A review of the magnetic susceptibility of guano deposits in caves

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Abstract. The study of environmental magnetic methods using magnetic susceptibility parameters in cave guano deposits has not been widely discussed, especially in Indonesia. This method is relatively inexpensive, fast, affordable, and non-destructive. Environmental magnetism is associated with environmental changes such as climate change and anthropogenic effects. After a brief introduction to the fundamental of environmental magnetism, we describe several case studies regarding the properties of magnetic minerals and magnetic grains. This study was complemented with XRF results to identify the elemental composition.

1. Introduction

Environmental magnetism is a method used to study the magnetic properties of sediments. Deposits can record and store information on changes in ancient environments [1-2]. These changes include climate change [3], anthropogenic effects [4], and vegetation [5].

Environmental magnetic studies on various suspended sediments in lakes [6-7], rivers [8-10], sea [11], soils [12-13], and cave sediment have been done [14]. Cave sediments such as guano are bat or bird droppings that settle over a long period [15]. Bat guano is clastic sediment. Clastic sediment is sediments carried from the external environment into the cave. Guano is rich in phosphate minerals associated with clay, quartz, gypsum [16-19].

Also, bat guano contains heavy metals [20]. Therefore, guano contains magnetic minerals, although not on many levels, they contribute as an indicator of environmental change [21]. One of the parameters used in environmental magnetism is magnetic susceptibility [22-24]. Magnetic susceptibility describes the properties of magnetic minerals contained in deposits.

Mineral properties can find out based on the type [25-27], composition, shape, grain type, and grain size of magnetic minerals. The advantages of using this method are that it is relatively cheap, fast, non-destructive, and affordable [28-29]. During the last few years, especially in Indonesia, not many have studied the application of environmental magnetism to guano, especially cave guano. Therefore, in this paper, we carry out an in-depth study related to the basic methods of environmental magnetism, the nature of guano magnetic minerals, and guano geochemistry.
2. Fundamentals of Environmental Magnetism

Environmental magnetism (environmental magnetism) is one of the fields that applies the rock magnetic methods. Other fields of rock magnetism methods that have developed are paleomagnetism, volcanomagnetism, biomagnetism, magnetoclimatology, agromagnetism, and exploration/industry. One of the magnetic parameters is magnetic susceptibility [30-32]. Mineral properties depend on the type, concentration, composition, shape, grain type, and grain size [33-34].

Magnetic susceptibility is the degree to which a material is magnetized when an external magnetic field was applied. If the magnetization ($\mathbf{M}$) is parallel and proportional to the external magnetic field ($\mathbf{H}$), then the constant for proportionality expressed in magnetic susceptibility per unit mass ($\chi$). This can be expressed through equations $\mathbf{M} = \chi \mathbf{H}$. The equation shows that for parallel and proportional $\mathbf{M}$ and $\mathbf{H}$, magnetic susceptibility is a scalar quantity.

Magnetic susceptibility depends on the type of magnetic minerals, magnetic mineral concentration, magnetic mineral composition, grain size and shape, and domain. There are four magnetic domains, namely multi-domain (MD), single domain (SD), pseudo-single domain (PSD), and superparamagnetic (SP). [35-36]. Changes in the ratio of SP grains among other grains in rock, soil, or sediment are thought to be a reflection of changes that occur in the environment. A relatively new study is cave guano sediment. [20].

Information about the presence of SP grains is known by measuring the magnetic susceptibility at two different frequencies. This is caused by the nature of SP grains are sensitive to changes in frequency. The difference in magnetic susceptibility within a decade of different frequencies is known as the frequency-dependent susceptibility (FDS) parameter. FDS represent with magnetic susceptibility per unit mass ($\chi_{FD}$), namely $\chi_{FD} = \chi_{LF} - \chi_{HF}$ or $\chi_{FD} (%) = (\chi_{LF} - \chi_{HF})\chi_{LF} \times 100\%$ where $\chi_{LF}$ and $\chi_{HF}$ are mass unit susceptibility at low frequencies and frequencies, respectively height [37].

Interpretation of the $\chi_{FD}$ value is <2% virtually no superparamagnetic grains, 2-10% a mixture of SP grains and SP grains that are not coarse or SP grains <0.005 m, 10-14% almost all SP grains, and >14% rare values, wrong measurements, anisotropy, weak samples or contamination. In the study of mineral magnetic properties, this method can combine with other methods such as XRD [38-40], XRF [21], SEM [41-42].

3. Magnetic Susceptibility of the Cave Guano

The study of guano magnetic minerals showed that the range of magnetic susceptibility values of guano deposits in several caves in Sumatra, Kalimantan, and Sulawesi varied (table 1). The magnetic susceptibility value at low frequency ($\chi_{LF}$) is high enough so that it has ferrimagnetic properties. However, the source of magnetic minerals in each cave is different. The high magnetic susceptibility in the upper layer of 0-5 cm Baba cave [43], Bau-Bau cave [44], Mampu cave [20] indicates an anthropogenic influence (human activity) as evidenced by the discovery of remains archeology. Meanwhile, in a Liang Besar cave [41], Bubau cave [20], Solek cave [21], the low magnetic susceptibility value indicates that the guano formed is still naturally without anthropogenic influence. In other words, it is the result of climate change. Therefore, the high and low magnetic susceptibility of guano in caves can cause by anthropogenic effects and also climate change [3-4].

Guano fluctuates in the depth variation of its susceptibility value (figure 1). The same result was also obtained by [20] that magnetic susceptibility fluctuates at various depths illustrating that the magnetic mineral concentration also varies. This variability is most likely due to being controlled by environmental changes such as climate change. If the guano sample is measured at two different frequencies, so the frequency-dependent susceptibility ($\chi_{FD}\%$) will obtain. $\chi_{LF}$ and $\chi_{FD}$ relationship to find out the domain of guano. In a study conducted by [21], the $\chi_{FD}$ value ranged from 0.13% to 3.19%. Guano in Solek cave contains multi-domain magnetic grains (MD) and a mixture of a single domain and superparamagnetic (SD-SP) (figure 2a). Meanwhile, the percentage of $\chi_{FD}$ guano in the Mampu cave ranges from 1.65% to 35.53% [20], Guano in Mampu cave contains multi-domain (MD), a mixture of a single domain (SD) and superparamagnetic (SP), and superparamagnetic (SP) grains (figure 2b). These results indicate that the low $\chi_{FD}$ guano of the Solek cave is natural, namely climate
change. Meanwhile, the high percentage of $\chi_{FD}$ guano in the Mampu cave was due to anthropogenic influences (human activities in the cave).

Table 1. Magnetic susceptibility of several caves in Indonesia.

| No. | Name of the cave                  | Magnetic susceptibility value (x10^{-8} m^3/kg) |
|-----|----------------------------------|-----------------------------------------------|
| 1   | Baba cave, West Sumatera^{[43]}  | 240.91 – 461.94                               |
| 2   | Bau-Bau cave, East Kalimantan^{[44]} | 1.61 – 3.28                                   |
| 3   | Mampu cave, South Sulawesi^{[20]} | 3.5 - 242.6                                    |
| 4   | Bubau cave, South Sulawesi^{[20]} | 8.6 - 106.5                                    |
| 5   | Solek cave, West Sumatera^{[21]}  | 86.8 - 2204.2                                  |
| 6   | Liang Besar cave, South Kalimantan^{[45]} | 11.1 – 22.4                                 |

Figure 1. The variation of magnetic susceptibility to depth in (a) Solek cave [21] (b) Mampu and Bubau caves [20]

4. Geochemistry of Guano Caves
The XRF method is a complementary method to validate the magnetic susceptibility results. Based on XRF guano data from Solek cave, Mampu cave, and Bubau cave there are differences in elemental composition [20-21] (table 2). Solek cave contains quite high Al and Si elements. These results indicate that guano contains quartz and phosphate minerals. Meanwhile, guano in Mampu and Bubau caves contains high Ca and P elements. These results indicate that guano contains phosphate and gypsum minerals (CaSO$_4$.2H$_2$O).

The content of heavy metals (Cu, Zn, Cr, Pb, Fe) in the guano of the Mampu cave was higher than that of Solek cave and Bubau cave. These results illustrate the presence of anthropogenic influences in Mampu cave. Meanwhile, the Solek cave and Bubau cave were affected by climate change. The results of this study [20-21] agree with the magnetic susceptibility study.
Through this study, the presence of phosphate mineral content in guano can be identified. Phosphate minerals such as hydroxylapatite \([\text{Ca}_5(\text{PO}_4)_3(\text{OH})]\), ardealite \([\text{Ca}_2(\text{SO}_4)(\text{HPO}_4)\cdot 4\text{H}_2\text{O}]\), brushite \([\text{Ca}(\text{PO}_3\text{OH})\cdot 2\text{H}_2\text{O}]\), taranakite \([\text{K}_3\text{Al}_5(\text{PO}_3\text{OH})_6(\text{PO}_4)_2\cdot 18\text{H}_2\text{O}]\) \cite{17, 19, 42, 43}. With this mineral phosphate content, the guano has the potential as an organic fertilizer \cite{48-49}.

![Figure 2](image1.png)  
(a) Solek Sumatran cave \cite{21}  
(b) Mampu cave South Sulawesi \cite{20}

**Table 2.** The elemental composition of guano in several caves in Indonesia

| Element | Solek cave\cite{21} | Mampu cave\cite{20} | Bubau cave\cite{20} |
|---------|---------------------|---------------------|---------------------|
| Mg      | 1.134               | 2.415               | 6.665               |
| Al      | 26.217              | 6.256               | 3.243               |
| Si      | 45.973              | 8.552               | 14.153              |
| P       | 3.244               | 15.067              | 16.428              |
| S       | -                   | -                   | 3.372               |
| Cl      | -                   | 0.118               | 0.713               |
| K       | 2.358               | 0.399               | 16.936              |
| Ca      | 3.39                | 54.822              | 33.294              |
| Ti      | 1.898               | 0.707               | 0.472               |
| Cr      | -                   | 0.041               | 0.011               |
| Mn      | -                   | 0.387               | 0.189               |
| Fe      | 13.813              | 7.45                | 3.379               |
| Ni      | -                   | 0.021               | 0.013               |
| Cu      | -                   | 0.405               | 0.134               |
| Zn      | -                   | 0.712               | 0.284               |
| Pb      | -                   | 0.004               | 0.002               |

5. **Summary and Study Benefits**

The magnetic susceptibility of several cave guano deposits in Indonesia has been studied. Guano contains ferrimagnetic minerals. Magnetic minerals contain magnetic grains such as multi-domain (MD), single-domain and superparamagnetic (SD-SP) mixtures, and superparamagnetic (SP). Also, from XRF data, guano deposits contain quartz, gypsum, and phosphate minerals. Thus, the source of magnetic minerals is known. The phosphate content is high enough so that it has potential as an organic fertilizer.

Based on this study, we can study magnetic mineral sources such as ancient climate change and anthropogenic effects (human activity in caves). This study is easy to integrate with the X-Ray Fluorescence (XRF) method. For further research, it is necessary to study using other complementary
methods such as X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to study mineral types, grain size, and mineral morphology.

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