement of some magnetic properties have been performed on vertical profile from South Sulawesi caves (Mampu and Bubau) by using low cost, rapid, sensitive and non destructive magnetic method. The aim is to attempt to use magnetic characters as a fingerprint for anthropogenic pollution in the caves. Guano samples were collected every 5 cm at a certain section of Mampu and Bubau cave, South Sulawesi, starting from surface through 300 cm in depth of mampu Cave and 30 cm of Bubau Cave. The magnetic parameters such as magnetic susceptibility and percentage frequency dependence susceptibility were measured using the Bartington MS2-MS2B instruments and supported by X-Ray Fluoroscence (XRF) to know their element composition. The results show that the samples had variations in magnetic susceptibility from 3.5 to 242.6 x 10^{-8} m^3/kg for Mampu Cave and from 8.6 to 106.5 x 10^{-8} m^3/kg for Bubau Cave and also magnetic domain. Then, the XRF results show that the caves contain several heavy metals. Magnetic and heavy metal analyses showing that the magnetic minerals in caves are lithogenic (Fe-bearing minerals) in origin and anthropogenic (Zn content) in the caves.

1. Introduction

Guano is one of the deposits on the cave floor from the rest of the process of digestion (feces) of bats or birds containing mineral component [1]. Deposits of guano mostly contain carbon, nitrogen, phosphate or sulphate minerals [2]. Not infrequently chitin substance ($C_{18}H_{26}N_2O_{10}$) could be found in bat guano in large quantities [3]. Chitin derived from insect fragment, the structural component from bat feces. The sediment of guano will undergo deposition a few meters after thousands of years [1].

During the process of precipitation in the cave for thousands of years, guano could record environmental changes that occur for pasttime [3]. Environmental changes stored in the cave can be seen from variation of magnetic mineral concentration of guano. Despite the presence of magnetic minerals in sediments is very small, but has a great influence and can serve as proxy for environmental change [4]. The magnetic minerals transport process in the cave occur in wet and or dry state through water, wind and animal cave [5].

The magnetic mineral properties can be determined by using magnetism method [6]. Magnetic susceptibility is described as the ratio of total magnetization induced to the intensity of the magnetic field generating magnetization [7,8]. Specific mass magnetic susceptibility (χ) is a function of concentration, grain size and mineralogical mineral magnetic found in the sediment [9]. Measurement of magnetic properties using magnetic susceptibility can identify magnetic mineral concentrations due to rapid, cost-effective, efficient, non-destructive, and affordable measurements [7,4]. Magnetism methods have been utilized into a wide range of environments to provide a fast, low cost and sensitive characterization of sediments [10]. Environmental alterations have been well documented from lake sediments [11,17], marine sediments [12,16] and archaeological [13], based on magnetic mineral properties.

Magnetic susceptibility may be affected by elemental composition especially Fe. The Fe content in the guano sample is proportional to the magnetic susceptibility value increase [7]. In this study, we measured the guano from Mampu and Bubau caves using magnetic susceptibility test and X-Ray Fluorescence (XRF) test. Then the magnetic parameters will be compared with the chemical method. The measurement result is expected to be a proxy for environmental change.

2. Methods

Guano sampling was carried out from two sites in South Sulawesi. The both sites are located in Mampu cave (4^o 32' S, 120^o 22'E) and Bubau cave (3^o 52' S, 119^o 89'E). The samples were taken vertically with 5 cm intervals for Mampu cave depth until 300 cm and Bubau cave depth until 30 cm.

Figure 1. Location of sampling site

The samples were packed into polyethylene bags then shipped to Geophysics Laboratory in State University of Padang. In the laboratory, guano samples were opened from polyethylene bags and placed inside a tightly secured cylindrical plastic holder.

Firstly, all samples were treated for mass-specific magnetic susceptibility measurements by Bartington MS2B instrument. Measurements of magnetic susceptibility were performed at two different frequencies, 0.47 kHz for low frequency magnetic susceptibility (χ_{LF}) and 4.7 kHz for high frequency magnetic susceptibility (χ_{HF}) with the 1.0 sensitivity setting. Each sample was measured three times to obtain average value with an air reading before and after each series for drift correction.

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The mass spesific frequency dependent susceptibility χ_{FD} could be obtained from percentage ratio $\chi_{LF} - \chi_{HF}$. This parameter can detect superparamagnetic grains.

To be compared with magnetic susceptibility data, selected guano samples were examined with chemical method using X-Ray Fluorescence (XRF). The analysis of XRF was performed in order to obtain element composition of mineral magnetic containing in guano. XRF measurements were carried out by using PANalitical type Epsilon 3 at Chemical Laboratory in State University of Padang. The XRF samples were guano from representative samples from upper section of the cores from Mampu cave and Bubau cave.

3. Results

3.1 Magnetic Susceptibility

Figure 2 shows relation of magnetic susceptibility profile in low frequency (χ_{LF}) and frequency-dependent susceptibility (χ_{FDS}) from Mampu and Bubau cave. The χ_{LF} profile of Mampu cave could be divisible by two zones. High susceptibility zones were represented in upper from surface until 10 cm. It shows range value between 242.6 x 10^{-8} m^3/kg and 124 x 10^{-8} m^3/kg. Higher magnetic susceptibility value could be founded in surface. Low susceptibility zones could be seen from depth of 20 cm until 300 cm with range between 37.9 x 10^{-8} m^3/kg and 3.5 x 10^{-8} m^3/kg. Lower magnetic susceptibility value could be founded in 300 cm. Most of magnetic susceptibility values below 100 x 10^{-8} m^3/kg. After 100 cm depth, values of χ_{LF} has a relative steady with low value and there s no significant change. While values of χ_{LF} in Bubau cave is different than Mampu cave. Magnetic susceptibility in surface tends to be low value of 20.1 x 10^{-8} m^3/kg. In contrast to 20 and 25 cm depth, χ_{LF} value tend to increase strongly with high value of 98.6 x 10^{-8} m^3/kg. Then decreased significantly at a depth of 30 cm with lowest value of 7.4 x 10^{-8} m^3/kg.

Guano samples from Mampu cave has varying χ_{FDS} values with lowest value 1.65 % to highest value 35.53 %. Frequency dependent susceptibility value (χ_{FDS}) on Figure 2 shows a more complicated trend across section. There are many maximum peaks of χ_{FDS} and fluctuative each sequence on Mampu cave. The Maximum χ_{FDS} values (> 10%) depicted at 5cm, from 30 cm to 40 cm, 55 cm, 65 cm, 110 cm, 140 cm, 175 cm to 185 cm, 220 cm, 240 cm, 270 cm, 280 cm, and 300 cm.The are two peaks value (>30%) observed at 215 cm and 250 cm depth. This case could be considered as erroneous measurements [7]. The χ_{FDS} profile of Bubau cave shows variation values from 0 % to 8.25 %. It seems different with χ_{FDS} values with Mampu cave. There is no significant change of χ_{FDS} values in the Bubau cave. Generally χ_{FDS} values increase from 10 cm to 25 cm then decrease strongly until value of 0 %. On χ_{FDS} value of 0 %, it also could be considered as error in measurement.

Figure 3 and 4 explain relation of χ_{FDS} % versus χ_{LF} showing guano samples in each Mampu cave and Bubau cave. The χ_{FDS} values which are smallest or closer to zero (< 2%), usually dominated by multidomain (MD) grains. Values range between 2 - 10% indicates mixture of stable single domain (SSD) and superparamagnetic (SP). Values which are greater than 10 % indicates superparamagnetic (SP) [7].

Dissemination of grains size each section in Mampu cave evenly. Generally, most of grains size in Mampu cave and Bubau cave on the low magnetic susceptibility values. Grains size of sample from Mampu cave are largely dominated by mixture of SSD and SP magnetic grains, while grains size of sample from Bubau cave consist of MD and mixture of SSD and SP magnetic grains.

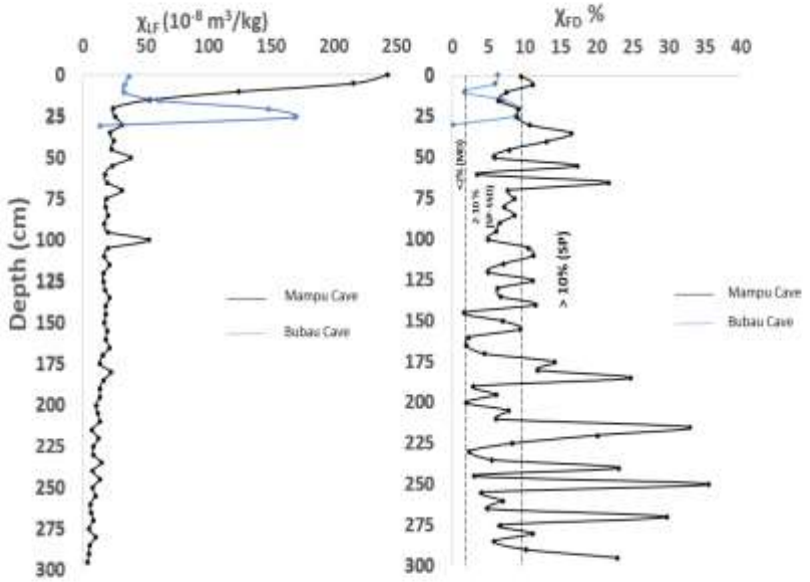

Figure 2. The magnetic susceptibility value in low frequency (χ_{LF}) and frequency-dependent susceptibility (χ_{FDS}) versus depth from Mampu and Bubau cave.

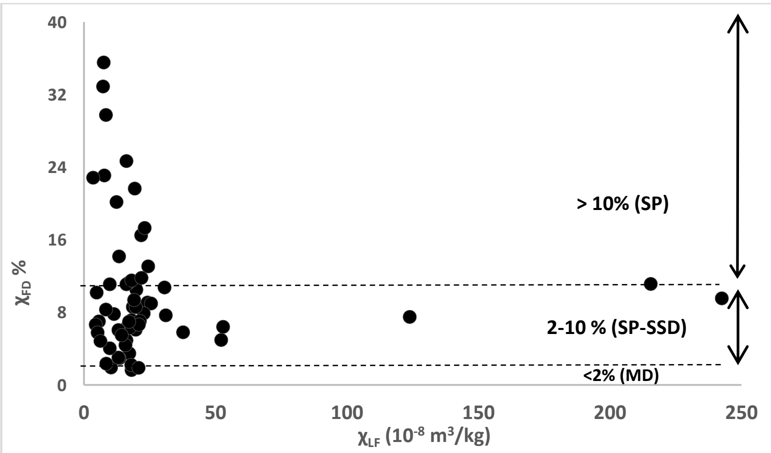

Figure 3. χ_{FDS} % versus χ_{LF} of guano from Mampu cave, South Sulawesi.

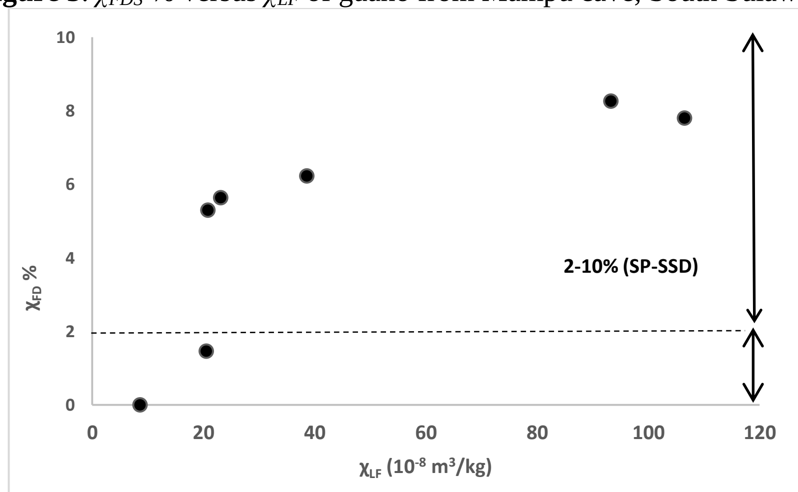

Figure 4. χ_{FDS} % versus χ_{LF} guano from Bubau cave, South Sulawesi.

3.2 Geochemistry

Table 1 shows XRF results that represent variation of element composition of surface sample from both caves. Data from XRF shows presence of element such as (Fe and Ni) which are part of ferromagnetic elements, paramagnetic (K, Mg, Mn, Ti, Al and Ca) and diamagnetic (Pb, Cu and Zn). Ca is a high concentration element with percentage 54.822% in Mampu cave and 33.294% in Bubau cave. While Pb is a low concentration element found in the Mampu cave with percentage 0.004% and 0.002 % Bubau cave. Concentration S is not present in the Mampu cave than Bubau cave with percentage 3.372%. Concentration of Fe in the Mampu cave is greater (7.45%) than Bubau cave (3.379 %).

Table 1. XRF results showing element composition.

Composition Element	Mampu Cave %	Bubau Cave %
Mg	2.415	6.665
Al	6.256	3.243
Si	8.552	14.153
P	15.067	16.428
S	-	3.372
Cl	0.118	0.713
K	0.399	16.936
Ca	54.822	33.294
Ti	0.707	0.472
Cr	0.041	0.011
Mn	0.387	0.189
Fe	7.45	3.379
Ni	0.021	0.013
Cu	0.405	0.134
Zn	0.712	0.284
Pb	0.004	0.002

4. Discussion

As comparation to magnetic susceptibility value of above 250 x ^{8} m^3/kg 10 in surface obtained from cave sand in Western Cape, South Africa [14]. High magnetic susceptibility in Mampu cave (above 100 x 10^{-8} m^3/kg) in upper section could be indicated high concentration of ferrimagnetic in the guano deposits. By looking at the condition in the Mampu cave, the cause may come from anthropogenically altered material occurred through human activities. It also confirmed by any archaeogical remains in the cave. The enhancement of magnetic susceptibility value could relate human occupation that took place in the Maronia cave, Greece where tt 15 cm and 100 cm depth have peaks of magnetic susceptibility value of 53 x 10^{-8} m^3/kg and 52.2 x 10^{-8} m^3/kg. These layers also could be indicated by records of the anthropogenic influence. Moreover, magnetic susceptibility could be good proxy for intensity of human activity and degree of magnetic susceptibilty enhancement appears to be a good indicator of occupation longevity and intensity. The low magnetic susceptibility values in Mampu cave occur naturally without influenced by human activity [14].

The magnetic susceptibility pattern in Bubau cave look different and not similar than Mampu cave. The Low magnetic susceptibility value (χ_{LF}) founded in surface. Bubau cave seems has not any archaeological remains. It is difficult to determine magnetic susceptibility pattern because the samples taken only to depth of 30 cm and not the same as the depth of Mampu cave. But it looks that Bubau cave is natural and not found evidence which is affected by anthropogenic influence. In other words, guano samples of Bubau cave formed by climate alteration.

Data from geochemical analysis by using XRF, shows relatively high concentration of calcium in sediment. Calcium is one of element of gypsum ($CaSO_4$.$2H_2O$) found in the cave sediment [13]. Mampu cave and Bubau cave are mostly composed of several high concentration elements including paramagnetic. In addition, there is good correlation between magnetic susceptibility value with concentration or abundance of magnetic mineral particularly Fe. Concentration of Fe in the Mampu cave is greater than Bubau cave. This is what causes susceptibility value of Mampu cave higher than Bubau cave. Heavy metal shows as a carrier of magnetic properties into the cave. Generally, it could be conclude that when magnetic susceptibility and metal concentrations are both high particularly Fe, mostly the source indicated from anthropogenic influence [18].

5. Conclusion

Magnetic susceptibility value on guano samples from mampu cave is higher than Bubau cave. This is influenced by concentration of Fe that causes the increase of magnetic susceptibility value. Variation of susceptibility from Mampu cave tend to decreasing after 10 cm depth. Grains size from both caves predominantly consist of mixture SSD and SP magnetic grains.

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