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Analysis of chemical elements of the rocks on the coastal areas in the Eastern Bolaang-Mongondow District, North Sulawesi Indonesia

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Abstract. The chemical elements making up the rocks located on the coastal areas in the Eastern Bolaang Mongondow were successfully mapped and investigated by employing the XRF method. The rocks collected from the Central Buyat, South Buyat, Motongkat and Jiko coastal areas of the sub-districts were milled until the size was close to 120 mesh. The samples were characterized and measured to obtain the chemical elements deposited inside the rocks. It was found that the elements which make up the rocks are relatively different depending on the coastal locations. The silicon (Si) was the highest percentage of all elements found and followed by iron (Fe), calcium (Ca) and aluminum (Al). The composition of Si deposited in the rocks from Buyat coastal area was of 42.4% which the biggest percentage compared the rest of the samples. The Iron (Fe) element had a chemical composition recorded at 28.9% that was the highest figure in which rocks were obtained from Jiko coast. The aluminum (Al) composition was relatively similar for all samples collected from that location and observed at 10%.

1. Introduction

The chemical elements, such as *the rare earth elements* (REE) which have an atomic number from 57 until 71, are very essential for technological applications used by people. Those materials have a magnetic property and can be used as alloy substances as energy storage. The REE are also useful for renewable energy technology, an electrical car, LED lamps, *wind power* as well as are important of weapon industry. They are deposited inside stones, sands, and crust expanding from zero to ten kilometers below the ground. The spread of those elements is not uniform depending on the geological age and volcanic activity [1].

The Indonesia country has the longest beach line in the world after Canada. It is giving the unique landscape in which their appearances, such as colors and environments are significantly different each other. It indicates, that chemical elements, compositions, and material structure are unique each coastal line. The coastal line latitude measured from the surface of seawater and beach profile influence the chemical elements compositions [2][3][4].



The Eastern Bolaang Mongondow District (BOLTIM) is consists of sub-districts which have coastal lines, they are *Kotabunan, Tutuyan, Motongkat, and Nuangan*. If they are watched physically materials, or minerals deposited in coastal lines not only uniqueness and interesting to carry out a study but also explored for supporting a regional development.

The study of the contents of the precious elements and minerals inside stones has been conducted for hundreds of years. The gold and cuprum materials were metal substances that the most explored and treaded for years. The materials, however, were mixed with other elements, such as *iron oxide copper-gold (IOCG)* as published previously [5]. The iron ores were found inside stones and to analyze them using *Laser-Induced Breakdown Spectroscopy* method [6]. The tungsten deposited inside rocks was characterized by utilizing radioactivity of an isotope [7]. Meanwhile, silicon material widely used for semiconductor industry was discovered on crusts mainly in sands and soils called a *silicate*. The method to measure the Silicon content also employs Si isotope between silicate and iron [8] while, cuprum element was analyzed using methods INAA, ICP-MS, and LA-MC-ICP-MS [9].

The study and exploration of the minerals content on the coastal area are still limited in Indonesia because of environmental considerations. However, some coastal areas have been investigated of the minerals deposited inside rocks and sands. Authors [10] were successful to characterize of the chemical compositions on the coastal zones employing gamma-ray methods. It was found that the calcium element deposited inside calcium carbonate, or calcite dominated of the materials on the beach rocks. The method of *computer Controlled Scanning Electron Microscopy (CCSEM)* was applied to measure the chemical data and mineral ores of the coastal sediments [11]. While the *rare earth elements* have been discovered on the sands of a desert and beach using a spatial distribution whereby the results found that there was a correlation with inland and beach materials [12]. The radiometric technique was used in analyzing a sediment motion on the beach by detecting a gamma rays [13].

The minerals deposited inside sands have been well mapped and classified [14]. Authors classified simplicity of the minerals in sands with ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ and Ca content. The mineral investigation inside sands and sediment using a portable XRF (*X-ray fluorescence*) has been reported by authors previously [15]. The XRF was powerful to detect the chemical elements, K, Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn, Rb, Sr, Zr, Pb, U, S, As, Br, Mo and Hg, but it was not accurate for P, V, Cr, Ni, Se, Ag, Cd, Sn, Sb, I, Ba and Bi. Meanwhile, the combination methods, XRD, XRF, TG, and SEM were successful to measure minerals of titanium, quartz, and iron-rich structures and alloy iron-titanium [16].

As previously mentioned, it was found that the methods can be employed in analyzing the chemical elements deposited inside rocks, sands, and soils. This study was to map and to investigate the chemical elements deposited in rocks in some regions located on the coastal areas in the Eastern Bolaang Mongondow District, North Sulawesi Province, Indonesia by using XRF. The procedures conducted as follows: Collecting the rocks taken from the coastal area; milling the rocks until their size close to 120 mesh; and characterizing the samples.

2. Methods

2.1. Material Preparations

The rocks were obtained from four the coastal areas of the Motongkat, Central Buyat, South Buyat and Jiko sub-districts in Eastern Bolaang Mongondow District, North Sulawesi Province. Then the rocks were crushed using a heavy tool and they were milled and screened passing the particles with size 120 mesh.

2.2. Measurement

The particles obtained were shipped to the Central Lab belonged by The State Malang University for a measurement. The characterization of samples using XRF (Merk : PANalytical, Type : Minipal 4) followed by methods previously reported [17][18]. The XRF employed was to know the element composition that made up the rocks as previous investigations [19][20][21]. The procedures as

follows: The samples prepared were put inside the XRF instrument (The MiniPal 4) and then were rotated and the measurement of elemental compositions was conducted for 1200 seconds. The standard each element was available to find the sample content (in concentration) and the measured intensities and the data were obtained.

3. Results and Discussion

The data obtained are the composition of the element which makes up of the rocks in some coastal areas in Eastern Bolaang Mongondow as shown in Table 1. The chemical composition of elements is significantly different from each other. There are some rare elements appear in the table but in the low percentage for all locations.

Table 1. The element compositions deposited in rocks located in Motongkat, Central Buyat, Buyat and Jiko coastal areas

No	Element	Symbol	Composition (%)			
			Motongkat	Central Buyat	South Buyat	Jiko
1	Aluminum	Al	9.7	10.0	9.8	10.0
2	Silicon	Si	39.3	39.6	42.4	36.3
3	Phosphorus	P	0.57	0.68	-	-
4	Kalium	K	2.42	3.21	3.04	3.17
5	Calcium	Ca	21.4	18.4	17.3	18.1
6	Titanium	Ti	1.33	1.10	1.33	1.47
7	Vanadium	V	0.073	0.075	0.080	0.10
8	Chromium	Cr	0.072	0.068	0.071	0.078
9	Manganese	Mn	1.68	0.59	0.68	0.81
10	Iron	Fe	22.0	24.8	23.8	28.9
11	Copper	Cu	0.15	0.13	0.13	0.16
12	Zinc	Zn	0.03	-	0.01	-
13	Strontium	Sr	0.71	0.69	0.68	0.55
14	Barium	Ba	-	-	-	0.09
15	Europium	Eu	0.3	0.4	0.3	0.3
16	Rhenium	Re	0.3	-	0.2	-

The strontium element, a soft silver was discovered in all coastal regions whose percentages were 0.71% (Matongkat), 0.69% (Central Buyat), 0.68% (South Buyat) and 0.55% (Jiko). The Sr that is prepared with barium in the form of an oxide is widely used in the high technology devices, such as color television cathode ray tubes which it resists the X-ray emission and it is added on the fireworks for a red color [22].

The barium element was only discovered in South Buyat sub-district coast observed at 0.2%. This metal generally alloyed with aluminum, is employed as a cleaner of unwanted gases in vacuum columns and tubes in electronic apparatuses. Since it is easily condensed, barium is suitable for gases cleaner and is attracted to O₂, N₂, CO₂, and H₂O [23]. Fig. 1 shows the XRF spectra of a chemical element discovered on the coast in the Matongkat sub-district and is plotted as an intensity with respect to energy. To find the element appearing in the spectrum should be compared with the data which are available. The manganese element was found in quite a high percentage in this regional coast recorded at 1.68%. The metal is very applicable in the modern technology and life as well as is widely used in an alloy with iron [24].

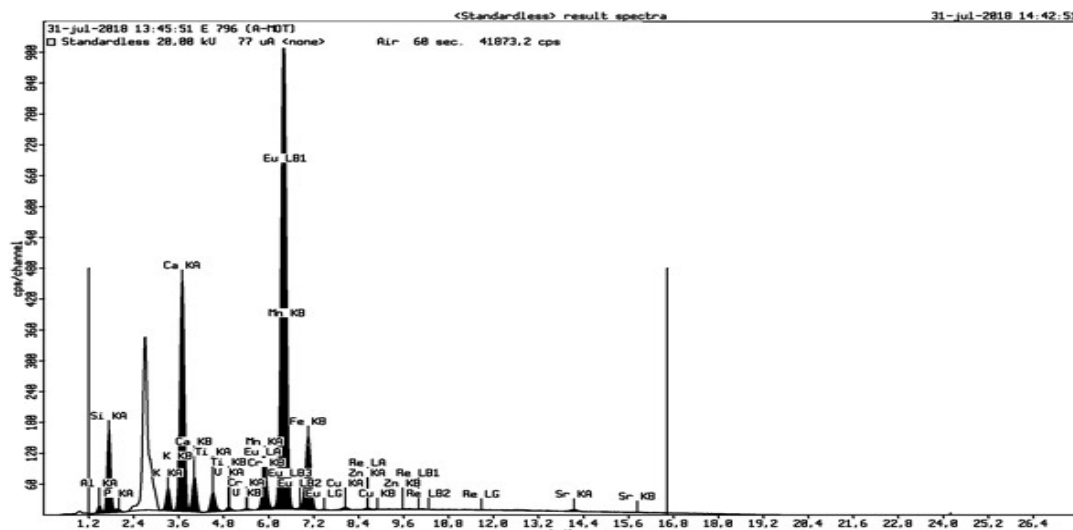


Figure 1. The XRF spectrum of the chemical elements appearing inside rocks obtained from Matongkat coastal region.

The other rare materials found were europium and rhenium whose composition is similar at 0.3% while, iron, copper, and zinc was of 22.0, 0.15 and 0.03%, respectively. Iron metal was also in high composition discovered in all regional coasts in order to it is perspective of an exploration for industrial needs.

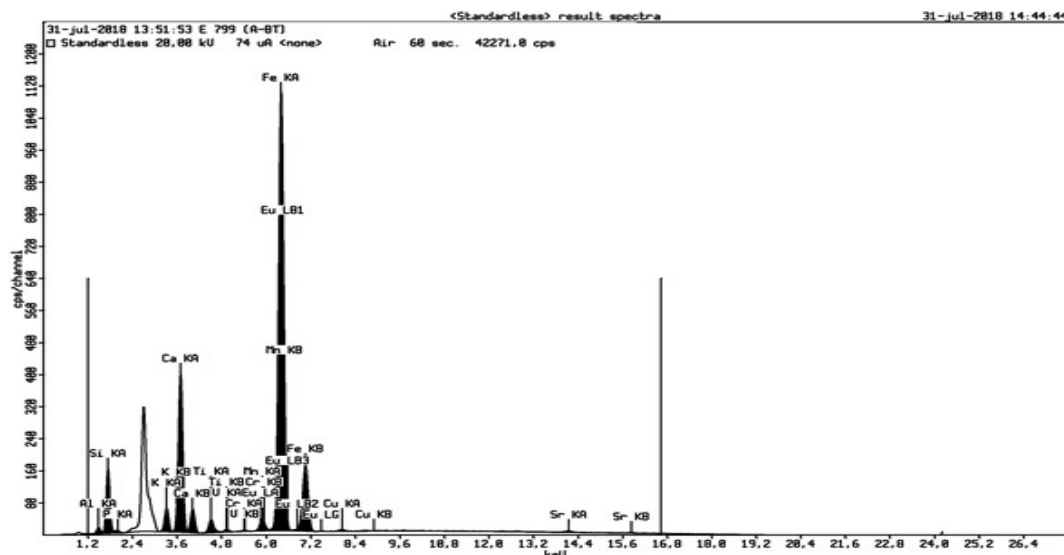


Figure 2. The element composition inside rocks obtained from Central Buyat coast.

The vanadium and chromium measured were recorded at 0.073 and 0.072% which were similar to other places as described below. Kalium, calcium, and titanium are relatively high proportion discovered on the coastal area in Motongkat sub-district whereby percentages are 2.42, 21.4 and 1.33, respectively. Three elements are also exploited economically for their compositions are significantly big. These materials are very used in the chemical industry; kalium and calcium are widely used in fertilizer and food industries, and titanium is applied in a semiconductor-based

device. The composition of a chemical element found in the coastal area in Central Buyat is relatively different if compared to Motongkat sub-district coast as shown in Fig. 2. The zinc, barium, and rhenium elements did not appear in the spectrum but the iron was significantly increased to 24.8%. The aluminum, silicon, and calcium are the slightly different compared with the previous region in which their compositions were of 10.0, 39.6 and 18.4%.

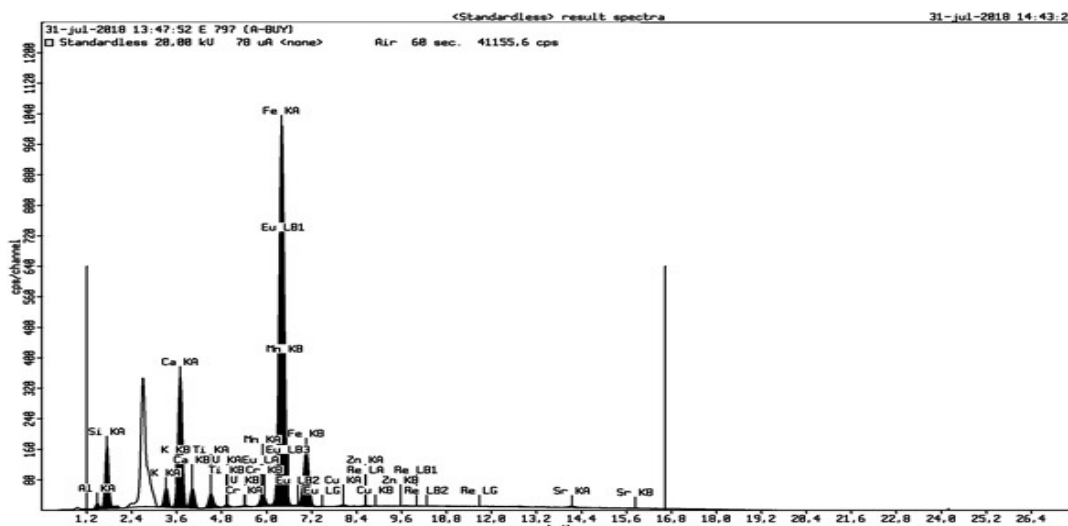


Figure 3. The element composition inside rocks obtained from South Buyat coast.

The silicone composition was the biggest discovered inside rocks of the coastal region in South Buyat Sub-district and was observed at 42.4% as drawn in Fig. 3. The phosphorous and barium did not appear in the XRF spectrum. The aluminum element was recorded at 9.8% which was relatively same with another sub-district zone. The kalium which was produced for agricultural-based products was observed at 3.04% that was similar to other coastal regions.

Calcium that has been produced for building development utility has a big portion in South Buyat coastal region appearing at 17.3%. The titanium which was the most applicable in semiconductor devices was discovered at 1.33 that was similar to that of Motongkat sub-district and was only slightly different with the rest of coastal regions.

The vanadium, chromium and manganese compositions were recorded at low portions of 0.080, 0.071 and 0.68% and were comparable with that of other areas. The iron element gave a higher percentage of composition that was a number 23.8%. If compared with other coastal areas, iron is possible to conduct an exploration in Eastern Bolaang Mongondow District. The copper, zinc, and strontium were the low portions that were of 0.13, 0.01 and 0.68%. Meanwhile, the europium and rhenium which were included in the rare material were observed at 0.3 and 0.2%, respectively.

The coastal Jiko rocks were not found the three elements as follows phosphorus, zinc, and rhenium as presented in Fig. 4. The highest chemical element composition belonged to silicon followed by iron, calcium, and aluminum whose their percentages were of 36.3, 28.9, 18.1 and 10.0%, respectively. The middle compositions were kalium, titanium, manganese, strontium, and copper. The titanium was the biggest percentage compared with other locations which were observed at 1.47%. While, the lower elements were vanadium, chromium, barium, and europium were noted at 0.10, 0.078, 0.09 and 0.3%. The chemical and physical properties of the heavy materials found in coastal areas could be referred to the previous work [25]. While the characteristics and properties of the Rare Earth Element were investigated in the Western Indonesia [26].

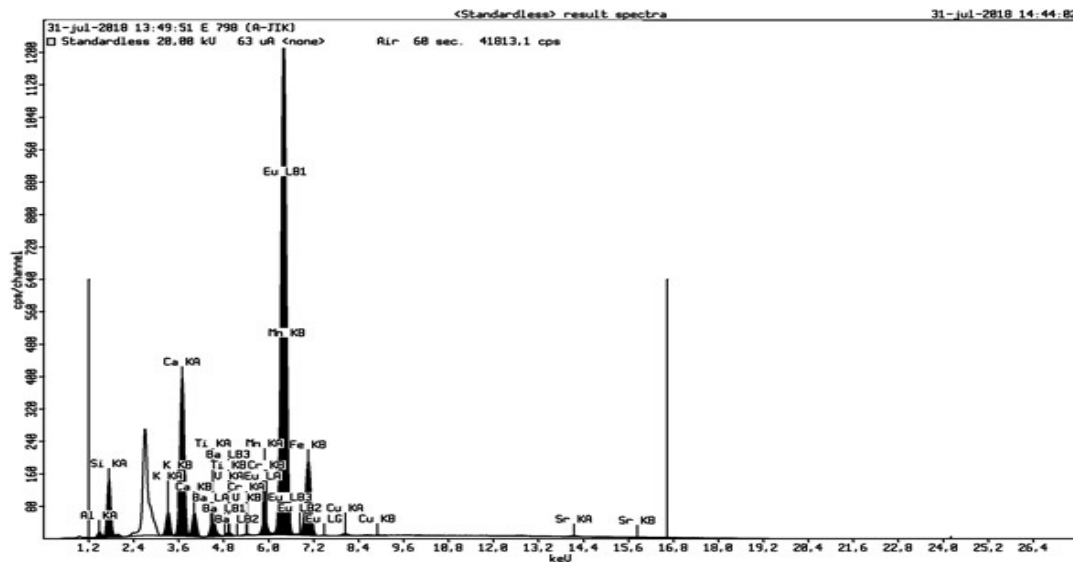


Figure 4. The XRF spectra of chemical elements made up of the rocks obtained from the Jiko coast.

4. Conclusions

The compositions of the chemical elements which were contained in the rocks of the four coastal regions in Eastern Bolaang Mongondow District were successfully determined to employ an XRF measurement. It was found that the iron, aluminum, and silicon were the highest portions of the rocks discovered of all coastal locations. The kalium, calcium, and titanium were in the middle portions spread from 1.10 to 21.4% which were possible to be carried out an exploration. The rare materials, such as vanadium, chromium, manganese, strontium, europium, barium and rhenium were also discovered in all coastal areas but the gold deposit was not discovered. The exploration of the materials was possible to be conducted since some chemical elements were in big percentages.

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