



Analysis of the heavy metal content of Mimpji Cave sediments in the Maros Karst Area, South Sulawesi, Indonesia

Vistarani Arini Tiwow

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Makassar, Indonesia

Abstract

Research has been carried out to determine the heavy metal content of sediments in the Mimpji Cave in the Maros Karst Area. Cave sediment samples were taken at three points, namely at the mouth of the cave, the middle of the cave, and the cave's exit. The testing method used on cave sediment samples is X-ray fluorescence (XRF) to determine the heavy metal content. The results show that the cave sediment samples contain heavy metal elements such as Fe, Ag, Ni, Zn, V, Pb, Cu, Cr, Zr, Ga, Co, and Ir. Lead (Pb) at 11.4 g/cm^3 is the heavy metal element with the highest density. Heavy metals are indicated as materials that carry magnetic properties in caves. The source influences the high concentration of heavy metals. The elements contained in the sediment are indicated to be caused by geological factors, namely from the weathering of cave-forming rocks; climate change factors, namely material from outside the cave, which is transported into the cave via wind; and anthropogenic factors, namely human activity. In the sediment samples, rare earth metals such as lithium (Y), vital materials with strategic potential, were also found.

Keywords: Sediment, heavy metals, Mimpji cave, Maros karst area

Introduction

Karst is often found in many areas with carbonate rocks or other rocks that are readily soluble. As a result of the dissolution process, a unique hydrological system is formed. The hydrological system of karst areas is greatly influenced by secondary porosity, which causes water to enter the underground flow system and cause dry conditions on the surface. Karst areas in Indonesia have a strategic function in absorbing carbon dioxide (CO₂). It is related to Indonesia's position in the tropical region, which is influenced by the global atmospheric movement system. Global atmospheric movements that influence CO₂ levels in tropical regions include movements caused by the intertropical convergence zone (ITCZ) phenomenon (Haryono & Adji, 2004)^[7].

The Maros-Pangkep Karst area has around 521 caves with stalactites, stalagmites, pillars and other cave ornaments. These are natural formations in the form of karst chambers formed in underground limestone fields. Both stand-alone and are connected to other rooms due to the dissolution process by water or geological activity that occurs in an area. Natural caves can form in extrusive igneous rocks, lava, limestone, or carbonate rocks. Most of the caves formed in Indonesia are caves formed from limestone. Most cave ornaments still form crystals; a few have already passed the crystallization stage (Achmad, 2011)^[1].

The cave ecosystem is one of the most vulnerable on earth and is where the process of adaptation and evolution of various organisms occurs (Rahmadi, 2007)^[13]. One of the caves in South Sulawesi is Mimpji Cave in Bantimurung Bulusaraung National Park, Maros Regency. Mimpji Cave is a geological site in a cave formed by natural processes. It is located in Bantimurung Hamlet, Jenetaesa Village, Simbang District, Maros Regency, South Sulawesi. This cave has become widely known to the public along with the fame of Bantimurung waterfall. This type of horizontal cave has a length of around $\pm 1,415$ meters and penetrates a karst hill (Ramdani *et al.*, 2015)^[14].

The cave sediment studied is guano, which comes from the faeces (faces) of bats that breed in Mimpji Cave and has been sedimented with soil (Rahmadhani *et al.*, 2013)^[12]. One of the microelements that influence the quality of guano is Fe (iron), which is magnetic. Iron does not come from bat droppings but rather through the transport of sediment brought from the external environment into the cave so that it accumulates and settles on the cave floor. In other words, cave sediment is associated with material that enters the cave in the summer and rain through water, wind, or animals. Apart from that, material from outside the cave can also come from human activities. Research regarding the geochemical analysis of cave sediments has yet to be widely discussed. Moreover, sedimentary deposits, especially in Indonesia, are widespread in Sumatra, Java, Kalimantan, Sulawesi, Nusa Tenggara, and Papua as cave deposits (Suwarno & Idris, 2007)^[17].

The magnetic mineral of a material, in this case guano, is influenced by the iron (Fe) content, which is a ferromagnetic element. Even though the amount of Fe in magnetic minerals is small, it can be detected. Environmental magnetic studies have proven that a material's magnetic mineral is associated with heavy metal content (Cowan *et al.*, 2017^[5]; Wnuk *et al.*, 2020)^[18]. Several studies have reported the results of heavy metal content analysis using X-ray fluorescence (XRF). Rifai *et al.* (2018)^[15] reported that Mampu Cave and Bubau Cave in South Sulawesi contain heavy metals such as Cr, Mn, Fe, Ni, Cu, Zn, and Pb. The Fe concentration in Mampu Cave (7.45%) is greater than the Fe concentration in Bubau Cave (3.379%). Bubau Cave is still natural and not influenced by anthropogenic activities, so the cave sediments were formed by climate alteration. Putra *et al.* (2019)^[11] reported that in Solek Cave, West Sumatra, Indonesia, cave sediments contain the element Fe, which is ferromagnetic; the elements Ti, Mg, Al, K and Ca, which are paramagnetic;

and Si and P, which are diamagnetic. A study of heavy metals in cave sediments was also carried out by Arsyad *et al.* (2022) [3] that the bat cave sediments of the Rammang-Rammang Karst Area contain heavy metals such as iron (Fe), zinc (Zn), copper (Cu), zircon (Zr), and neodymium (Nb). Fe is associated with other heavy metals such as Zn, Cu, Zr, and Nb.

Thus, this research aims to analyze the heavy metal content of the sediments of Dream Cave in the Maros Karst Area using the X-ray fluorescence (XRF) method. XRF is a method for determining the chemical composition of all types of materials. These materials are in the form of solids,

liquids, powders and filters. The XRF method is fast, accurate, non-destructive (does not damage the sample), and requires easy sample preparation.

Materials and Method

Sediment sampling in Mimpi, Maros Karst Area, Bantimurung Bulusaung National Park, Maros Regency (Figure 1). Samples were taken on the cave floor at the mouth of the cave, middle of the cave and exit at varying depths. The samples were cleaned, dried, crushed, and sieved with a 100-mesh sieve. The sample was weighed with a mass of 10 g and then tested for elemental content.

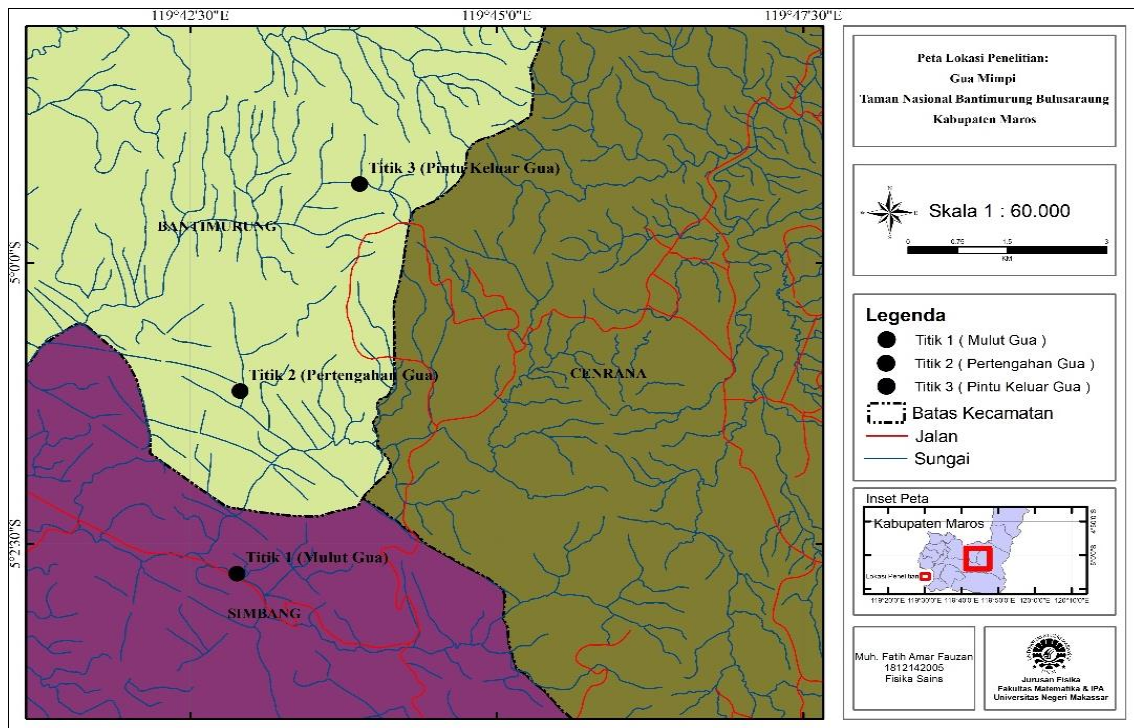


Fig 1: Sampling location

Testing of elemental content in sediments in Dream Cave using the XRF method. The tool used to analyze this material is the PANalytical Epsilon 3 XRF Instrument Spectrometer type. Testing was conducted at the Instrument Chemistry Laboratory, Department of Chemistry, FMIPA UNP. Before testing, sample preparation is carried out. Based on the ASTM library and the XRF spectrometer manual, the material's surface to be analyzed must be flat, smooth and clean. The sample's analyzed surface is cleaned using alcohol/acetone and waited until it dries. Once dry, it is placed in a plastic sample holder so that vacuum and energy calibration can be carried out, and then the sample can be tested to determine the element content.

Results and Discussion

Table 1 shows the elemental content of XRF testing results in sediment samples from the Mimpi Cave in the Maros Karst Area, South Sulawesi, Indonesia. At each sampling point based on depth, the dominant elements contained in the sediment were iron (Fe) and aluminium (Al). The element content varies at each point. The elements zirconium (Zr) and lithium (Y) were found at site one at point F3 at a depth of 8-12 cm, respectively, containing 0.264% and 0.097%. The element gallium (Ga) was found

at site 1 point F3 at a depth of 8-12 cm (0.026%) and site 2 point F19 at a depth of 32-36 cm (0.015%). The element iridium (Ir) is only found at site 3 point F21 at a depth of 0-4 cm (0.01%). Meanwhile, the element rubidium (Rb) was not found at site 1 point F1 at a 0-4 cm depth. The element cobalt (Co) was also not found at site 1.

The XRF test results show that the elements iron (Fe), nickel (Ni), and cobalt (Co) are included in the category of ferromagnetic elements. The element chromium (Cr) is included in the category of antiferromagnetic elements. The elements aluminium (Al), magnesium (Mg), titanium (Ti), calcium (Ca), manganese (Mn), potassium (K), vanadium (V), strontium (Sr), zirconium (Zr), lithium (Y), rubidium (Rb), and iridium (Ir) are included in the category of paramagnetic elements. The elements silicon (Si), phosphorus (P), silver (Ag), zinc (Zn), lead (Pb), copper (Cu), and gallium (Ga) are included in the category of diamagnetic elements. A study of cave sediment content was also carried out by Putra *et al.* (2019) [11] in Solek Cave, West Sumatra, Indonesia, that cave sediments contain the element Fe, which is ferromagnetic, the elements Ti, Mg, Al, K and Ca which are paramagnetic, and Si and P which are diamagnetic.

Table 1: Element content of Mimpri Cave sediment samples in the Maros Karst Area, South Sulawesi, Indonesia

Element		Element Content (%)					
Chemical Formula	Element Name	Site 1		Site 2		Site 3	
		F1 (0-4 cm)	F3 (8-12 cm)	F15 (16-20 cm)	F19 (32-36 cm)	F21 (0-4 cm)	F30 (36-40 cm)
Fe	Iron	55.259	54.576	48.835	50.111	54.976	49.907
Al	Aluminum	23.574	23.449	17.379	16.844	13.908	24.804
Si	Silicone	5.709	4.386	1.169	0.926	3.306	8.242
Ti	Titanium	4.427	4.234	4.57	4.705	5.138	4.082
P	Phosphor	3.281	2.336	9.981	9.612	5.811	2.395
Ca	Calcium	3.046	3.44	12.592	12.321	7.307	2.463
Mn	Mangan	1.714	2.324	0.303	0.293	1.739	2.728
Ag	Silver	1.288	3.63	3.38	3.452	5.477	3.927
K	Potassium	0.436	0.158	0.032	0.068	0.061	0.109
Ni	Nickel	0.216	0.255	0.116	0.109	0.15	0.197
Zn	Zinc	0.22	0.234	0.213	0.215	0.517	0.254
V	Vanadium	0.18	0.161	0.138	0.137	0.157	0.151
Sr	Strontium	0.179	0.127	0.625	0.515	0.633	0.116
Pb	Lead	0.164	-	0.161	0.152	0.174	0.162
Cu	Copper	0.16	0.174	0.178	0.203	0.281	0.144
Cr	Chromium	0.147	0.12	0.109	0.115	0.118	0.08
Zr	Zirconium	-	0.264	-	-	-	-
Y	Lithrium	-	0.097	-	-	-	-
Ga	Gallium	-	0.026	-	0.015	-	-
Rb	Rubidium	-	0.009	0.01	0.01	0.01	0.014
Co	Cobalt	-	-	0.209	0.196	0.227	0.225
Ir	Iridium	-	-	-	-	0.01	-

XRF analysis was carried out to identify the element content in cave sediment samples. The presence of the Fe element was identified, thought to come from the external environment transported through the wind into the cave. The Ca content is indicated to originate from carbonate rocks which contain karst minerals such as calcite (CaCO_3), aragonite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) but can also occur in other rocks formed from other water-soluble minerals such as gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) (McFarlane & Lundberg, 2018^[9]; Arsyad *et al.*, 2020a^[2]; Arsyad *et al.*, 2020b).

Table 1 also shows that the element content in the Mimpri Cave sediment samples includes heavy metals. These elements are Fe, Ag, Ni, Zn, V, Pb, Cu, Cr, Zr, Ga, Co, and Ir. These elements have a density value above 5 g/cm³. However, among all the heavy metal elements, the highest density is the element lead (Pb) at 11.4 g/cm³. The Pb element is found at all sites. At sites 2 and 3, the presence of Pb is almost at a depth of 40 cm. Heavy metals are indicated as materials that carry magnetic properties in caves. The source influences the high concentration of heavy metals. Magnetic mineral content can occur naturally due to climate factors and the location where this source acts as a contaminant (Rifai *et al.*, 2018)^[15].

The presence of high concentrations of heavy metals indicates that the environment of Mimpri Cave has changed from a natural cave to a polluted cave. The environment is categorized as polluted if changes have occurred and shifted from its original condition (Misno *et al.*, 2016)^[10]. These results align with research conducted by Rifai *et al.* (2018)^[15], who found that Mampu Cave and Bubau Cave contain heavy metals such as Cr, Mn, Fe, Ni, Cu, Zn, and Pb. The Fe concentration in Mampu Cave (7.45%) is greater than the Fe concentration in Bubau Cave (3.379%). Bubau Cave is still natural and not influenced by anthropogenic activities, so the cave sediments were formed by climate alteration. A study of heavy metals in cave sediments was also carried out by Arsyad *et al.* (2022)^[3] that the Kelelawar Cave

sediments of the Rammang-Rammang Karst Area contain heavy metals such as iron (Fe), zinc (Zn), copper (Cu), zircon (Zr), and neodymium (Nb). Fe is associated with several other heavy metals, such as Zn, Cu, Zr, and Nb. The correlation obtained is dominantly positive, where the location of the Kelelawar Cave causes the abundance of Fe in magnetic minerals in a karst environment and is also influenced by climatic factors. Fine grains of magnetic minerals are distributed into the cave via wind. Meanwhile, grains of coarse magnetic minerals come from the external environment and are transported into the cave during the rainy season.

Effect of heavy metals identified in samples on health and the environment. Iron metal (Fe) is one of the metals most commonly found in the earth's crust, a silvery-white metal that can be formed in nature as hematite. Fe metal is an essential metal whose presence in specific amounts is needed by living organisms, but excess amounts can cause toxic effects. The high Fe metal content will have an impact on human health, including causing poisoning (vomiting), intestinal damage, premature ageing, arthritis, bleeding gums, cancer, kidney cirrhosis, constipation, diabetes, diarrhoea, dizziness, fatigue, hepatitis, hypertension, insomnia and sudden death (Supriyanti & Endrawati, 2015). Manganese metal (Mn) is a metal cation with chemical characteristics similar to iron and a density of 7.86 g/cm³. In the soil, Mn is in the form of manganese dioxide compounds. Manganese is a trace nutrient that is essential for plants and animals. This metal plays a role in growth and is an essential component of the enzyme system. Manganese deficiency can result in stunted growth and disrupted nervous system and reproductive processes. In plants, manganese is an essential element in metabolic processes (Misno *et al.*, 2016)^[10].

Zirconium (Zr) is an element in nature resistant to high temperatures. Zirconium does not occur in free form in nature but in zirconium silicate in zircon (ZrSiO_4) and zirconium oxide in baddeleyite (ZrO_2). Zirconium is often

found in volcanic rocks, basalt and granite. Zirconium is not a rare element, but because it is the most common mineral, it is very resistant to weathering, and the distribution of this element is limited. Zirconium and its salts are generally low toxic. The estimated intake of food is around 50 micrograms. When it enters the body, most zirconium is not absorbed by the intestines, and when absorbed, it tends to accumulate in the bones rather than in the tissues (Junita, 2013)^[8].

Lead (Pb) is a type of metal that is soft and blackish brown and is easy to purify; in scientific language, it is called plumbum, and Pb symbolizes this metal. This metal is prevalent and widely known by ordinary people. It is due to the large amount of lead used in factories, which causes the most poisoning in living creatures. Lead is also widely used in human life to make batteries, ammunition, metal products, and medical equipment (Misno *et al.*, 2016)^[10].

Copper (Cu) in nature can be found as a free metal; this metal is widely used in factories that produce electrical equipment and glass. The heavy metal Cu is classified as an essential heavy metal, meaning that even though Cu is a toxic heavy metal, this heavy metal element is needed by the body, even in small amounts. Therefore, Cu is also included in the essential metals for humans, such as Fe and others. Cu's toxicity will only work and show its effects if this metal has entered the organism's body in large quantities or exceeds its tolerance value for dyes usually mixed with other metals (Junita, 2013)^[8].

Zinc (Zn), this metal, has a shiny bluish-white colour and is quite reactive with acids, alkali metals and other non-metals, and if it is in an impure state, it will become reactive with acids to release hydrogen. Zinc occurs widely in several minerals. Zinc is usually used as an alloy metal, for example, brass (copper+zinc). The zinc compounds that are widely used are ZnO and ZnS, which are used to make white paint, and ZnS is used to coat television picture tubes (Harling, 2018)^[6].

In the Mimpi Cave sediment samples, especially in sample F3, the element lithium (Y) had an elemental composition of 0.097% and was included in one of the rare earth metal elements. Rare earth metals are irreplaceable. It is due to the unique nature of rare earth metals, so until now, no other material has been able to replace them. If there is, the resulting ability is not as good as rare earth metals. The nature of rare earth metals, used as high-tech materials and have no substitute, makes them vital materials with strategic potential (Suprpto, 2008)^[16].

Conclusion

Mimpi Cave sediment samples from the Maros Karst Area contain heavy metal elements such as Fe, Ag, Ni, Zn, V, Pb, Cu, Cr, Zr, Ga, Co, and Ir. Lead (Pb) at 11.4 g/cm³ is the heavy metal element with the highest density. Heavy metals are indicated as materials that carry magnetic properties in caves. The source influences the high concentration of heavy metals. The elements contained in the sediment are indicated to be caused by geological factors, namely from the weathering of cave-forming rocks; climate change factors, namely material from outside the cave, which is transported into the cave via wind; and anthropogenic factors, namely human activity. In the sediment samples, rare earth metals such as lithium (Y), vital materials with strategic potential, were also found.

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