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# Heavy mineral concentrations in the sandstones of Amij Formation with particular emphasis on the mineral chemistry and petrographic characteristics of monazite, western desert of Iraq

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The heavy minerals in the clastic unit of the Lower Jurassic Amij Formation exposed in the western desert of Iraq were studied. The uppermost part of the clastic unit contains thin, placer-like black sandstone horizons that are radioactive and abnormally rich in heavy minerals (0.6–56%), dominated by opaque (65%) and transparent (35%) heavy minerals. The minerals, in the order of decreasing abundance are pseudorutile, goethite, zircon, hematite, magnetite, monazite, rutile, leucoxene, tourmaline, ilmenite, chromite, and few others. Electron probe microanalysis (EPMA), microscopic and autoradiographic observations and analysis showed that the monazite is monazite-(Ce) type with an average composition of $(Ce_{0.39}Nd_{0.16}La_{0.19}Pr_{0.04}Sm_{0.02}Gd_{0.02}Eu_{0.01}Y_{0.04}Th_{0.06}U_{0.01}Ca_{0.05}Fe_{0.01})(P_{0.98}Si_{0.03})O_4$.

Monazite consists predominantly of REE-oxides (57.93%) and $P_2O_5$ (29.31%), with minor amounts of $ThO_2$ (6.60%), $Y_2O_3$ (1.92%), $UO_2$ (0.76%), CaO (1.14%), $SiO_2$ (0.69%), and $FeO_t$ (0.17%). The dominant compositional substitution operating between REE and P were a mixture of the complex cheralite type substitution ($[REE]_{-2}$ [Th][Ca]) and the coupled huttonite type substitution ($[REE]_{-1}$ $[P]_{-1}$ [Th][Si]). The chondrite-normalized REE distribution patterns of monazite show enrichment in LREE with positive Eu- and Pr-anomalies of 1.46 and 9.13, respectively. The median values of $(La/Sm)_{CN}$ and $(La/Nd)_{CN}$ ratios are 4.35 and 1.97, respectively. Zircon which is the dominant transparent mineral is Hf-rich that is composed of 30.61% $SiO_2$, 57.58% $ZrO_2$, 7.03% $HfO_2$, 2.04% $Y_2O_3$, 0.56% $ThO_2$, 0.19% $UO_2$, and 0.19% $Al_2O_3$ corresponding to a formula $(Zr_{0.909}Hf_{0.065}Th_{0.004}U_{0.001}Y_{0.031})_{\Sigma 1.011}(Si_{3.966}Al_{0.028})_{\Sigma 0.999}O_4$. Rutile and tourmaline form 7% and 4% of the heavy minerals. Ilmenite which is one of the predominant heavy minerals forms 2.5% of the opaques because it is pervasively altered to Ti-Fe oxides. In addition of zircon and monazite, the chemical compositions of most of the other heavy minerals are also given in this study. The expected dominant source of heavy minerals and their host sandstones are most probably the felsic igneous and metamorphic complexes of the Arabian Shield, currently located ~600 kms to the south of the studied area. The heavy minerals were carried from the source area by northward moving rivers and sorted out by ocean waves as black sand concentrations at the delta mouth along the southern beaches of the Neo-Tethys Ocean under passive margin tectonic setting. This border was apparently bordering the current western part of Iraq during Upper Jurassic period.

## 1. Introduction

Heavy mineral studies have benefited from technology advancements of single-mineral analytical techniques such as electron probe microanalysis (EPMA) and Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) (Mange and Wright, 2007). Interest is generated by those interested in provenance studies, as well as their economic importance. Monazite in particular has attracted much scientific and economic interest (e.g., Levinson, 1966; Overstreet, 1967; Graeser and Schwander, 1987; Nickel and Mandarino, 1987; Masau et al., 2002; Huminicki and

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Hawthorne, 2002; Mange and Morton, 2007; Linthout, 2007) for it accommodates significant quantities of lanthanides (REE and Y) and phosphorus, and in many occurrences, the actinide thorium (Th). Monazite-(REE)$PO_4$ is an anhydrous rare-earth elements orthophosphate with monoclinic structure (space group $P21/n$, $Z = 4$) where the larger trivalent rare-earth element (REE) cations are located in a polyhedron, coordinated by nine oxygen atoms (Huminicki and Hawthorne, 2002; Boatner, 2002). It is basically a Ce-phosphate with ideal formula of $CePO_4$ where Ce can partially be replaced up to few per cent by other light rare earth elements (LREEs) and Gd, and by some tenths of percent of Eu and heavy rare earth elements (HREEs) (Nagy and Draganits, 1999). In addition to cations of LREEs, monazite may also incorporate significant amounts of thorium, and to a lesser extent, uranium, such that it represents a principal thorium ore, and a secondary source of uranium (Boatner, 2002). Monazite is widely distributed as an accessory mineral in acidic igneous rocks (granites, rhyolites, pegmatites), and gneisses (Boatner, 2002) and also in carbonatites, charnockites, migmatites, and quartz veins (Rapp and Watson, 1986). Monazite of metamorphic origin has been reported, particularly in Ca-poor rocks (Nagy and Draganits, 1999; Pan, 1997; Lanzirotti and Hanson, 1996; Akers et al., 1993; Grauch, 1989; Kiesl et al., 1983). It may also be found as a heavy mineral in alluvial deposits (placers) such as black beach sands, where it forms important economic deposits in many countries including the United States, Australia, South Africa, Sri Lanka, Brazil, India, Malagasy, and Canada (Boatner, 2002). These detrital deposits were formed by the weathering and erosion of granitic and other related host rocks. The formation of such monazite placer deposits is attributed to its mechanical and chemical stability such that it survives metamorphic and sedimentary cycles for 100s million years (Rapp and Watson, 1986). In addition to the economic importance of monazite as the source of REE, Th and U, it also has many scientific applications. Monazite has been used in provenance studies as tectonic indicator (Drost et al., 2004); geochronology for Th-U-Pb age dating (Krenn et al., 2009; Kusiak et al., 2006; Gonzalez-Alvarez et al., 2006; Yang et al., 2006; Williams et al., 2007), and in geothermometry and geobarometry (Gratz and Heinrich, 1997, 1998; Andrehs and Heinrich, 1998).

The heavy minerals and their host clastic lower part of the Amij Formation including a proposed heavy-mineral placer deposit, very rich in opaques and transparent minerals (zircon, monazite, rutile, and tourmaline and others) form the uppermost part of the sandstone unit exposed in the western desert of Iraq are studied. The study gives particular emphasis to monazite which is the main source of radioactivity of the Amij Formation. The Lower Jurassic Amij Formation is best exposed in Amij valley area (locally called Wadi Amij), some 50 km east of Rutba City (Fig. 1). Anomalous radioactivity in Amij Formation was reported by Rohan (1979) and Polytechnic (1980) which were followed by subsequent studies investigating the source of radioactivity and its possible economic importance. However, the main source of the radioactivity were not fully identified until the work of Ismail (1996) who described monazite to be the main cause of the radioactive anomaly, with a minor contribution from zircon. Before the study of Ismail (1996), zircon was considered as the main radioactivity source by most of previous studies. The importance of Amij Formation is also highlighted by Al-Bassam (2007) as an important formation for its heavy minerals content.

The description includes the mineralogical, geochemical, optical, autoradiographic and separation characteristics of monazite as well as its provenance, which forms ~8% of heavy minerals within the studied sandstones. In addition to monazite, data about the associated heavy minerals and their host sandstones will also be described and discussed in some detail.

## 2. Geology

The rocks of Amij Formation were introduced as a new formation within the stratigraphic column of western desert of Iraq by Buday and Hak (1980) (Figs. 1 and 2). They subdivided the formation into two rock units, the lower coastal deltaic or coastal closed basin sandstone unit, and the upper carbonate unit of shallow coastal marine origin (Fig. 3). The age of the formation is not agreed upon, ranging between Liasic to Bathonian. Since the introduction of Amij Formation, it was studied by many researchers (e.g., Karim and Ctyroky, 1981; Al-Mubarak and Amin, 1983; Jassim et al., 1984; Hussein, 1984; Al-Naqib et al., 1986; Qaddouri, 1986; Al-Sinjeri, 1987; Al-Hadithi, 1989; Kaseer et al., 1992). The thickness of the lower clastic unit of Amij Formation varies between 9 and 21 m and that of the upper carbonate unit reaches 30 m (Al-Naqib et al., 1986). It is unconformably overlaying the Hussainiyat Formation (Lower Liassic) and unconformably overlain by the sandstones of Muhaiwir and Saggar formations (Jassim et al., 2006) (Fig. 2).

The Amij Formation was the focus of many studies because of its anomalous radioactive nature that was reported by Rohan (1979) and Polytechnic (1980) (e.g., Al-Kazzaz, 1985; Al-Najim and Hakki, 1986; Al-Amiri, 1988; Al-Salihi, 1989; Al-Ameer et al., 1993; Ismail, 1996; Gayara and Ismail, 1996). Ismail (1996) was the first to fully establish the real causes of radioactivity in Amij Formation and concluded that the main source of such anomalous radioactivity is mainly monazite and to a lesser degree zircon; meanwhile the previous studies attributed the radioactivity mostly to zircon. The currently studied heavy mineral-rich horizons occur as few centimetres thick each, blanket-like, highly concentrated black sandstone beds alternating with white sandstones which were deposited as beach sands along the southern coast of the Tethys Sea during Jurassic Period. The economic significance of this occurrence is not fully studied although its radioactivity has been detected by carborne survey.

The western desert is part of the Stable Shelf tectonic division of Iraq which includes formations ranging in age from Permo-Carboniferous to Tertiary. These formations were deposited in continental to shallow marine environments, and are separated by regional to local unconformities (Fig. 2). In spite of the relative stability of the area, it has been affected by tectonism that may be observed in the sedimentation modes and is reflected in regional structural features that controlled structural development of the sedimentary basin. The most important structural feature is the Rutba Uplift which is the extension of the Hail-Rutba Arch. The effect of this structure is evident from the lack of sedimentation and presence of unconformities during Mesozoic and Cenozoic periods (Buday and Hak 1980). These events have affected the mode of sedimentation during Jurassic period in the form of sedimentation cycles characterized by clastic strata forming the lower part, separated by unconformities from older units, and covered by carbonate strata surrounding the Rutba Uplift which are exposed in the east of Rutba City. The western desert has very low relief, ~2 m/km with a NE-SW regional strike of the Jurassic formations (Fig. 2).

## 3. Sampling and methodology

225 samples were collected from the Amij Formation along 20 sections that were exposed in 17 trenches dug within the Amij Valley and 3 trenches to the northeast of the valley (Fig. 1). The samples comprised 185 sandstones and 40 claystones.