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Mineralogical and Geochemical Characteristics of Dur Al-Najaf Gemstones from Al-Najaf Province, Central Iraq

Basim H. Soltan [1], Muqdad T. Sadkhan [2], Maher M Mahdi [3*], Hussein B. Ghalib [4]

[1,2,3]Geology Department, Science College, University of Basrah, Basrah, Iraq.
[4] Director of the Scholarships and Cultural Relations Department Ministry of Higher Education and Scientific Research, Baghdad, Iraq.

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Correspondence:
Name: Maher M Mahdi

Email: maher.mahdi@uobasrah.edu.iq

ABSTRACT

Dur Al-Najaf is considered one of the most distinguished semi-precious stones in Iraq, especially in the province of Najaf. A field survey is conducted in the areas within the Bahr Al-Najaf region and among the recent sediments and the Dibdibba Formation. The study aims to analyze the mineral and chemical makeup of this semi-precious stone, to categorize its type, to provide an overview of its typical attributes, and to ascertain the origin and geographical distribution of these semi-precious stones. The samples underwent examination from a sedimentological, mineralogical, and geochemical perspectives. Four distinct samples of stones, each representing a different color variant, underwent examination to explore their petrology through polarized light microscopy and mineralogy via XRD analysis. Additionally, three more stones were subjected to SEM analysis. The results reveal three types of these stones which are pure type, oily type (gray), and Al-Husseini type (reddish brown). Results of XRD, XRF, and EDX analysis show that these stones are various forms of pure sedimentary quartz mineral. Some of these stones contain impurities that give them varying colors, such as gray, which may have resulted from a high concentration of CaO, or red to reddish color, resulting from high FeO concentrations. These stones represent pieces of quartz minerals included in the components of the Dibdibba Formation, which resulted from the erosion and crushing of igneous rocks from the Arabian Shield that spread to wide extents in the Najaf Plateau.

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الخصائص المعدنية والجيوكيميائية لأحجار در النجف من محافظة النجف وسط العراق

باسم حميد سلطان [1] ، مقداد طاهر سدخان [2] ، ماهر منديل مهدي [3*] ، حسين بدر غالب [4]

[1،2،3]قسم علم الارض، كلية العلوم، جامعة البصرة، البصرة ، العراق.

[4] مديرية إدارة الابتعاث والعلاقات الثقافية بوزارة التعليم العالي والبحث العلمي، بغداد، العراق .

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احجار كريمة

معدنية

العراق

المراسلة:

الاسم: ماهر منديل مهدي

Email: maher.mahdi@uobasrah.edu.iq

الملخص

يعتبر در النجف من أبرز الاحجار شبه الكريمة في العراق وخاصة في محافظة النجف الاشرف. تم إجراء مسح ميداني في مناطق مختارة من داخل منطقة بحر النجف وبين الرواسب الحديثة بالإضافة إلى رواسب تكوين دبدبة. سعت هذه الدراسة إلى تحليل التركيب المعدني والكيميائي لهذه الأحجار الكريمة وتصنيف نوعها وتقديم لمحة عامة عن صفاتها النموذجية، والتأكد من الأصل والتوزيع الجغرافي لهذه الأحجار. درست العينات من الناحية الرسوبية والمعدنية والجيوكيميائية خضعت أربع عينات مختلفة من الأحجار الكريمة للفحص لاستكشاف خصائصها الصخرية من خلال الفحص المجهري للضوء المستقطب ومعدنيتها عبر تحليل XRD حيث تمثل كل منها لونًا مختلفًا، بالإضافة إلى ذلك، خضعت ثلاث عينات أخرى لتحليل SEM. حيث تم العثور على ثلاثة أنواع من هذا الحجر: النوع النقي، النوع الزيتي (الرمادي)، النوع الحسيني (البني المحمر). أظهرت نتائج تحليل XRD و XRF و-SEM EDX أن هذه الأحجار هي أشكال مختلفة من معدن الكوارتز الرسوبي النقي. تحتوي بعض هذه الأحجار على شوائب تعطيها ألوانًا مختلفة، مثل الرمادي الناتج عن تركيز عالٍ من أوكسيد الكالسيوم، أو اللون البني الناتج عن تراكيز عالية من اوكسيد الحديد. تمثل هذه الأحجار قطعًا من معادن الكوارتز الموجودة في مكونات تكوين دبدبة، والتي نتجت عن تآكل وسحق الصخور النارية من الدرع العربي التي انتشرت على مسافات واسعة في هضبة النجف.

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Introduction

Dur Al-Najaf is a precious or semi-precious stone that is shaped like a pebble or gravel and is found in the Najaf desert area in the center of Iraq (Figure 1). This stone is subjected to repeated polishing after it is transported by torrential water over long distances, which gives its distinctive characteristics, such as luster, transparency, and high purity (Ford and Vodacek, 2020). These stones date back to the geological formation of the Najaf region, and pebbles were known and used during the pre-Islamic Era (Al-Attiyah, 2006). The shiny pebbles are famous in the land of Al-Najaf, where effected by many natural factors such as dust, rain, heat, type of rock in the region, thermal extremes, drought, and sand type, formed these shiny pebbles (Al-Attiyah, 2009). The people of Al-Hira old city (near Al-Najaf City) knew the shiny stones of Dur Al-Najaf that adorned the surface of the Najaf Desert in addition to the desert flower structures. As such, the residents of Al-Hira, and after them, the people of Kufa in early Islamic periods used the land of Najaf as a refuge for hunting and wandering, especially during the spring. Given the presence of shiny pebbles in this region, they called it Al-Bariq (the shiny land), but this term is no longer used (Al-Attiyah, 2009). The area extends west of the noble city of Najaf to the so-called Najaf Sea, which is a depression or a wide valley that represents part of the western desert of Iraq (Figure 1), for a distance of

approximately 100 kilometers. The colors of the pebbles of different shapes and sizes vary, and the pebbles appear with a distinct transparency that distinguishes them from other types of pebbles. Samples of these stones are collected by gem collectors and shepherds at specific times, especially after a rainy day, as the rain washes away the pebbles, and the sun after rain increases their luster, making them easier to notice and distinguish from other stones. The Najaf people know the seasons and the places for gathering the pebbles, and because the pebbles are abundant in the Najaf Desert, they were called it the Dur of Al-Najaf (The word Dur in Arabic means shining precious stone). These pebbles are found in all the lands of Najaf, including the southern areas of Kufa City, beyond the famous Wadi al-Salam cemetery, and the lands between Al-Hira and Al-Najaf (Fig. 1).

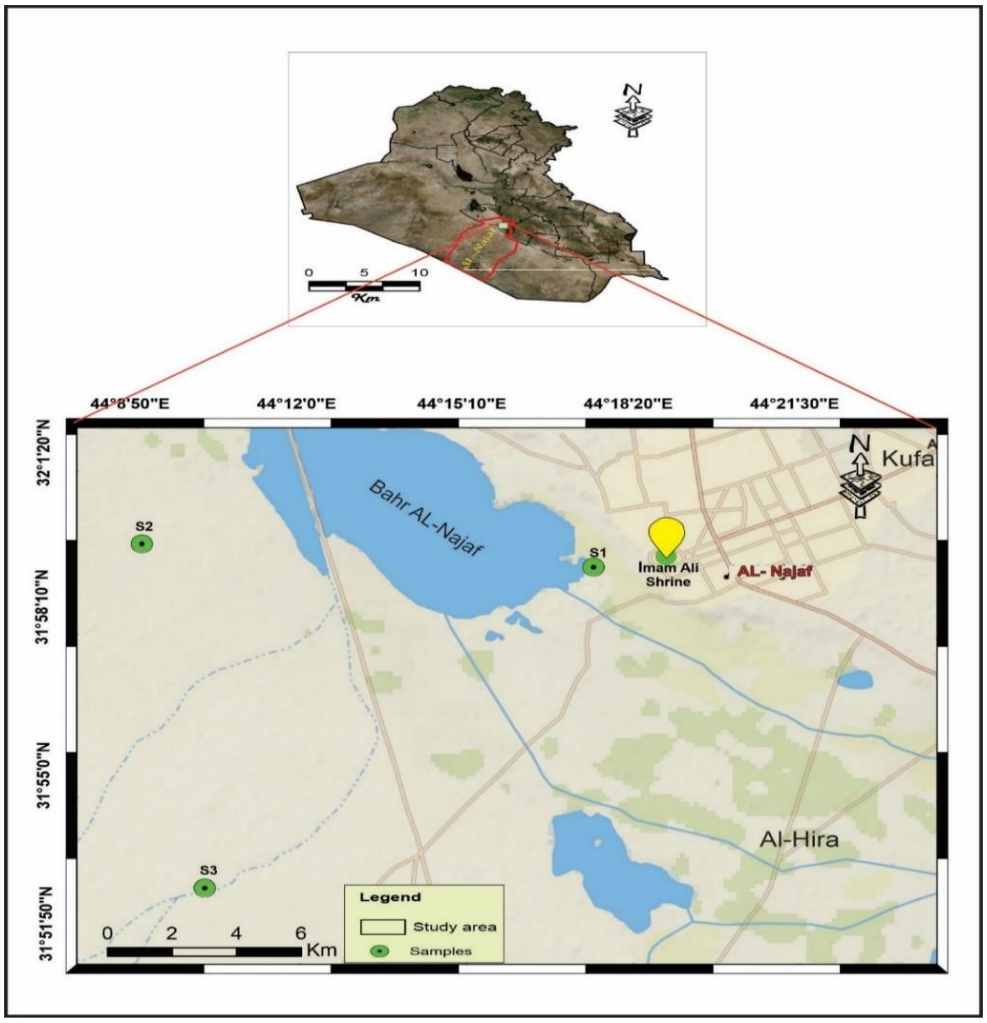

Fig.1. Study area (Bahr Al-Najaf) and samples collecting locations (S2, S3) (Google Map, 2022).

Dur Al-Najaf gemstones are regarded as semi-precious because they are collected from an area close to the shrine of Imam Ali in Najaf City, Iraq, and the stones are gaining a high status among Muslims (Plate 1: a). The stones are also valued for their other distinctive natural characteristics, such as luster, hardness, and purity, especially after being polished and cut by skilled craftsmen in Najaf City (Plate .1: b).

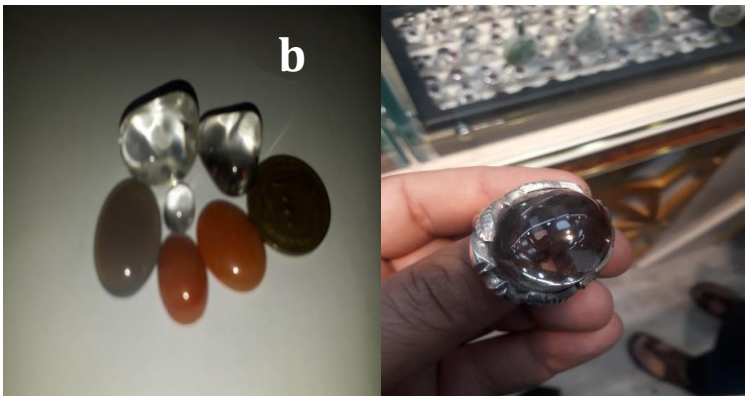

Plate1. (a) Different polished types of Dur Al-Najaf stones; (b) A beautiful and distinctive ring made of Dur Al-Najaf stone.

Dur Al-Najaf varies according to its sources and types, and is classified locally based on colors, states, and sizes as follows (Plate 1a):

1- The bright (white) Dur or the bright star in analogy to the planets or the bright stars.

2- The oily Dur is named for its oil-like color and because it is shiny, with a color gradient from gray to black. It is believed to be a type of smoky quartz.

3- Al-Dur Al-Husseini, whose color ranges from brownish red to bright red.

4- Al-Dur abu-Sha'rah (sha'arah in Arabic = hair), which is a distinct stone containing hair-like thin lines that may appear as a single line or a group of lines; this type of stone may be exposed to a natural condition in its form to appear in this form of formation, and hair-like lines are visible inside the transparent stone from all directions (Al-Abtahi, 2008). Unfortunately, no specimen of this type was found in the study area or in the local market.

The craft of Dur al-Najaf has been known in all its various stages, such as collecting, punching, and crafting, for a long time in this city (Plate 1 b). This trade contributes to increasing the city's economy, as this commodity is popular given its high demand among the clergy, locals, expatriates, and tourists from different countries, especially those from Iran, Lebanon, the Arab Gulf states, Pakistan, Afghanistan, and India. Thus far, this form of gemstone has not been studied in detail, except for a limited study by Ali (2000), one of the researchers of the Iraqi General Company for Geological Survey and Mining (Al-Attiyah, 2006). He studied the mineral and chemical composition of these stones and described them as one of the forms of quartz minerals found in the Bahr al-Najaf region.

Various references indicate that this stone has many medical and psychological benefits, as it is believed that it increases the positive energy in humans, prevents insomnia and nightmares, reduces stress and work pressures, and strengthens focus and visual sense, which are believed to be related to the electrical properties and trace proportions of some radioactive elements in quartz crystals such as uranium and radon (Al-Abtahi, 2008; Al-Maarouf, 2014; Jia-Huan *et al.*, 2016; Oniya *et al.*, 2022). The price of these stones in the Iraqi markets ranges between 2$ and 15$ per 1 gram, depending on the type, purity, and proximity to Najaf City (information from local sellers).

Aim of study

This study aims to characterize the mineral and chemical composition of this semi-precious stone, classify the type, describe the general characteristics, and determine the sources and locations of these semi-precious stones in this area.

Geological setting of Bahr Al-Najaf region

Bahr Al-Najaf (Najaf Sea) is located at the western edge of Najaf City and overlooks its plateau. Its basin extends toward an area of approximately 750 km^2, and the lowest point height is approximately 11 m above sea level. The surface is generally covered with recent clay and silt sediments. The outcrops cover large areas of Bahr Al-Najaf, and most of these outcrops are from the deposits of the Dibdibba and Fatha Formations in the north and eastern north (Ghalib *et al.*, 2019) (Figure 2). At the western end of Bahr Al-Najaf, there are exposures of the Euphrates and Nafayil Formations (Sissakian and Fouad, 2015). Bahr Al-Najaf depression is located on the boundary between the stable shelf (Salman Zone) and unstable shelf and passes through Heet-Abu Jir fault systems, with few parts falling within the Najaf basin (Al-Attiyah, 2009; Sissakian and Fouad, 2015; Ghalib, 2017). The Bahr Al-Najaf region represents a high cluster of fractures toward the east of the Heet-Abu Jir fault system, while the Najaf plateau represents the descending block according to the regional structural map (Al-Attiyah, 2009). The stratigraphic situation of the study area includes several exposed formations on the surface extending from the Paleocene to the Quaternary age (Buday, 1980). The most important geological formations surveyed in the study area are as shown in the geologic map below (Figure 2).

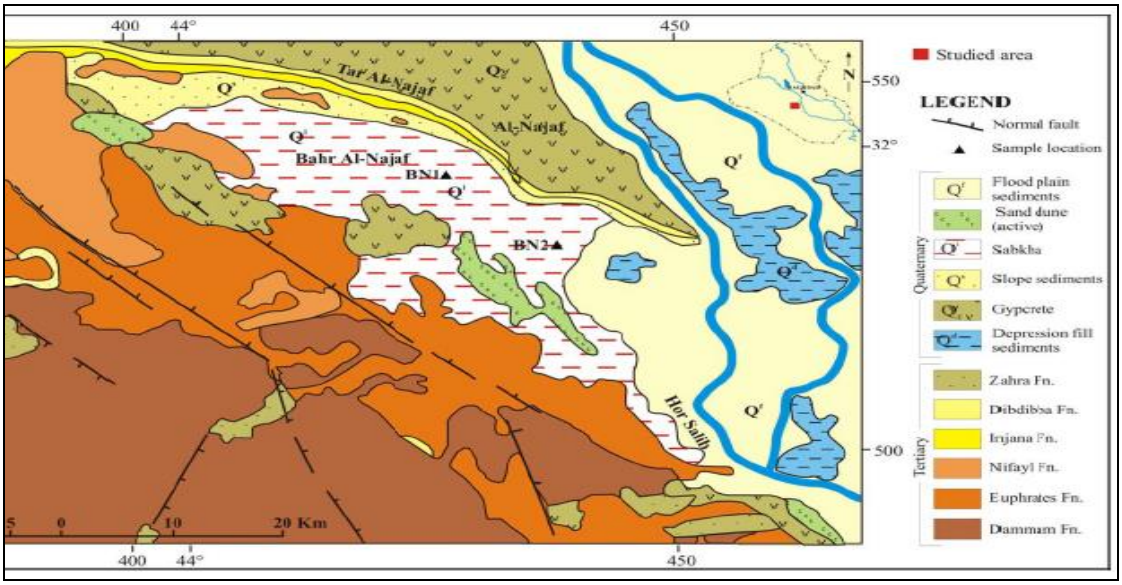

Fig.2. Geological map of Bahr Al-Najaf area (Benni *et al.*, 2012)

According to Daoud (2000) and Al-Jaberi and Mahdi (2020), these sediments belong to the Quaternary period, dating to approximately 1.75 million years ago. These sediments were exposed as terraces or successive layers on the edges of the Bahr al-Najaf depression, especially at its northern sides (Plate 2A). These types are fluvial sediments, sabkha, sand dunes, and alluvial and aeolian sediments (Daoud, 2000). Sissakian *et al.* (2015) pointed to the Quaternary sediments that come from the flood plain of the Euphrates River and exploded geological formations in the Tar Al-Najaf area in the northern parts, whose sediments are transported from the Western Desert, west of the study area, through the seasonal valleys. The

climate of the studied area is dry or semi-arid, thereby increasing the erosion of the unconsolidated rock. The weathering factor reduces the presence of groups of unstable minerals that make up the majority of the total components of heavy minerals. Depending on the presence of four sedimentary cycles in the sedimentary column of this area, there is a variation in the rates of minerals that appear in the variable higher cycles (Benni *et al.*, 2012).

Dibdibba Formation

The Dibdibba Formation (Pliocene-Pleistocene) covers outcrops in two areas in Iraq; the first is the Basrah and Dhi-Qar regions; and the second is the Najaf-Karbala plateau, which is a mixture of different sizes of sand and gravel deposits and pebbles (Plate 2: B, C, and D), with variable igneous, metamorphic, and sedimentary origins, derived from the erosion of the Arabian Shield rocks in the Arabian Peninsula (Al-Attiyah, 2009). It was transported by rivers with sedimentary loads and deposited in the form of fan river deposits. The thickness of the Dibdibba Formation, which is exposed at outcrops in the Najaf Plateau, is approximately 13 m in the northwestern part, then decreases toward the southeast until 2 m is reached. It consists of solid gravel sand rocks whose grains are interwoven with carbonate matrix and sometimes consists of white to brown brittle sands mixed with pebbles. Clay balls are present within the sand on the surface in contact with the Injana Formation (Al-Attiyah, 2006; Sissakian *et al.*, 2015). In the northwestern part, the formation includes layers of successive solid sand with alluvial and thin layers of gypsum or anhydrite. The age of the Dibdibba Formation goes back to the period extending from the Upper Miocene to the Pleistocene era, and it asymmetrically covers the formation of the hole in the southern regions of Iraq, while harmonically, it covers the formation of the Injana in the areas of the Najaf plateau (Al-Attiyah, 2009). The Dibdibba Formation is an important feature of the Najaf Governorate from an economic point of view, as it is an important source of sand for construction or industrial purposes and can be used in the manufacture of glass after making some improvements (Daoud, 2000; Sissakian *et al.*, 2015). This formation consists of intersecting sandstone layers with a solid layer of celestite mineral and consists of a thick sandstone at the bottom that ends with layers of unconsolidated fine sand (Alabbassi *et al.*, 2016).

Materials and Methods

A geological survey was conducted in the areas of the Dibdibba formation sediments outcrops in the Bahr Al-Najaf region (31°42′– 32°8′ N, 43°40′– 44°24′ E), where Dur Al-Najaf stones are expected to be found, eight pieces are collected from those areas. Information about these stones is collected, and different sizes and types of stones are obtained in the Najaf markets specialized in selling them. In addition, six pieces are purchased and examined to determine their physical properties, such as color, hardness, and specific density. Four pieces (one from each type) are of different colors analyzed at the Building Research Center in Baghdad to investigate their petrology by polarized light microscopy and mineralogy by X-ray diffractometer (Model: D-6000 XRD, using CuBF sources in wavelength, v = 1.54056 Å at 60 kV and 80 mA). In addition, three pieces (Pure type DN1, Oily type DN2 and Al-Husseini type DN3) are analyzed using scanning electron microscopy (Model FEI Nova NanoSEM 450) in the laboratories of the Physics Department at the University of Basrah to perform a comprehensive mineral and chemical diagnosis and determine the impurities present in the impure types of Dur Al-Najaf stone that led to their different colors compared with the common transparent stones. Three pieces are analyzed using X-ray fluorescence

(Model: Spectro Xepos XRF, Germany) in the laboratories of the Department of Geology at the University of Baghdad to determine their chemical composition.

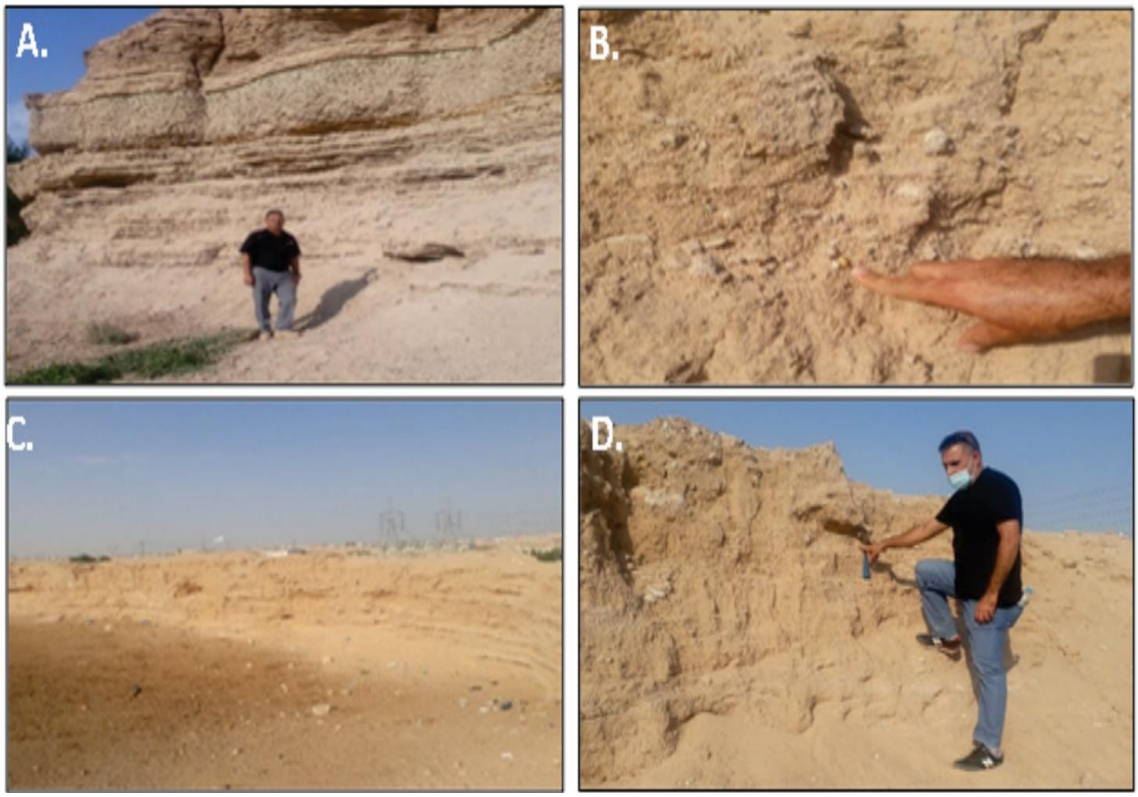

Plate 2. (A). Recent sediments outcrops in edges of Bahr Al-Najaf (B.) Pieces of Dur Al-Najaf stones in the study area (C, D) Outcrops of Dibdibba Formation clastics.

Results

1. Petrological and mineralogical study

Dur Al-Najaf stones are collected from separate and far-flung areas in the Bahr Al-Najaf region. In addition, the pieces are obtained from the local market in Najaf City (Plate 3: A and B) and distinguished by their colors (transparent with a glassy luster, semi-transparent white, reddish to brown color, and a single gray stone), which are the main stone types known locally (Al-Maarouf, 2014), with a density ranging between 2.611 and 2.635 gm/cm$^{3.}$ Their sizes range between approximately 1 and 5 cm. A monocrystalline quartz mineral has well-known optical properties (Plate 4: A); it is colorless in normal plane polarized light, while it has homogeneous parallel extinction and first-order gray to yellow interference colors (Gotze, 2009; Nesse, 2012), which can reflect the igneous origin of the source rocks of these stones; sometimes, it contains impurities and fine silicate grains in areas of limited fractures in its structure as poikilitic textures (Plate 4: B) (Mahdi and Soltan, 2021). These stones have been analyzed mineralogically using X-ray diffraction to determine their mineral composition, and the results showed that these stones consist of pure monocrystalline quartz mineral in a normal form (Figure 3).

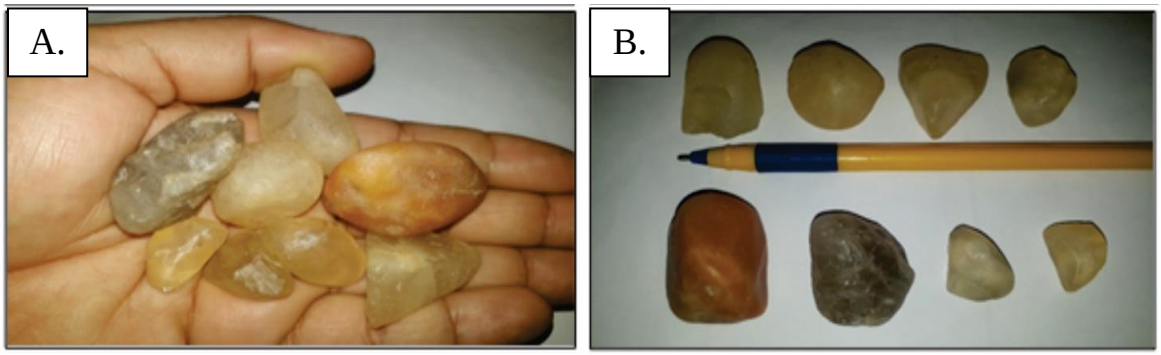

Plate 3. (A). The collected stones from the study area (B) Types and sizes of Dur Al-Najaf stones.

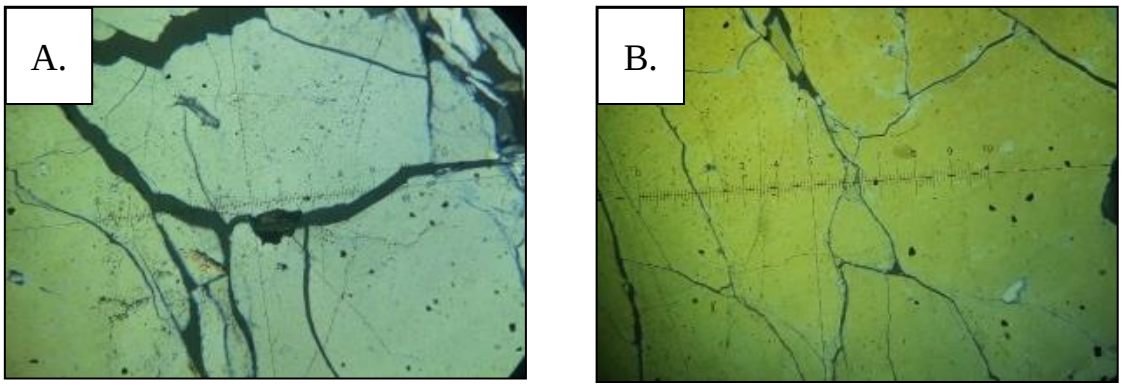

Plate 4. (A). Monocrystalline quartz grains of Dur Al-Najaf stones (40X- X.P.L.). (B) Poikilitic texture in quartz grains (40X- X.P.L.).

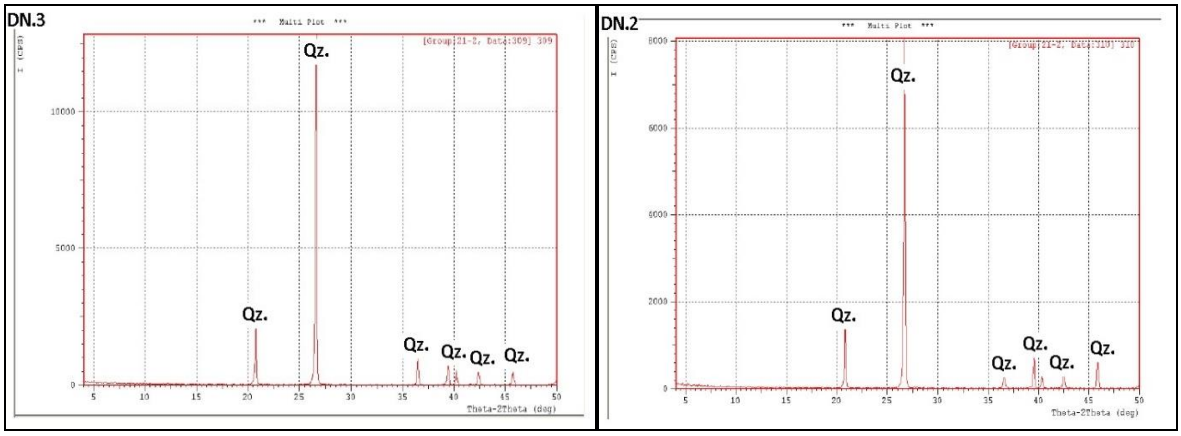

Fig.3. X-ray diffraction pattern of Dur Al-Najaf gemstones.

2. Geochemical study

Several samples are analyzed using SEM-EDX to determine the total chemical composition of the various types of Al-Dur stone. The focus is on the Al-Husseini and oily types, and the results show that the pure type of Dur Al-Najaf stone has a high purity and is composed mainly of silicon and oxygen (Figure 4. A). The samples of AL-Husseini stone type contained relatively high concentrations of iron oxide (5.99%) and strontium (0.55%) (Figure 4.C). Iron may be the cause of the red hues of the stone (Fritsch and Rossman, 1988). In addition to strontium, silicon (39.25%), and oxygen (57.83%), as well as calcium and titanium, with concentrations of approximately 0.26% and 0.31%, respectively (Figure 4.B), the last two elements may be the cause of the different shades of gray in these stones (Cohen and Makar, 1982).

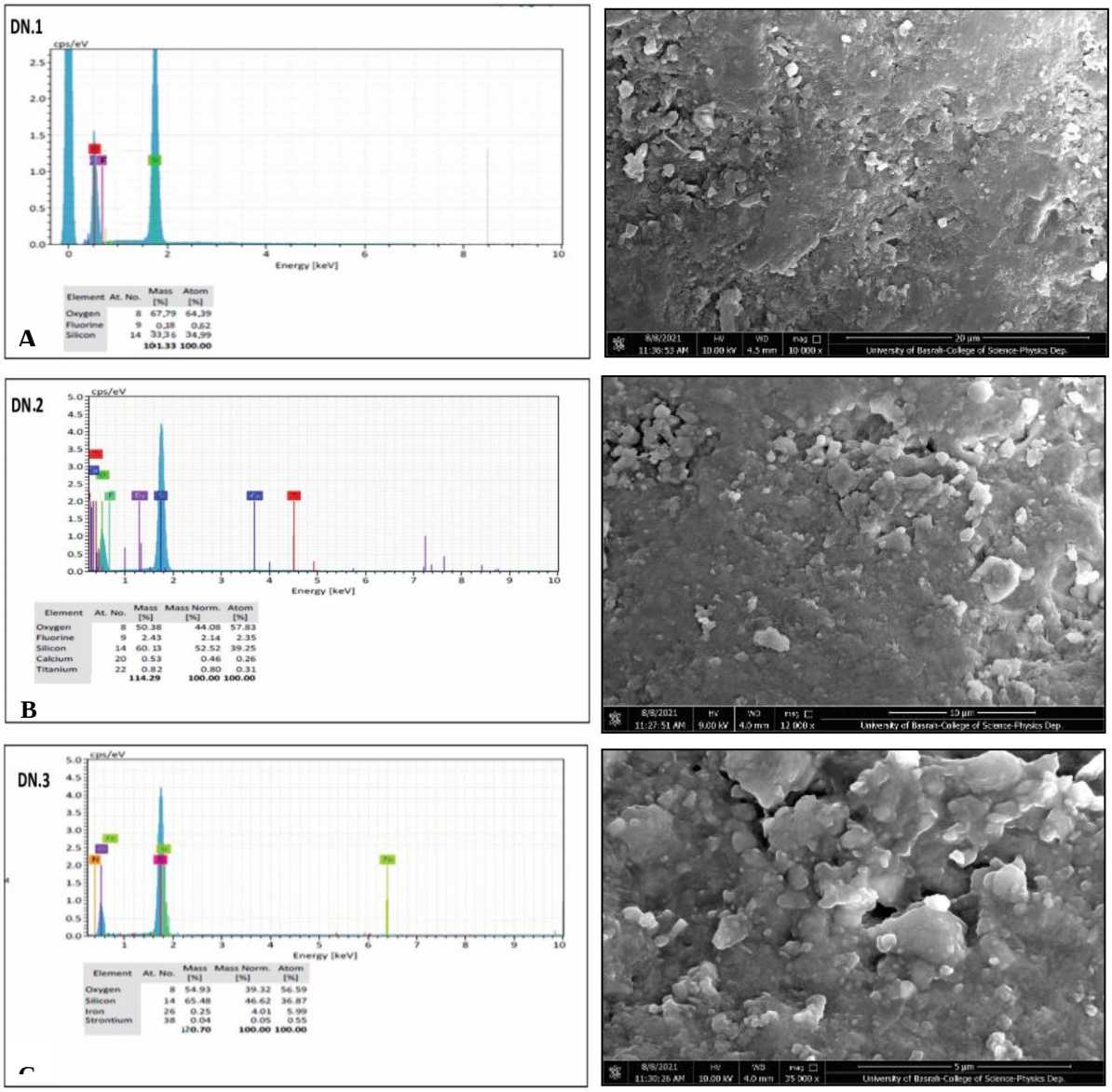

Fig.4. SEM-EDX analysis of Dur Al-Najaf gemstones, with SEM-images showed the surface morphology of these stones.

The chemical composition of these stones is shown in table (1). The stones have various forms of sedimentary quartz mineral and contain very high concentrations of SiO_2 ranging between 95.18% and 97.98%, as well as minor concentrations of other major oxides whose levels converged in the three types but low in the pure type (DN.1). The oily type (DN2) contains a high concentration of CaO, reaching a rate of 1.21%, which could be the cause of the distinctive gray color of this type because it contains a relatively high concentration of this oxide. The reddish (Al-Hosseini) type (DN3) is distinguished by its higher concentration of FeO, which reachs 2.823% explaining the brown colors of this type of Dur Al-Najaf. There is a belief that Dur al-Najaf is a moonstone, which is a type of feldspar mineral (Iamsupa *et al.*, 2016), but chemical analysis indicated that these stones are quartz minerals. The various concentrations of iron oxide observed in these stones (Table 1) may be attributed to the fact that they came from various igneous rocks within the Arabian Shield rocks, which range between granite and granodiorite rocks, which constitute the source of sediments in this region.

Table 1. Chemical analysis of different types of Dur Al-Najaf stones.

Oxides (%)	DN.1	DN.2	DN.3
SiO_2	97.98	97.26	95.18
Al_2O_3	0.251	0.251	0.260
CaO	0.158	1.21	0.107
MgO	0.789	0. 812	0.812
FeO	-	0.12	2.823
TiO_2	< 0.008	< 0.013	< 0.005
F	<0.12	<0.08	<0.141
Total	99.178	99.654	99.281

Discussion

Dur Al-Najaf stones have existed since the formation of the Najaf region, and ancient people who settled in these areas were known to collect and obtain these stones since the pre-Islamic period. This region is characterized by the presence of shiny or sparkling pebbles due to several reasons, such as the type of sediments and geological formations (Dibdibba Formation), which are derived from the erosion of the Arabian Shield rocks (specially granite and granodiorite igneous rocks) in the Arabian Peninsula, the rocks are transmitted later for thousands of kilometers and exposed to various and long processes of erosion, cracking, and polishing during different geological times, accompanied with unevenness of rain and heat, drought, thermal extremes, which made all of these factors contribute to the formation of these stones forming an attractive shiny gravels or gemstones (Saleh *et al.*, 2021; Soltan and Mahdi, 2022). Other studies such as Alabidi *et al.* (2020) indicate that the source of the sediments of the Quaternary period was not the rocks of the Arabian Shield but the sedimentary cover on the edges of the Arabian Shield, and they were moved over short distances to their present location. However, sedimentary and regional studies on the region support that these sediments, which contain within them pieces and stones of Durr al-Najaf, moved from distant geological areas.

Conclusion

Dur Al-Najaf is composed of quartz, which is one of the forms of crystalline quartz stones; thus, it cannot be considered a type of moonstone, which is usually formed from feldspar minerals. Dur Al-Najaf stones are randomly distributed in the Bahr al-Najaf region, especially within the sediments of the Dibdibba Formation and the recent sediments scattered in the region, which were from Arabian Shield rocks from neighboring Saudi Arabia. The types of Dur Al-Najaf include the pure type, the Al-Dur Al-Husseini, and oily Dur. The Al-Dur Al-Husseini stone has a red or reddish-brown color due to the presence of iron oxide, while the gray color of the oily Dur stone is due to calcium and strontium content. Therefore, the chemical composition has played a fundamental role in the formation of different types of these stones. Dur Al-Najaf gemstones are regarded as semi-precious stones because they are collected from an area close to religious places, especially for the Muslim community in Iraq.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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