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Study of *Unio* shells in the Quaternary deposits, southern Iraq

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Abstract. Shells are useful in evolutionary biology and paleobiology. Freshwater shells compose the main types of mollusks, and can use as a key for ecological variations. Shell samples in the present study were collected on the highway of Nasyriah city- Samawa city, southern Iraq. The study area contains a large accumulation of shells at 6-7m depths, especially at 7m depth. The main types of these shells are *Unio*, *Corbicula*, and *Melanoides tuberculata*. *Unio* was the most species common in the study area. *Unio* species were used to detect the paleoenvironment in Quaternary deposits, in southern Iraq. Calcite and aragonite are the common minerals in the *Unio* shells. According to the distribution and percentage of calcite and aragonite in the *Unio* shells, it was found the calcite at 6m is more than 7m, whereas the aragonite at 7m is highest compared to 6m. Under X-Ray Fluorescence analyzers, found that calcium oxide, silica, magnesium oxide, and phosphor oxide are the major oxides in the *Unio* shells, while Zn, Sr, Pb, and Rb are the main trace elements. Strontium (Sr) has a high concentration in the *Unio* shells at 7m than 6m, while magnesium (Mg) is found in a high concentration at 6m than 7m. According to trace and some of the major elements concentrations, the paleotemperature, paleosalinity, and water contamination of rivers at 6m are more than 7m, and the river water at 7m depth was fresh water with a high abundance of nutrients and climate was suitable to growth mollusks shells like *Unio* shells.

1. Introduction

The bivalve shells are used as environmental indicators [1]. Trace elements are incorporated into the bivalve shells according to the concentration of these elements in the water [2]. This is also affected by water salinity and temperature [3]. The observation of heavy metals in the aquatic environment involves detecting the metal in biota, sediments, and water [4,5,6,7]. The tolerance of mollusks' bivalves has made them an ecosystem monitoring [8]. The level of trace metal contamination of aqueous organisms is a result of a balance between metal loss and metal uptake [9]. The palaeoenvironmental recorders can be detected by the use of mollusks. The three-layered shell of *Unio* species of an outer thick periostracum, a prismatic layer, and a thick nacreous layer, as well as the aragonite mineralogy [10, 11, 12]. A number of authors have studied the mineralogy of *Unio* shells, such as the study of Gregoire (1961) [13] have revealed that *Unio* shells had a few crystals collection of aragonite. Taylor et al. (1969) [14] found two arrangements of the nacreous layers in several species of *Unionidae*. A study by Dauphin et al. (2017) [15] concluded the mineralogy and composition of a nacroprismatic bivalve species: *Unio* pictorum and explained that the prismatic layer of *Unio* is aragonite, and the inner structure of the prismatic units strongly differs from those of the calcitic layers. Lyubas et al. (2019) [16] used *Unio* freshwater shells

as indicators of paleoclimate changes compare to the present in the Pleistocene and Pliocene deposits of ancient rivers in Russia. The main objective of this study was the reconstruction of some parameters of the aquatic environment in the Quaternary period, in southern Iraq.

2. Location of the study area

The study area is located in the north of Nasyriah city. The study area consists of Quaternary sediments in southern Iraq (Figure 1).

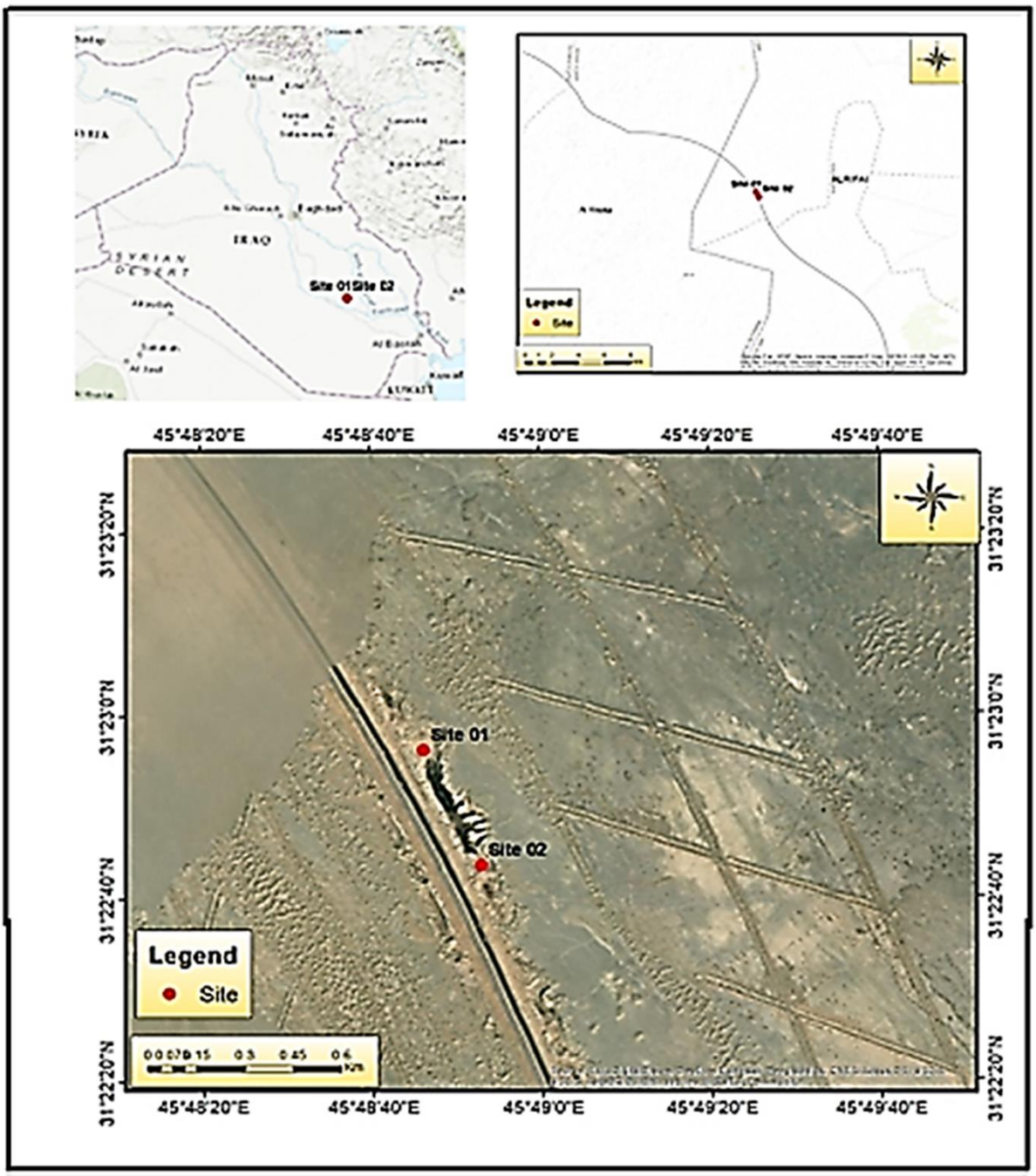

Figure 1. Map of the study area.

3. Materials and methods

Subfossil shells are the materials for this study, these shells are freshwater bivalve mollusks, belonging to the genera *Unio* [16]. The depths of 6 and 7m for two sites (S1 and S2) of outcrop Quaternary deposits (Figure 2,3,4) are chosen to study the *Unio* shells in the highway of Nasyriah - Samawa cities. The deposits in the study area are terrigenous sediments composed of sand, silt, and clay (Figure 4). The *Unio* samples were put in an acid-washed polyethylene bag. Grinding the shells by a glass mortar. X-ray fluoresces (XRF) and X-ray diffraction (XRD) are applied in this study to reveal of minerals and chemical composition of *Unio* shells.

Figure 2. *Unio* shells Shells at 6m.

Figure 3. *Unio* shells Shells at 7m.

4. Results

4.1. Mineralogy study

Calcite and aragonite are the common minerals in the *Unio* shells. According to the distribution and percentage of calcite and aragonite in the *Unio* shells, found the calcite at 6m is more than 7m, whereas the aragonite at 7m is highest compared to 6m.

4.2. Geochemical study

According to X-Ray Fluorescence (XRF) analyzers for *Unio* shells, it was estimated that calcium oxide, silica, magnesium oxide, and phosphor oxide are the major oxides, while Zn, Sr, Pb, and Rb are the main trace elements (Table 1).

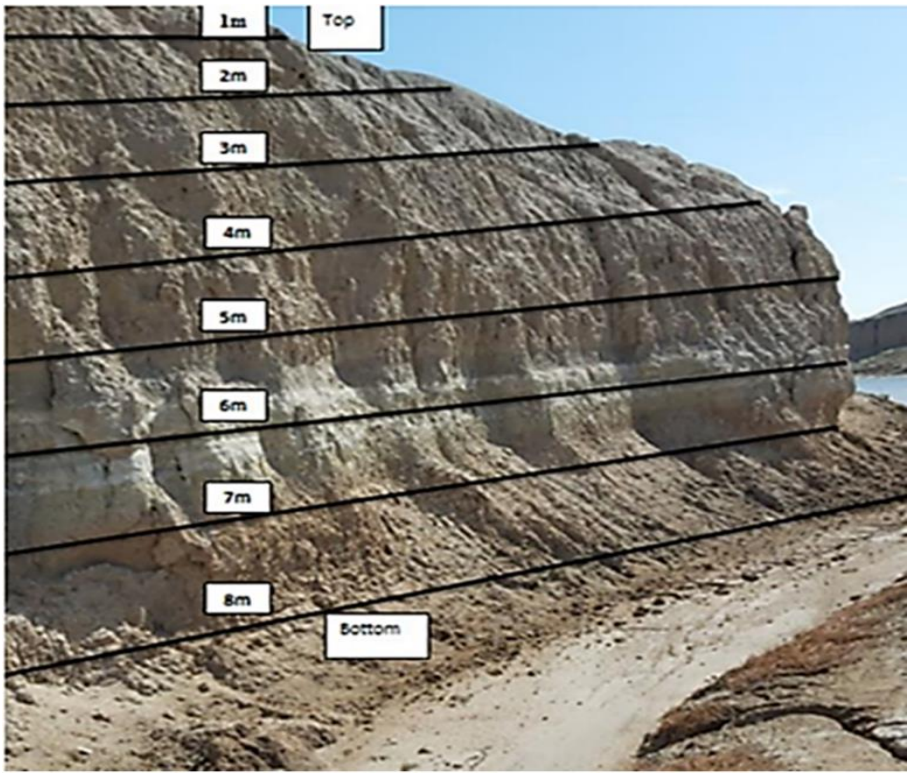

Figure 4. The sequence layers from the top to the bottom in the study area.

Table 1. The XRF analysis results of *Unio* shells for the studied sites.

	S1		S2	
Elements	**6m**	**7m**	**6m**	**7m**
SiO_2 %	0.2188	0.0016	0.2672	0.0022
MgO %	0.2199	0.1394	0.2596	0.1282
P_2O_5 %	0.2119	0.2065	0.2155	0.2172
CaO %	55.49	55.95	55.6	55.86
MnO %	0.05792	0.02919	0.05438	0.02715
Zn ppm	12.131	11.087	12.86	10.581
Rb ppm	0.641	0.366	0.683	0.384
Ba ppm	0.00858	0.00831	0.00849	0.00824
Pb ppm	1.946	1.265	1.862	1.386
Sr ppm	1152	1380	1173	1376

5. Discussions

Mollusk is the second most phylum on the earth [17]. The shell shapes reflect the environment and their phylogenetic history [18, 19, 20, 21]. The chemical composition of bivalves shells can be used as monitoring contamination and detect the different environmental conditions [22,23,24,25,4,5]. The adaptability of the mollusks has made them a preferred organism as an indicator of the ecosystems [7,8,9]. XRF analysis of hard body parts of bivalves can give a piece of information for biomineralization and the interaction between the surrounding environment and organisms. XRD

analysis revealed two main layers in the *Unio*, the outer layer constitutes calcite and the inner layer constitutes aragonite. The high abundance of *Unio* shells at 6 and 7m depths gave an indication of the freshwater environment. The high accumulation of shells at 7m gave an indication of suitable conditions in that period of Quaternary Formation to grow and to provide the appropriate nutrients for reproduction. [25,26] The rate of *Unio* shells in the river was present in a high accumulation in the nutrient silty clay channels. Major and trace elements in the bulk *Unio* shells are displayed and summarized in Table 1, which emphasized that calcite is higher in the *Unio* shells at 6m depth compared with 7m, which may probably be due to the increase of calcium ions in the river water, these ions uptake by *Union* shells to build their skeleton. The aragonite layer in the *Unio* shells at 7m is highest than 6m. The elements contained in the mollusk shells are suitable to concentrate in the calcite or aragonite according to their ionic radii [27]. Strontium (Sr) has a high concentration in the *Unio* shells at 7m than 6m, while magnesium (Mg) is found in a high concentration at 6m than 7m. [28,29,30] Indicated that the Sr element is more suitable to concentrate in the aragonite than the calcite layer. [31,32] Mentioned that Sr^{+2} substitutes more readily for Ca^{+2} in the aragonite than calcite. [27] The magnesium showed more preferential concentration in calcite rather than aragonite in shell growth. The Mg^{+2} content in the outer calcite layer is increased with increased environmental temperature, but not so regular as Sr concentration. The Mg content in the skeleton may be used for paleotemperature reconstruction, decrease the calcium elements and increase magnesium giving an indicator of high paleotemperature at 6m depth compare with 7m depth. An increase in the calcite layer with an increase in the Zn, Pb, Si, Mn, and Rb presented in large concentrations in *Unio* shells at 6m than 7m. [29] Mentioned the Zn, Pb, and Si which have small ionic radii and are present in a higher concentration in the calcite than aragonite. [29] Showed the concentration of Pb, Zn, and Mn, in the mollusks shells are higher when increasing the water salinity. In addition, the high accumulation of Mn, Zn, Pb, and Ba may have been attributed to sediments and water contamination at 6m than 7m, all of these showed the river at that time in 7m depth was fresh water with a high abundance of nutrients and climate was suitable to growth mollusks shells like *Unio* shells.

6. Conclusions

(1) The high abundance of *Unio* shells at 6m and 7m depths gave an indication of a freshwater environment, and the great number of shells at these depths gave a clear evidence to appropriate conditions for growth and generation.
(2) The aragonite layer in the *Unio* shells at 7m depth is more than 6m, while the calcite presence was reversed.
(3) Strontium has a high concentration in the *Unio* shells at 7m than 6m, while magnesium is found in a high concentration at 6m than 7m.
(4) Strontium was found in the aragonite layer, while magnesium is concentrated in the calcite layer of *Unio* shells.

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