



ISSN NO. 2320-5407

Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/7480
DOI URL: <http://dx.doi.org/10.21474/IJAR01/7480>



INTERNATIONAL JOURNAL OF
ADVANCED RESEARCH (IJAR)
ISSN 2320-5407
Journal Homepage: <http://www.journalijar.com>
Journal DOI:10.21474/IJAR01

RESEARCH ARTICLE

DETERMINATION OF RARE EARTH ELEMENT CONTENTS IN THE PULMODDAI-BASED MONAZITE.

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Manuscript Info

Manuscript History

Received: 24 May 2018
Final Accepted: 26 June 2018
Published: July 2018

Keywords:-

heavy minerals, monazite,
radioactivity, Pulmoddai mineral sand
deposit, Sri Lanka.

Abstract

Rare earth elements (REE) have become significant to our technological world as they have unique magnetic, phosphorescent and catalytic properties. The demand for REE has increased in recent past because they can be employed as both metals and alloys. The Pulmoddai deposit is the largest known heavy mineral sand deposit in Sri Lanka which extends to about six kilometers in length and with an average width of hundred meters (Ref?). According to predictions it contains six million tons of heavy mineral sands with high radioactivity. Monazite is a mineral containing thorium which can be used instead of uranium for nuclear power generation and is common in the Pulmoddai deposit. The study was aimed to diagnose the common heavy minerals using physical and optical properties, estimate the heavy mineral composition of Pulmoddai deposit and to quantify the rare earth element contents in Pulmoddai based monazite. A sand sample was collected up to 50 – 75 cm depths and heavy minerals were separated through gravitational and magnetic separations. Monazite was microscopically recovered using the optical microscopes. Rare earth element analysis was done using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). According to the results obtained, ilmenite, garnet, rutile, zircon, spinel, silimanite and monazite were major heavy minerals present in the mineral sand deposit and their concentrations were 83.31 %, 4.64 %, 2.48 %, 2.10 %, 1.40 %, 2.42 % and 1.38 % respectively. The REE percentages contained in monazite were Cerium (28%), Lanthanum (15%), Neodymium (10%), Promethium (3%), Samarium (2%), Gadolinium (2%) and Yttrium (1%). About 3.87g of cerium can be obtained by 1kg of Pulmoddai mineral sand. Due to the higher cerium concentration, value of the Pulmoddai monazite is considered to be economically enhanced and avenues for value addition by extraction of REE from Pulmoddai monazite should be critically evaluated.

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Introduction:-

The Pulmoddai deposit is the largest heavy mineral sand deposit in Sri Lanka which extends to six kilometers in length with an average width of 100 meters (Ref?). It is estimated to contain six million tons of heavy sand with an average composition of 70-72% ilmenite, 8-10% zircon, 8% rutile and 0.3% monazite. These heavy minerals carry a huge economic value as they consist of rare earth elements (REEs). (Thilakanayaka, 2015)

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pulmoddai beach sand deposit is the most important non-ferrous mineral reserve in Sri Lanka to date. It contains minerals which consist of titanium, one of the most expensive and important metals in the world. Ilmenite (FeTiO_3) and rutile (TiO_2) are found in massive concentrations in the Pulmoddai beach sand deposit. (Samanthi, 2017) therefore, Pulmoddai sandy beach is known as the black gold of Sri Lanka. (Sirimanna, 2014) This deposit extends from Nilaveli to Kokilai lagoon mouth.

Rare earth elements are a set of seventeen chemical elements including the fifteen lanthanides, scandium and yttrium. They are also known as “The seeds of technology” (by Japanese) and “Technology metals” (by US Department of Energy) for these elements as those elements have become irreplaceable to our world of technology. (Rare Element Resources Ltd, 2016) They help to fuel global economic growth, maintain high standards of living, and create products that help to save lives. (Rare Earth Technology Alliance, 2017)

As the technology is rapidly developing, it is possible to confirm that over the coming decades the REEs will be in more demand and valued, providing the producing countries with a very important competitive advantage in the international market. (Ortiz et al., 2014)

The rare earths were discovered in 1787 by Swedish Army Lieutenant Karl Axel Arrhenius. (Hedrick, 2000) Although they are known as rare earths, they are not rare. Those elements are relatively abundant in the earth's crust but, rarely concentrated into mineable ore deposits. (Geology.com, 2017) Because they display similar chemical behavior the rare-earth elements proved difficult to separate. Rare earths were first produced commercially in the 1880s in Sweden and Norway from the rare-earth mineral monazite. (Hedrick, 2000)

Rare earth minerals contain one or more REEs as major metal constituents. So far, a total of about 200 distinct species of rare earth minerals have been described. (Kanazawa et al., 2006)

Monazite is one of the major rare earth mineral which contributes highly in beach radioactivity and also an important ore for thorium, lanthanum, and cerium. It has a monoclinic crystal system displaying complex crystal habits, commonly flattened or elongated. Monazite occurs in massive or as rolled grains and its color varies from pale yellow to dark brownish red, having a white streak and resinous luster with an oily surface. (Rutley, 1916)

Monazite is primarily found in granites, pegmatites and carbonatites (Gosen et al., 2014) and secondary occurrence is as placer deposits, marine and beach sands. Monazite sands usually consist of monazite naturally concentrated with other heavy minerals, such as magnetite, rutile, ilmenite, zircon, garnet, etc.

The objectives of this study were to diagnose physical and optical properties of common heavy minerals and to estimate the mineral composition of Pulmoddai deposit and to quantify the REE contents in Pulmoddai based monazite.

Methodology:-

Mineralogical Analysis:-

The sand samples were collected down to 50-75cm depths from heavy mineral accumulations in the beach. Then, those samples were packed and labeled. The bulk sample was first air dried and the dry weight was noted down. Then, the sample was sieved through a 2mm size sieve (ASTM). Then again the sand portion with the size less than 2mm was sieved through a 1mm sieve (ASTM). The sieved fraction was kept for further separation and the other fractions were weighed, packed and labeled.

The sieved sample was separated in the Wilfley table into heavies and non-heavies. When the machine was fed with sand, sand was moved along the table with water. The heavy minerals were filled into a gas funnel kept after the Wilfley table and light minerals were filled into another gas funnel. Then, those separated were put into dishes and kept in an electric oven to dry within 110-180°C.

The oven dried portion of heavies was taken for the heavy liquid separation. The separation funnel was filled with 50ml of sodium polytungstate. About 50g of (the representative sample of) heavies' was taken using the sample splitter and added into the separation funnel through a funnel wound with a paper. Then the mixture was stirred well using a clean glass rod. The setup was allowed to settle down for 20 minutes. The sink portion and the float portion

were separated into labeled filter papers and they were washed with tap water until the sodium poly tungstate is totally removed. Washed sand samples were kept for oven dry at about 110°C. The dried samples were weighed, packed, labeled and kept for further analysis.

The sinks portion of the heavy liquid separation was used for the magnetic separation. At first, the magnetite in the sand sample was removed using the free fall magnetic separator. For the removal of magnetite, voltage in the free fall magnetic separator was set at 0.25 V. The sample was placed in a plastic tray and it was rotated by hand, keeping on the magnets. Then, the magnetite was arranged in between the cavity of magnets. The other minerals didn't act upon the magnetic field. They were fallen along within the tray. Then that magnetite was removed by hand.

Magnetite free sand sample was separated further into different magnetic fractions of minerals using inclined chute magnetic separator which was set its inclinations/ampere at 0.3 A/15°, 0.4 A/15°, 0.55A/15°, 0.8A/15°, 1.2A /15° and 1.2A /5° respectively (Figure 3). As the machine vibrated continuously, minerals were separated according to their magnetic susceptibility in the descending order. The separated fractions were weighed, packed, labeled and stored for further analysis.

All the magnetic fractions and the floats of the heavy liquid separation were studied under the microscope. For this purpose, the stereo binocular microscope (MEIJI Techno EMZ 13TR) and the polarizing microscope were used.

Using inclined chute magnetic separator, monazite is separated within the magnetic fraction 0.55A/15° to 1.2 A/5° and monazite could be recovered at 85% purity. These magnetic fractions still contains impurities such as hornblende, spinal and rutile. Then, monazite was further purified by selectively removal of impurities using the microscope. The purified monazite was grinded using an agate pestle and mortar in order to make a fine powder.

Chemical Analysis:-

The powdered monazite samples were digested in aqua regia using Microwave digester CEM MARS 6 and REE analysis was done using the Thermo iCAP Q ICP-MS analyzer. The quantities of monazite and acids used in digestion and the adjustments for the microwave digester in digestion of monazite have been mentioned in Table 1 and Table 2 respectively. The flow diagram of the procedure for REE analysis has shown in Figure 1.

Results:-

Monazite is a yellowish brown to reddish brown or greenish brown mineral with a resinous to vitreous luster. It is a translucent phosphate with monoclinic crystal system and poor cleavages. The streak is white in color. The hardness of monazite lies in the range 5-5.5 while the specific gravity lies in the range 4.6-5.4. When the monazite sands were observed through the stereo binocular microscope they were viewed as grains with oily surfaces. Monazite is an isotropic mineral and when the microscope stage was rotated in cross polarized light, a shadow was observed on the monazite grain four times in 360°. The mineral fractions observed through the stereo binocular microscope are presented in Figure 2 and Figure 3. These minerals are in between 63-1000 µm sieve size.

The REE composition of monazite was more than 61%. The most abundant elements were cerium, lanthanum and neodymium. Their abundances were around 28%, 15% and 10% respectively. About 3.87 grams of cerium can be produced using 1kg of Pulmoddai mineral sand.

The results of REE analysis (ICP-MS) have been shown in Table 3.

According to the results, the major heavy minerals present in the mineral sand deposit were ilmenite, garnet, rutile, zircon, spinal, silimanite and monazite. Their concentrations were 83.31 %, 4.64 %, 2.48 %, 2.10 %, 1.40 %, 2.42 % and 1.38 % respectively.

Discussion & Conclusion:-

Using the Wilfley table, the minerals were separated according to their specific gravity. The mechanism of this machine is as the winnowing process with a fan (*kulla*). The inclined table oscillates backward and forward. The minerals with higher specific gravity (heavies) remain moving a short distance while minerals with lesser specific gravity move forward. Here the silt and clay particles were washed out and wet sieving was not necessary to remove silt and clay. The principal of operation of the Wilfley table has shown in Figure 4.

At the heavy liquid separation process, the minerals with higher density than that of the liquid were sunk and the minerals with lower density were floated on the liquid. The best heavy liquid suited for the heavy liquid separation is bromoform (tribromomethane; SG=2.89). But, in this research, sodium polytungstate (SG=2.85) was used alternatively as the bromoform liquid is expensive and the specific gravity difference of the two liquids was very small. The liquid- sand mixture must be well stirred and kept for about twenty minutes to separate floats and sinks. Additionally, the separated portions should be washed with water until the liquid is removed. Otherwise, the sand sample would get caked when dried.

At the inclined chute magnetic separator, the minerals are separated according to their magnetic susceptibility property. There, the minerals with higher magnetic susceptibility were getting separated in lower current values and minerals with lower magnetic susceptibility were getting separated in higher current values. Before separating sand by the inclined chute magnetic separator, magnetite must be removed by the free fall magnetic separator. Otherwise, magnetite would get clustered at the gutter of the inclined chute magnetic separator. Then the sand samples would not be separated properly.

Physical properties of the minerals were used in identifying the minerals. The separated minerals were observed through a stereo binocular microscope and further an optical microscope was used to ensure the minerals. It was because the optical properties of the minerals are unique. At the stereo binocular microscope, the color, streak, luster, crystal habit, cleavage, transparency and hardness of minerals were checked and at the polarizing microscope the optical properties (refractive index, pleochroism, isotropic/ anisotropic, uniaxial/biaxial, relief, dispersion and birefringence) of the minerals were checked.

The mineral percentages of all the portions were estimated by observing through the microscopes. Here, the volume ratios are obtained and those volume ratios were converted to weight ratios using the density values of minerals.

When using the ICP-MS analyzer, we must keep remember not to use samples with mass over 0.5 g. Otherwise, the machine would collapse due to the high pressure.

Due to higher rare earth element composition, value of the Pulmoddai monazite is considered to be economically enhanced and avenues for value addition process such as extraction of REE from Pulmoddai monazite should be critically evaluated.

List of tables:-

Table 1:-The quantities of monazite and acids used in digestion

| | Sample A | Sample B | Sample C | Sample D | Sample Blank1 | Sample Blank2 |
|-----------------------------|----------|----------|----------|----------|---------------|---------------|
| Monazite/g | 0.1003 | 0.0997 | 0.0994 | 0.1015 | - | - |
| HNO ₃ (69.0%)/mL | 6 | 6 | 1.5 | 1.5 | 6 | 1.5 |
| HCL/mL | - | - | 4.5 | 4.5 | - | 4.5 |

Table 2:-The adjustments for the microwave digester in digestion of monazite

| Field | Adjustment |
|---------------------|-------------------------|
| Name | ABC |
| Controltype | ramp to temperature |
| Vesseltype | Easy prep |
| Tempguard | ON-260 ⁰ C |
| Duotemp | OFF |
| Ramp time | 15 min |
| Hold | 12 min |
| Holding temperature | 160 ⁰ C |
| Pressure | No pressure adjustments |
| Power | 900W |
| Stirring | OFF |

Table 3:-The results of REE analysis (ICP-MS)

| | | Monazite A | Monazite B | Monazite C | Monazite D | Blank 1 | Blank 2 |
|-------|-----|------------|------------|------------|------------|---------|---------|
| 175Lu | ppm | 77 | 73 | 102 | 102 | 0 | 0 |
| 172Yb | ppm | 330 | 313 | 435 | 435 | 0 | 0 |
| 169Tm | ppm | 13 | 12 | 17 | 17 | 0 | 0 |
| 166Er | ppm | 1396 | 1323 | 1459 | 1451 | 0 | 1 |
| 165Ho | ppm | 165 | 157 | 217 | 218 | 0 | 0 |
| 163Dy | ppm | 1173 | 1125 | 1536 | 1544 | 0 | 1 |
| 159Tb | ppm | 817 | 779 | 1061 | 1062 | 0 | 0 |
| 157Gd | ppm | 7300 | 7087 | 9413 | 9368 | 1 | 4 |
| 153Eu | ppm | 168 | 158 | 224 | 222 | 0 | 0 |
| 147Sm | ppm | 5469 | 5325 | 6937 | 6887 | 1 | 5 |
| 146Nd | ppm | 33621 | 32621 | 41873 | 42103 | 8 | 30 |
| 141Pr | ppm | 9784 | 9586 | 12154 | 12117 | 2 | 9 |
| 140Ce | ppm | 91160 | 89765 | 110643 | 111693 | 19 | 77 |
| 139La | ppm | 49005 | 48041 | 59372 | 59758 | 9 | 37 |
| 89Y | ppm | 4906 | 4832 | 4283 | 4308 | 1 | 2 |

List of figures:-

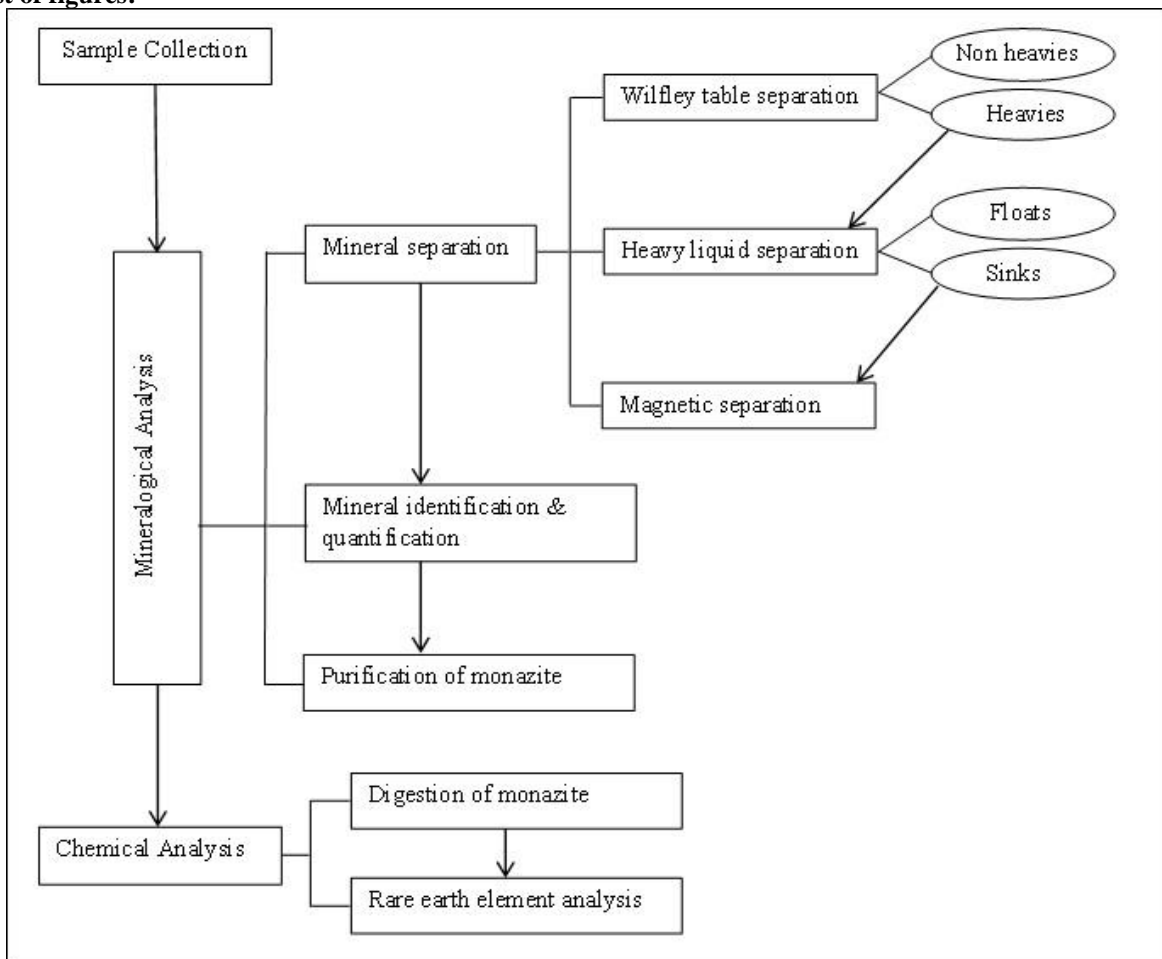


Figure 1:-The procedure for REE analysis



Figure 2:-Microscopic view of +2000 portion and monazite

Average Thoria and REE contents in SW Sri Lanka (Source: Unpublished Geological Survey Reports):-

| | Weight % | | | |
|--------------------------------|-----------------|------------------|-----------------|-----------------|
| | Induruwa (1949) | Kaikawala (1954) | Beruwala (1960) | Beruwala (1963) |
| ThO ₂ | 8.98 | 9.64 | 9.77 | 9.47 |
| Ce ₂ O ₃ | 26.87 | 28.03 | 27.30 | 27.55 |
| La ₂ O ₃ | 28.26 | 29.79 | 30.79 | 31.45 |
| Y ₂ O ₃ | 1.37 | 0.74 | 0.74 | 0.87 |
| P ₂ O ₅ | 28.06 | 26.74 | 27.09 | 27.25 |

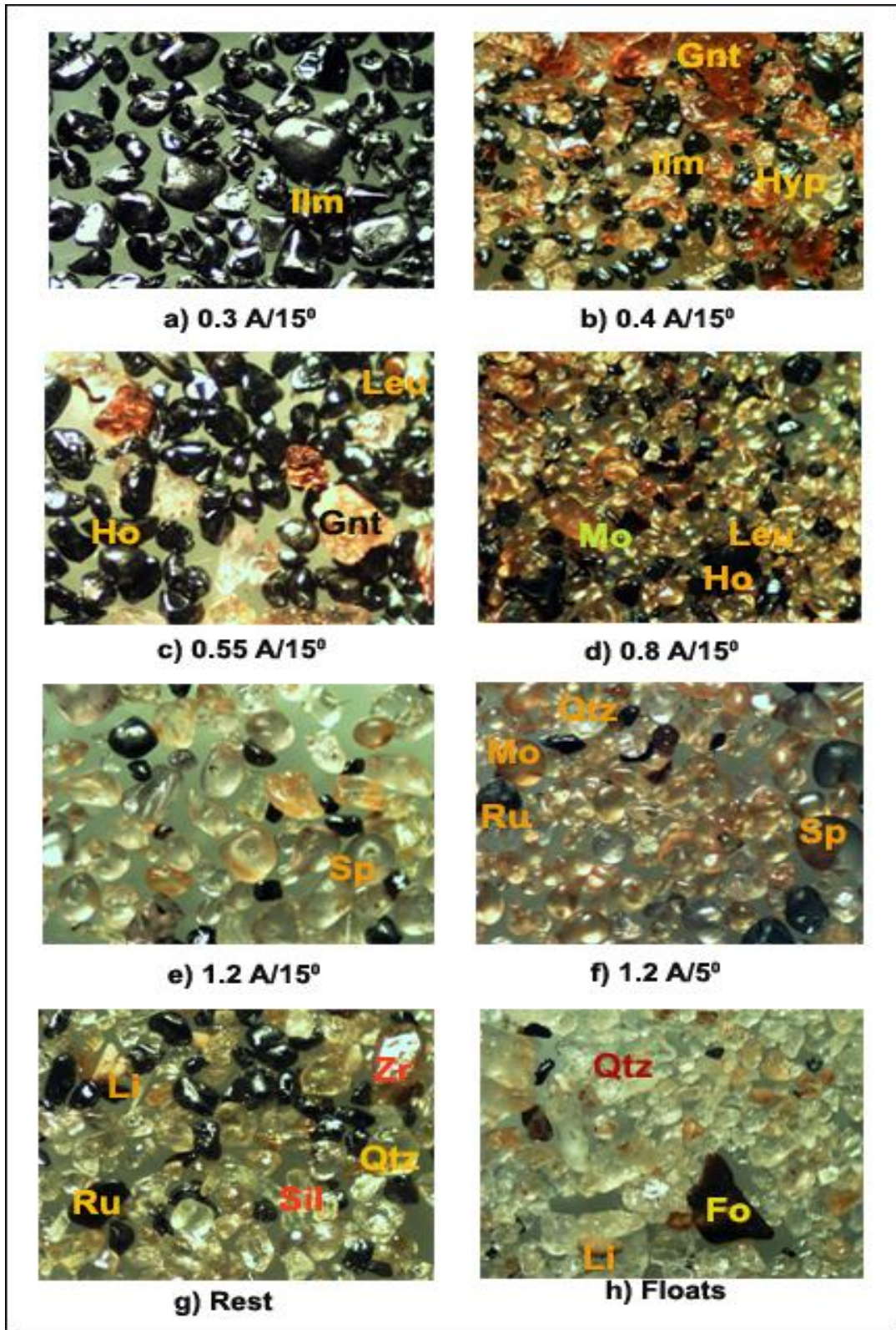
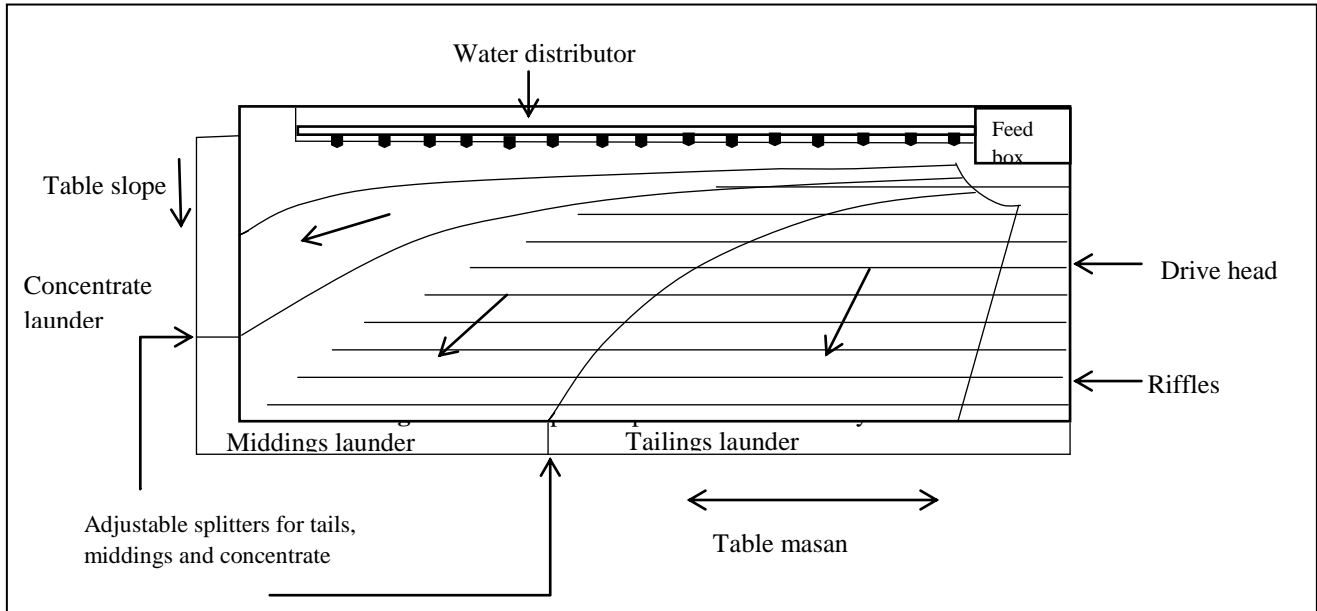


Figure 3:-Microscopic view of different magnetic separated samples fractions (Ilm- Ilmenite, Gnt- Garnet, Hyp- Hypersthene, Ho- Hornblende, Leu- Leucoxene, Mo- Monazite, Sp- Spinal, Ru- Rutile, Qtz-Quartz, Li- Limonite, Sil- Sillimanite, Zr- Zircon, Fo- Fossils)



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