MINERALOGY, GEOCHEMISTRY AND ECONOMIC POTENTIAL OF ZIRCON AND ASSOCIATED MINERALS IN DUBAYDIB SANDSTONE FORMATION, JORDAN

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ABSTRACT

This study was conducted to evaluate the zircon minerals in Wadi Al-Mezrab, South Jordan. Zircon at the study area belongs to the Middle member of the Dubaydib Formation of the Middle Ordovician age. The detailed petrographic study shows that the host rock is composed mainly of quartz, plagioclase, biotite, muscovite, and zircon, with small amounts of other heavy minerals such as rutile, tourmaline and monazite. The samples are composed of magnetic minerals that range in concentrations from 6.2% to 42% and non-magnetic range between 58% and 93.8%. The gravity separation using heavy liquids showed that the heavy minerals averages about 10%. Zircon grains are mostly clear, euhedral to rounded grains and exhibit elongated or stubbed prisms. Chemical analytical data indicate that the average content of Zr is 2.4%, Ce, La and Y percentages (in monazite) are 7.1%, 1.9% and 0.04%, respectively in concentrated samples and TiO₂ content is 6.8%. The results indicate positive relationships between the Zr, Ce, La, Y, and TiO₂. The highest percentage of Zr, TiO₂, and REE in non-magnetic mineral concentrates within the size fractions of less than 75 + 45 to -45 μm. The calculated result of % by weight showed; the highest content of Zr was 22.82, the ZrO₂% was 32, and the ZrSiO₄% was 49.14 of the less than 75 to 45 size fraction.

Keywords: Zircon; Ordovician Dubaydib sandstone; geochemistry; Economic potential; Jordan

INTRODUCTION

Zircon (ZrSiO₄) is a nesosilicates mineral that is characterized high concentration of trace elements such as Hafnium (Hf) and rare earth elements (REE). In general heavy minerals are associated with zircon, particularly titanium minerals (e.g., rutile ilmenite and monazite) (Al-Malabeh et al., 2002; Nesse, 2000 and 2004; Sláma, 2008).
Naturally zircon occurs as a common accessory mineral in igneous rocks, in metamorphic rocks (Malone et al., 2008; Al-Fugha et al., 2012). Due to its hardness, durability and chemical inertness, zircon persists in sedimentary deposits and is a common constituent of most sands (Al-Malabeh et al., 2004; Malone et al., 2008; and Perrin, 1989). The study area is situated in south Jordan, near the borders with Saudi Arabia approximately 350 Km south Amman, 100 Km northeast Aqaba, and 17 Km southeast of Sahl As Suwwan (Fig. 1).

![Fig. 1: A) Jordan map show the study area location (maps.com, 1997) B) Geological map of the study area (JTM) (Al-Smadi, 2010)](image)

**GEOLOGICAL SETTING**

The outcroppings formations within the study area comprise of the Khreim Group (Hiswah Sandstone Formation) of Middle Ordovician that occur in the southwestern part of the study area and the Dubaydib Sandstone Formation of Late Ordovician age (Al-Malabeh, 1994; Madanat and Mehyar, 1999; and Al-Malabeh and El-Hasan, 2009), which outcrops mostly in the northeastern part of the study area (Fig. 1). Zircon minerals mainly occur in the middle member of Dubaydib Sandstone Formation (DB2) which has an age of the Middle Ordovician. Columnar section has been drawn from trenches in the study area (Fig. 2).
Zircon grains were separated using standard techniques of crushing, grinding, sieving, heavy liquid and magnetic separation, and then purified by hand picking under a binocular microscope. The samples separated into 600 to less than 45 μm size fractions by standard crushing and heavy liquid techniques, from fractions 125 to less than 45 μm. Zircon and other heavy minerals were separated using a heavy liquid Bromoform CHBr3 (S.G = 2.81), and undiluted Di-lodmethane CH2I2 (S.G = 3.3). The
separated minerals were then studied under the polarizing microscope, X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM).

RESULTS

This study describes in details the characteristics of zircon sand composition of Wadi Al-Mezrabi sandstone samples taken from the study area. Microscope was used to find out the primary and secondary minerals and their textures.

Petrography

Nine samples from four sites were selected to be in thin section. The sandstone was found to contain several primary minerals such as quartz (Fig. 3), plagioclase (the main constituents), and mica {e.g. muscovite biotite (Fig. 4), and iron oxides}. The secondary minerals include heavy minerals such as zircon (Figs. 5 and 6), hafnium, tourmaline, and titanium minerals (rutile and ilmenite). Zircons from most samples are clear, euhedral to rounded grains and exhibit elongated or stubbed prisms.

Fig. 3: Microphotograph shows contain fractured quartz grains, low concentration of zircon and very small, biotite, and high oxidation of sample Z ~ 4 {crossed polar (XPL) at a 10X.10X magnification}
Fig. 4: Microphotograph show Biotite (Bi), plagioclase grain, and quartz grains, from Z ~ 2, with magnification 10X*10X.
A) Biotite (Bi) with (XPL) 10X*10X magnification, B) Biotite (Bi) with (PPL) 10X*10X magnification.

Fig. 5: Microphotograph shows the quartz grain from sample Z ~ 2, unhedral, A) Not fractured quartz (Qz) grains, with crossed polar (XPL) at a 40X*10X magnification. B) Fractured quartz (Qz) grains, with crossed polar (XPL) at a 40X*10X magnification.

Fig. 6: Microphotograph shows the hexagonal shape of zircon (Zr) grain, A) Z ~ 2 with (XPL), B) Z ~ 2, with (PPL), both A and B taken with magnification 40X*10X.
Mineralogy

- **Binocular microscope**

  a. **Zircon ZrSiO₄**: Zircon is most abundant heavy mineral in this study area. The zircon grains have varied of colors including; colorless, yellow, brown, brown reddish, and black. Zircons from most samples are clear, euhedral to rounded grains and exhibit elongated or stubbed (Fig. 7). Zircon has a tetragonal symmetry but its internal crystal structure may often be damaged by bombardment from the decay of radioactive elements present in small amounts in many zircons (Klein, 2002).

  b. **Tourmaline {NaMg₃Al₆B₃Si₆O₂₇(OH, F)₄}**: Tourmaline forms the second most abundant heavy mineral in the examined samples. The majority of tourmaline grains are dark black or brown in color, angular to rounded prism in shape, and rounded to sub rounded triagonal shape (Fig. 8).

![Fig. 7: Zircon grains under binocular microscope with different shapes and colors](image1)

![Fig. 8: Tourmaline grains under binocular microscope with different colors and shapes](image2)

  c. **Titanium Minerals {Rutile (TiO₂) and Ilmenite (FeTiO₃)}**: The majority of rutile grains are black or brown to reddish brown in color, shapes vary and are commonly observed as elongated to rounded prism in shape, sub rounded, rounded to sub rounded, and often fragmented grains, with tetragonal system (Fig. 9).

  d. **Monazite (Ce, La, Nd, Th, Y) PO₄**: The color varies from pale yellow, brownish yellow to pale amber and light brown. Monazite grains are rounded to sub rounded, egg-shaped or spherical grains. It is characterized by a frequent brownish stain and surface pitting (Fig. 10).
Scanning Electron Microscope (SEM)

SEM study carried out by (FEI Quanta 200, Nether lands) scanning electron microscope equipped with EDAX for X-ray microanalysis in the Department of Earth and Environmental Sciences in the Yarmouk University SEM was used to characterize zircon morphologies and to identify association of zircon with other surrounding minerals. And in particular to determine chemical composition in the wet sieved fraction after separated by two heavy liquid. Three wet sieved fraction in the range from 75 μm to less than 45 μm were examined the zircon sand sample euhedral to rounded grains and exhibit elongated or stubbed prisms in shape (Fig. 11A). Monazite grains of the zircon sand sample are rounded to sub rounded, egg-shaped or spherical grains (Fig. 11B).

X-Ray Diffraction (XRD)

XRD analysis was used to identify the mineralogical composition of the studied samples of zircon sand after some process, The XRD instrument model PW 3040 diffractometer, was controlled by a PC-APD by NRA. Results recorded XRD analysis of the Z ~ G and Z ~ I samples indicate the presence of titanium minerals, zircon, and monazite (Fig. 12 and 13).
Fig. 11: Photographs under SEM, A) Zircon grains  
B) Monazite grains under SEM

Fig. 12: X-Ray diffraction pattern of representative Z~G sample

Fig. 13: X-Ray diffraction pattern of representative Z~I sample
**Inductive Coupled Plasma (ICP)**

All concentrated samples were analyzed using ICP technique (by NRA, Jordan) to determine the major oxides and the trace elements. The result showed that the highest percentage of Zr of the size fraction less than 75 µm to +45 µm was 22.82. These calculations of the results (in wt%) indicated that the ZrO₂ % is 32, and the ZrSiO₄ % is 49.14 (Table 1).

### Table 1: Recalculation of the result for the size fraction in the composite sample

<table>
<thead>
<tr>
<th>Size fraction</th>
<th>Wt</th>
<th>Zr</th>
<th>ZrO₂</th>
<th>ZrSiO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>+125</td>
<td>12.22</td>
<td>2.16</td>
<td>3.024</td>
<td>4.64</td>
</tr>
<tr>
<td>+90</td>
<td>22.4</td>
<td>2.07</td>
<td>2.9</td>
<td>4.45</td>
</tr>
<tr>
<td>+75</td>
<td>28.99</td>
<td>3.88</td>
<td>5.43</td>
<td>8.34</td>
</tr>
<tr>
<td>+45</td>
<td>34.89</td>
<td>22.82</td>
<td>32</td>
<td>49.14</td>
</tr>
<tr>
<td>Less 45</td>
<td>1.5</td>
<td>11.33</td>
<td>15.9</td>
<td>24.42</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this study, the values of Zr showed a positive correlation with TiO₂ %, and P₂O₅ % for sub-samples, and have showed a positive correlation with Y, Ce, La and Pb for sub-samples.

**ECONOMICAL VALUE OF THE STUDY AREA**

Zircon in the study area could be potential source of zirconium element ore. Exploitation of zircon and associated minerals could be of economic value which will increase the national income of Jordan. The economic potential of zircon in the study area could be improved by extraction of other materials such as REE, Monazite, radioactive elements (Th and U). Artificial zircon gemstones could be produced by smelting of the collected tiny zircon natural samples.

**CONCLUSIONS**

1. Field investigation showed that the zircon minerals occur in the middle part of Dubaydib Sandstone Formation (DB2) of Ordovician age.
2. The zircon is mainly concentrated in high percentages within the size fraction between 45 µm and 90 µm.
3. The highest concentration values of zircon that were concentrated in the size particles of (less than 90 μm to less than 45 μm) has averages range (of 65.4% to about 88%) of the total sample.

4. Qualitative studies using binocular microscope showed that the most abundant heavy minerals observed in the samples was zircon, which range between 70 – 80% in the heavy samples, and about 10% in the middle samples. The tourmaline grains range from 10 to 15% in the samples. The titanium minerals (rutile and ilmenite) range between 5 – 15%, and monazite range between 5 – 10%.

5. The results of SEM indicated that the shape of zircon grains of the zircon sand sample euhedral to rounded grains and exhibit elongated or stubbed prisms in shape. Monazite grains of the zircon sand sample are rounded to sub rounded, egg-shaped or spherical grains. Titanium minerals shapes vary and are commonly observed as elongated to rounded prism in shape, sub rounded, rounded to sub rounded, and often fragmented grains. Tourmaline grains shapes are commonly observed angular to rounded prism (slender to thick prismatic) in shape, sub rounded, rounded to sub rounded.

6. XRD analysis of the Z ~ G and Z ~ I samples indicate the presence of titanium minerals, zircon, and monazite.

7. Chemical analysis showed that there is a positive relationship between the Zr, Ce, La, Y and TiO₂.

8. The highest percent of Zr, TiO₂ and REE in non magnetic minerals concentrate (heavy minerals) is in the size fractions less than 90 + 45 to - 45 μm.

**RECOMMENDATIONS**

1. Detailed investigation in the study area and the surrounding areas are highly needed to determine the potential promise areas of zircon occurrence.

2. Feasibility studies of the zircon in the study area require further investigation to determine the exact amounts of the zircon ore.

3. Exploration of uranium in the whole area in order to determine the exact quantity and quality of the ore.

4. Investigations of REE and Monazite in the whole area in order determine the exact quantity and quality and industrial application.

5. Trenches and boreholes are highly needed for further prospecting.
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