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Analysis on the Relationship of Rare Earth Elements with Magnetic Mineral Concentration in Pumice around Sigura-gura

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Abstract: Rare earth elements are part of one of the strategic minerals and was included in the "critical minerals". Concentrations of rare earth elements are economically precious deposits that can be used as mining commodities. Pumice is the result of volcanic eruptions and it is one of the minerals containing the rare earth elements, one of which is found in Sigura-Gura, North Sumatra. The research aims to determine the composition of rare earth elements, the relationship between rare earth elements and magnetic mineral concentration, and to determine the concentration of magnetic minerals in pumice in Sigura-gura. The method employed is rock magnetic method with Bartington Magnetic Susceptibility Meter Sensor type B (MS2B), and X-Ray Fluorescence (XRF). Results indicated that Sigura-Gura pumice samples, and Sigura-Gura Waterfall have quite varied magnetic mineral concentrations with a range of values from 111,3 x 10^{-8}m^3/kg to 349,9 x 10^{-8}m^3/kg, with antiferromagnetic magnetic properties and grain types with almost no SP grains. Samples of Sigura-Gura pumice contain elements of Eu, Ce, and Y, while samples from Sigura-Gura Waterfall contain elements of Eu and Y. There is a correlation between the amount of magnetic minerals and rare elements, and the more elements are present in a sample, the lower the value χ_{lf} that is produce, and the greater the percentage of elements obtained, the smaller χ_{fd} (%) is obtained.

Keywords: Rare Earth Elements, Magnetic Minerals, Rock Magnetism, Magnetic Susceptibility, Pumice.

1. Introduction

One of the minerals contains a group of elements called the rare earth elements, including erbium (Er), gadolinium (Gd), ytterbium (Yb), praseodymium (Pr), samarium (Sm), neodymium (Nd), scandium (Sc), cerium (Ce), europium (Eu), thulium (Tm), lanthanum (La), dysprosium (Dy), terbium (Tb), holmium (Ho), lutetium (Lu) yttrium (Y), dysprosium (Dy) and promethium

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(Pm) [1]. Although they unstable isotopes, all rare earth elements found in the nature, but not in pure metal form and only in trace levels in natural materials [2]. Additionally, due to the urgent demand for new technologies, rare earth elements are now viewed as vital resources [3]. Rare earth elements have various potentials, which is in volcanic rocks so that it is interesting to be researched by the governments of many countries, including Indonesia. Many studies on volcanic materials has been done on the island of Sumatra, as the study of the pumice's magnetic susceptibility rating in North Tapanuli [4], examining the distribution pattern of volcanic material in Maninjau Lake [5], morphological characteristics and composition of magnetic mineral elements in Lake Maninjau sediments [6] and Maninjau Lake's pre-lava and post-caldera magnetic susceptibility analysis [7]. This volcanic rocks contain minerals that have a chemical composition with a certain ratio and atoms arranged systematically. Many minerals are found in these rocks, is magnetic minerals.

One of the natural materials that contain magnetic minerals is magnetized minerals. In general, certain diamagnetic, paramagnetic and ferromagnetic minerals can be found in nature. Of the three properties of magnetic materials, only ferromagnetic minerals are classified as magnetic minerals [8]. Ferromagnetics are usually grouped under the families of iron hydroxides, iron titanium oxides and iron sulfides. The minerals phyrhotite (Fe_7S_8) and Greigite (Fe_3S_4) belong to the iron sulfide family, goethite (α-FeOOH) to the iron oxide family, and magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3) to the iron titanium oxide family [9]. Many methods can be used in determining the concentration of magnetic minerals in rocks, one of which is the rock magnet ism method.

The rock magnetism method has been widely used to assess the content of magnetic minerals, rocks, sediments, volcanic ash, and other materials include many forms of magnetic minerals. In addition, in Pahae Julu, North Tapanuli, the magnetic susceptibility value of pumice has been examined using the rock magnetism method [4], Since no further research has been done regarding the content of rare earth elements in pumice in North Sumatra, where it was discovered that the area's rocks contain magnetic minerals, a study can be done to examine the relationship between rare earth elements and magnetic minerals in pumice in Sigura-Gura. Magnetic mineral concentrations can be determined from magnetic susceptibility measurement data, and rare earth elements can be found using X-Ray Fluorescence (XRF). The Magnetic mineral concentrations determined using the Bartington Magnetic Susceptibility Meter Sensor Type B (MS2B) were then analyzed to determine their relationship with rare earth elements.

2. Materials and Method

The research was conducted from the sampling, sample preparation, measurement, data processing and data analysis stages. Sampling was conducted at Sigura-Gura and Sigura-Gura Waterfall, North Sumatra (Figure 2). Before analysis, samples in the form of pumice were prepared by mashing and put into a 10 ml holder, and measured the mass. Samples that have been weighed using Ohauss Balance are measured for susceptibility using Bartington Magnetic Susceptibility Meter type Sensor B (MS2B) [10]. To find out the elements contained in the sample, several samples with different susceptibility values were taken and measured using X-ray fluorescence (XRF) [11]. The composition of our sample as well as the rare earth element composition present in the pumice sample was established using XRF data (Figure 1).

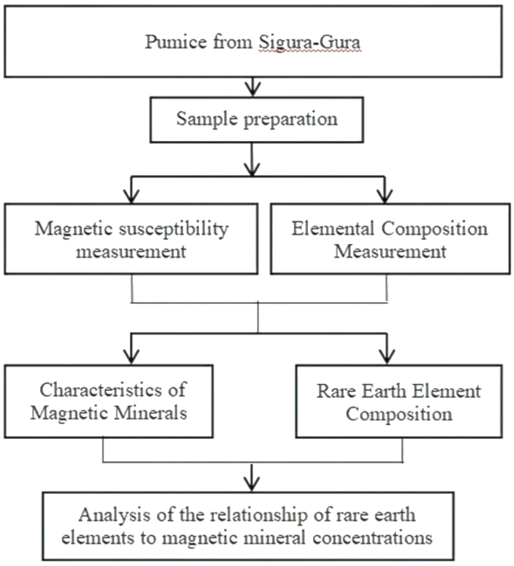


Figure 1. Research procedures to define the relationship between rare earth elements and magnetic mineral concentrations

Based on Figure 1, the analysis of the relationship between rare earth elements and magnetic mineral concentrations is obtained from the analysis of magnetic mineral characteristics and rare earth element composition. The samples used were 4 samples of pumice around Sigura-Gura. Sample preparation and measurement conducted at the Geophysical Laboratories, Department of Physics FMIPA and Chemistry Laboratory, Department of Chemistry FMIPA Padang State University. The research position was carried out in the area around Lake Toba (Figure 2).

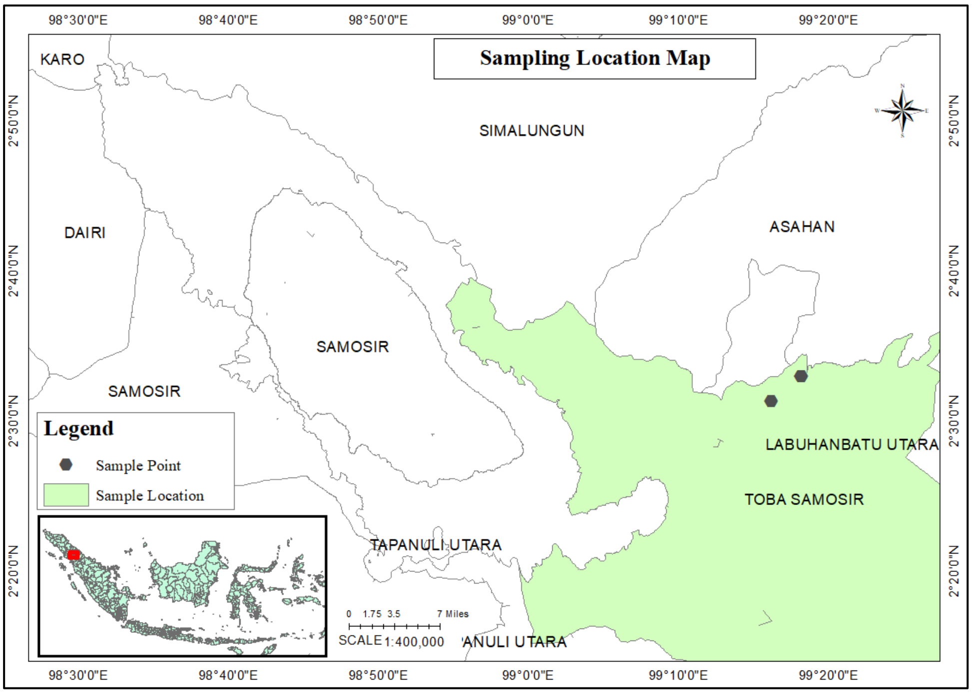


Figure 2. Sampling Location Map

Based on the Map in Figure 2, it can be seen that samples were taken at 2 points around Sigura-Gura, namely one point at Sigura Gura with coordinates S02.55009° E099.30318°, and one point at Sigura Gura Waterfall with coordinates S02.52207° E099.27027°. After taking measurements using Bartington MS2B, the results are obtained from two frequency, that is, low and high frequency, the measurement ratio at both frequency is referred to the magnetic susceptibility level obtained from the equation [10]:

$$\chi_{fd}\ \% = \frac{\chi_{lf} - \chi_{hf}}{\chi_{lf}} x\ 100\% \qquad (1)$$

where χ_{lf} is the mass unity susceptibility at low frequencies dan χ_{hf} is the high frequency mass unity susceptibility [12].

The measurement using X-ray fluorescence (XRF) generate data in form of rare earth element content and percentage of rare earth elements. [11], After that, the data is plotted between the Low Field value and to determine the correlation between magnetic mineral concentration and rare earth element content.

After obtaining data on magnetic mineral concentration and elemental composition, the relationship between magnetic susceptibility levels and rare earth elements was examined through analysis. Measurements using the Bartington Magnetic Susceptibility Meter type Sensor B (MS2B) produced magnetic susceptibility values that varied from each sampling location. The quantity of magnetic minerals formed by an elemental composition present in a material determines its magnetic susceptibility. Different mineral contents in each sample result in a different magnetic susceptibility value. To find the relationship between χ_{lf} and the rare earth elements present in a rock sample, can use a linear equation :

$$y = ax + b, \qquad (2)$$

Where y = independent variable, *x* = dependent variable, *a* = gradient / coefficient of variable *x*, where if the value of *a is* positive (+) then the value of the element on χ_{lf} has an effect, the more percent of the element, the higher the value of χ_{lf} , and if the value of *a is* minus (-) then the value of the element on χ_{lf} has no effect. *b* = constant, R^2 = level of confidence / determination, *r* = coefficient of correlation. The linearization curve has a determination value of $R^2 > 0.9$ (close to 1) [13].

3. Results and Discussion

Data from magnetic mineral abundance measurement at the low frequencies (χ_{lf}) and high frequencies (χ_{hf}) on pumice samples around Sigura-Gura as found in Table 1 and Table 2.

Table 1. Susceptibility values of pumice from Sigura-Gura

No.	Sample Name	Magnetic Susceptibility Value (10^{-8} m^3 /kg)		χ_{FD} (%)
		Low Field (χ_{lf})	*High Field* (χ_{hf})	
1	TOB 19-017-1	170,3	169,8	0,29
2	TOB 19-17-2	180,5	179,5	0,55
3	TOB 19-17-3	162,1	160,3	1,11
4	TOB 19-17-4	170,9	170,2	0,41
	χ_{Min}	162,1	160,3	0,29
	χ_{Max}	180,5	179,5	1,11
	$\chi_{Average}$	170,95	169,95	0,59

Table 1 presents measurements of samples from sigura-gura. Pumice with the χ_{lf} largest value is found in sample TOB 19-17-2 (180,5 x 10^{-8}m^3/kg), while pumice with the χ_{lf} smallest value is found in sample TOB 19-17-3 (162,1 x 10^{-8}m^3/kg) with an average value of (170,95 x 10^{-8}m^3/kg). The largest χ_{fd} *(%)* value is found in sample TOB 19-17-3 (1,11 %) and the smallest percentage χ_{fd} *(%)* value is found in sample TOB 19-17-1 (0,29 %) with an average value of 0,59 %.

Table 2. Magnetic Susceptibility Values of Pumice from Sigura-Gura Waterfalls

No.	Sample Name	Magnetic Susceptibility Value (10^{-8} m^3 /kg)		χ_{FD} (%)
		Low Field (χ_{lf})	*High Field* (χ_{hf})	
1	TOB 19-20-1	290,9	290,2	0,24
2	TOB 19-20-2	249,2	248,3	0,36
3	TOB 19-20-3	349,9	347,4	0,71
4	TOB 19-20-4	287,1	286,6	0,17
	χ_{Min}	249,2	247,4	0,17
	χ_{Max}	349,9	347,4	0,71
	$\chi_{Average}$	294,28	293,13	0,37
5	TOB 19-22-1	270	267,2	1,04
6	TOB 19-22-2	292	290,2	0,62
7	TOB 19-22-3	281,8	279,2	0,92
8	TOB 19-22-4	298,6	295,5	1,04
	χ_{Min}	270	267,2	0,62
	χ_{Max}	298,6	295,2	1,04
	$\chi_{Average}$	285,6	283,03	0,91
9	TOB 19-25-1	126,3	125,8	0,4
10	TOB 19-25-2	122,9	122	0,73
11	TOB 19-25-3	180,8	180,2	0,33
12	TOB 19-25-4	111,3	110	1,17
	χ_{Min}	111,3	110	0,33
	χ_{Max}	180,8	180,2	1,17
	$\chi_{Average}$	135,33	134,5	0,66

Based on Table 2, sample TOB 19-20 pumice from Sigura-Gura Waterfall which has the highest susceptibility value is sample TOB 19-20-3 with a value of χ_{lf} (349,9 x $10^{-8}m^3/kg$) and the sample that has the lowest susceptibility value is sample TOB 19-20-2 with the value of χ_{lf} (249,2 x $10^{-8}m^3/kg$) and value χ_{lf} average (294,28 x $10^{-8}m^3/kg$). With the value of χ_{fd} *(%) the* highest is 0,36 % which is found at TOB 19-20-2 sample, while the lower value is 0,17 % which is found in the TOB 19-20-4 sample.

Sample TOB 19-22 has the highest magnetic susceptibility value of (298,6 x $10^{-8}m^3/kg$) found in sample TOB 19-22-4, while the sample with the lowest susceptibility value is the TOB 19-22-1 sample with values χ_{lf} (270 x $10^{-8}m^3/kg$ /kg). The highest χ_{fd} *(%)* value is 1,04 % found at sample TOB 19-22-4 and the lowest χ_{fd} *(%)* data is 0,62 % found at sample TOB 19-22-2. In the TOB 19-25 sample, the highest magnetic susceptibility value is (180,8 x $10^{-8}m^3/kg$) found in the TOB 19-25-3 and the lowest magnetic susceptibility value is (111,3x $10^{-8}m^3/kg$) contained in the TOB 19-25-4 sample. The highest χ_{fd} *(%)* value is 1,17 % found in the TOB 19-25-4 sample and the lowest χ_{fd} *(%)* value is 0,33 % found at sample TOB 19-25-3.

The results of the measurements on the 4 samples show that changes in the magnetic susceptibility value in each sample indicate that the sample contains a variety of magnetic minerals with a range that is not too far away [14]. The difference in magnetic susceptibility values obtained is then plotted and can be seen in Figure 3.

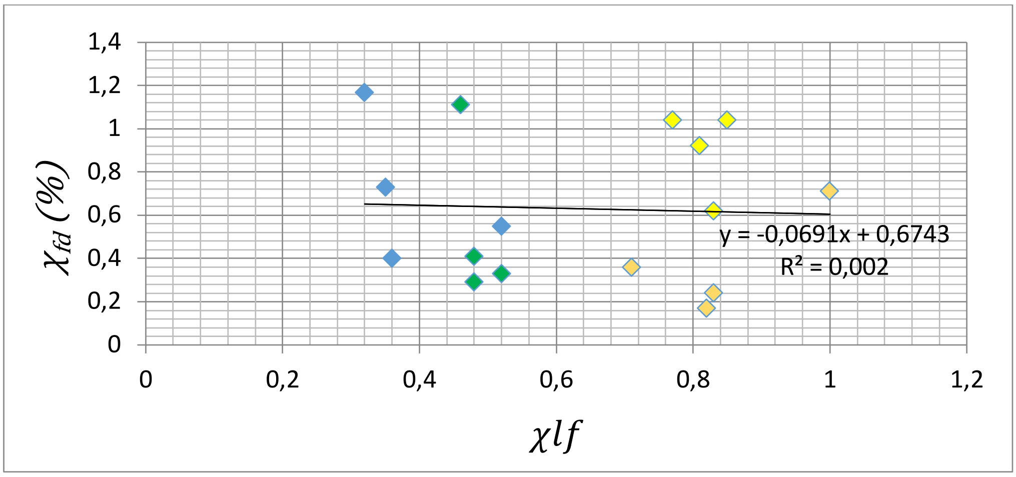


Figure 3. A plot of the relationship between χ_{lf} value and χ_{fd} *(%)* value to all samples

Figure 3 shows that the difference between the χ_{lf} value and the χ_{fd} *(%)* value in all samples is not too far away. On the Sigura-Gura sample (TOB 19-17) the green color can be obtained range of magnetic susceptibility varying from (162,1 x 10^{-8} m^3 /kg to 180,5 x 10^{-8} m^3 /kg), Sigura-Gura Waterfall sample (TOB 19-20) purple color, results for magnetic susceptibility varying from (249,2 x 10^{-8} m^3 /kg to 349,9 x 10^{-8} m^3 /kg), the sample of Sigura-Gura Waterfall (TOB 19-22) yellow color, magnetic susceptibility varying from (270 x 10^{-8} m^3 /kg to 298,6 x 10^{-8} m^3 /kg) and on the sample of Sigura-Gura Waterfall (TOB 19-25) the magnetic susceptibility value is obtained ranging from (111,3 x 10^{-8} m^3 /kg to 180,8 x 10^{-8} m^3 /kg). From different susceptibility values, the type of superparamagnetic grains obtained. The grain size of volcanic material is inversely proportional to the magnetic susceptibility value, the smaller the grain size, the greater the susceptibility value, this is caused by the reduction of the impector in volcanic material. [5]

Based on the data of magnetic susceptibility values obtained (Table 1 and Table 2), and the plot in Figure 3, the magnetic properties and types of superparamagnetic grains in each sample can be classified, so that it can be used to analyze the characteristics of magnetic minerals in each sample (Table 3).

Table 3. Magnetic mineral characteristics of the samples

No.	Sample Name	Magnetic Susceptibility		Magnetic Properties	Grain Type
		(χ_{lf}) (10^{-8} m^3 /kg)	χ_{FD} (%)		
1	TOB 19-17	162,1 - 180,5	0,29 - 1,11	Antiferromagnetics	Almost no SP granules
2	TOB 19-20	249,2 - 349,9	0,24 - 0,71	Antiferromagnetics	Almost no SP granules
3	TOB 19-22	270 - 298,6	0,62 - 1,04	Antiferromagnetics	Almost no SP granules
4	TOB 19-25	111,3 - 180,8	0,33 - 1,17	Antiferromagnetics	Almost no SP granules

Measurement of magnetic susceptibility values in Table 3 shows that, the range of magnetic susceptibility values of each sample varies. The difference concentration of the content of magnetic minerals in each samples is caused by differences in the magnetic properties of the samples. High magnetic susceptibility values indicate that samples tend to be ferromagnetic, while low magnetic susceptibility values indicate that samples tend to be diamagnetic. The magnetic properties of TOB sample 19-17, TOB sample 19-20, TOB sample 19-22, and TOB sample 19-25 are antiferromagnetic. [15]. And for the type of spheres in the TOB 19-17 sample, TOB 19-20 sample, TOB 19-22 sample, and TOB 19-25 sample, it was found that they almost did not have superparamagnetic spheres. [16] .

The magnetic grain size has a significant impact on any magnetic mineral's magnetic characteristics, the more superparamagnetic grains present, the lower the susceptibility value achieved [17]. The most significant element in the magnetic domain is the magnetic grain. because when measured at low and high frequencies, it will have the same magnetic susceptibility value [18]. Magnetic grains can often be detected in magnetic minerals. The more superparamagnetic grains present, the lower the susceptibility value achieved [19]. Susceptibility to magnetic fields ($\mathcal{X}$) is not only affected by the presence of diamagnetic and paramagnetic minerals, the amount of ferrimagnetic and antiferromagnetic minerals in a material also affects its magnetic susceptibility [20].

Elemental composition measurements were carried out using *X-Ray Fluoresence* (XRF). The samples measured consisted of 2 representative samples with varying susceptibility values. The elemental composition data obtained is the basic elemental composition and oxide composition of each sample (Table 4).

Table 4. XRF measurement results on the sample TOB 19-17-3 Sigura Gura Waterfall

Basic		Oxide	
Component	Concentration (%)	Component	Concentration (%)
Al	8,353	Al_2O_3	10,598
Si	42,926	SiO_2	56,239
P	3,412	P_2O_5	4,325
K	15,596	K_2O	9,792
Ca	10,692	CaO	7,243
Ti	0,865	TiO_2	0,669
Fe	14,165	Fe_2O_3	8,997
Y	0,034	Y_2O_3	0,018
Ce	0,063	CeO_2	0,034
Eu	0,175	Eu_2O_3	0,091

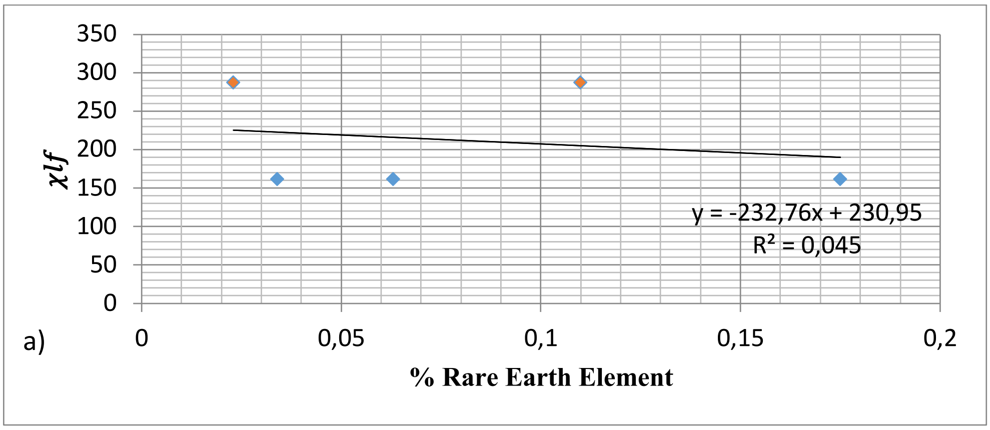
Based on Table 4, sample TOB 19-17-3 has a rare earth element content such as *Eu as* much as 0,175 %, *Ce* as much as 0,063 %, and *Y* as much as 0,034 %. The sample also contains Fe 14,165 % and Ti 0,865 %. The TOB 19-17-3 sample also has a dominant oxide content, namely SiO2 as much as 56,239 %, Al_2O_3 as much as 10.598%, K_2O as much as 9,792 %, P_2O_5 as much as 4,325 %, CaO as much as 7,243 %, and Fe_2O_3 as much as 8,997 %.

Table 5 . XRF Measurement Results on TOB 19-20-4 sample Sigura-Gura Waterfalls

Basic		Oxide	
Component	Concentration (%)	Component	Concentration (%)
Al	8,938	Al_2O_3	11,04
Si	54,233	SiO_2	66,604
P	3,308	P_2O_5	3,684
K	14,086	K_2O	7,748
Ca	8,129	CaO	4,775
Ti	0,768	TiO_2	0,515
Fe	8,028	Fe_2O_3	4,448
Y	0,023	Y_2O_3	0,011
Eu	0,11	Eu_2O_3	0,05
Yb	0	Yb_2O_3	0

Based on Table 5, sample TOB 19-20-4 has a rare earth element content such as Eu as much as 0,11 % and Y as much as 0,023 %. Fe 8,028 % and Ti 0,768% Sample TOB 19-20-4 also has a dominant oxide content of SiO2 as much as 66,604 %, Al_2O_3 as much as 11,04 %, K_2O as much as 7,748 %, P_2O_5 as much as 3,684 %, CaO as much as 4,775 %, and Fe_2O_3 as much as 4,448 %.

Pumice is a type of volcanic rock, and volcanic rocks typically consist of SiO_2 ranging from 48,29 % to 58,34 %, Al_2O_3 ranging from 12,49 % to 17,18 %, TiO_2 ranging from 0,49 % to 0,81 % and P_2O_5 ranging from 0,20 % to 0,41 % [21]. The results of the elemental composition obtained show the presence of Fe elements, where Fe is part of ferromagnetic elements, Ti, Al, K, and Ca elements which are paramagnetic elements and Si, and P which are part of diamagnetic elements [22]. One of the elements that compose magnetic minerals is Fe and Ti, the concentration of Fe and Ti determines its magnetic susceptibility value, the higher the amount of Fe and Ti in the sample, then the higher magnetic susceptibility grade, and the lower the Fe and Ti content of the sample, the lower the magnetic susceptibility value will be [23][24].



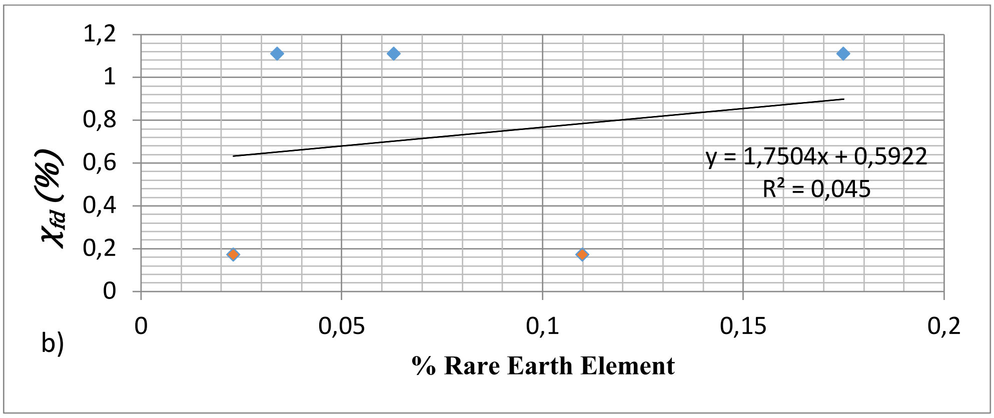


Figure 4. Relationship Graph a) Percentage from the rare earth elements with χ_{lf} b) Percentage from the rare earth elements with χ_{fd} (%)

Based on Figure 4, it can be seen that there was a relationship between the percentage from the rare earth elements and χ_{lf} and χ_{fd} (%) of each sample. In Figure 4a, we can see the relationship between the percentage of elements with the value of χ_{lf}Where the greater the percentage of elements obtained, the smaller the susceptibility value can be seen in the gradient (-232,76) with a reliability level of 0,045 or equivalent to 4,5 %. Figure 4b shows the relationship between the percentage of elements with the value of the susceptibility value, where the greater the percentage of elements obtained χ_{fd} (%) can be seen in the gradient (1,7504) with a confidence level of 0,045 or equivalent to 4,5 %.

4. Conclusion

Based on the measurements, the concentration of magnetic minerals is quite varied with antiferromagnetic properties and grain types with almost no SP grains. The results of elemental composition measurements show that the 2 samples contain rare earth elements, namely Eu, Ce, and Y. From the analysis, it can be concluded that there is a correlation between the elements of rare earths and magnetic minerals concentration, namely the greater the percentage of rare earth elements, the lower value obtained, and if the greater the percentage of rare earth elements, the lower the value. χ_{lf} obtained, and the greater the percentage of rare earth elements obtained, the smaller the χ_{fd} (%) value obtained.

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