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Biogenic Accumulations of Uranium in Recent Seas

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Abstract The objective of this study is to determine the geochemical role of molluscs in the distribution of uranium in the marine ecosystem. Biogeochemical studies are carried out on recent mollusc shells from the Caspian Sea, Sea of Japan, Sea of Marmara, Aegean Sea, Black Sea, Mediterranean Sea, Baltic Sea, and Indian Ocean, which differ from each other in terms of physical, chemical, geographic, and geochemical characteristics. In this study, nine Gastropoda and fifty-four Pelecypoda shells of different species are analyzed to document variations of uranium in seasonal layers, which were formed by the seasonal carbonate-organic phase of molluscs during their entire lives. Shell used in this study principally comprises three layers: upper (outer) prismatic, middle prismatic, and inner (mother-of-pearl) layers. In addition, when possible, the head, the middle, and the lower parts of the shells are used for analyses separately. Also, the biological accumulation rate values for each different mollusc species relative to the average uranium value in seawater are calculated. The BAR values of U in mollusc shells range between 11 and 216. Uranium concentrations in recent mollusc shells vary between 0.034 ppm and 0.65 ppm. Organic carbon values vary between 1100 and 9700 ppm in various mollusc species. The uranium and C_{org} concentrations in living mollusc shells are positively correlated. Both the uranium and C_{org} contents in mollusc shells are preferably dependent on the taxonomic characteristics of organisms. It has been observed that the uranium concentrations in the mineral-organic phase of molluscs are in good agreement with those of surrounding sediments. Therefore, the changes in the uranium concentrations in shell and sediment types are derived from the uranium concentrations in water.

Key words: uranium, mollusc shells, Gastropoda, Pelecypoda, biogeochemical, accumulation rate

1 Introduction

Biogeochemical investigations are important to determine the geochemical behavior of U (uranium) and the formation of U-rich zones in marine environments. Thus, the subject of U distribution in the marine ecosystem is important.

Uranium is a toxic radioactive metal and found in all living organisms. The U levels in various marine organisms are quite different. For example, the U percentages in various microorganism tissues change between 1.5 ppm and 98 ppm although the concentration in the environment remains the same (0.003 ppm). According to the results of experimental studies, U contents in the various microorganisms increased 15 to 350 times as the U showed 3000 fold increases in the environment (Letunova and Kovalski, 1978). It is possible to observe this change in both planktonic and benthic algae (Swanson, 1961; Baturin, 1975; Sakaguchi et al., 1978). Experimental studies are carried out on the marine and freshwater algae in an environment containing 1 ppm of U. The U concentrations in organisms relative to that of water (1 ppm) BAR (biological accumulation rate) for different algae species are as follows: 3900 for *Chlorella regularis*, 3400 for *Chlamydomonas reinhardtii*, 2300 for *Chlamydomonas angulosa*, 1900 for *Scenedesmus bijuga*, 1100 for *Scenedesmus obliguus* and 800 for *Scenedesmus choreloides* (Sakaguchi et al., 1978). Nakajima et al. (1973) and Sakaguchi et al. (1978) demonstrated experimentally the presence of high U concentrations in algae of marine organisms.

According to Baturin (1975), U concentrations in recent mollusc shells range between 0.01 ppm and 0.5 ppm with an average value of 0.11 ppm. The average biological accumulation rates relative to the average level of seawater vary in the range of 3–190.

Çağatay et al. (1987) and Degens et al. (1977) argued that U concentrates mainly as a form of metal-ion coordination in the living coccolith based on electron density (metal-stained) coccolith tests in the Black Sea sediments.

The grain size of the sediment sink for uranium establishes a potential for significant increases in the rate of uranium removal into suboxic/anoxic sediments during times of low oxygen bottom water levels and/or high productivity. This data supports the view that the marine cycle of uranium is sensitive to fluctuations in ocean chemistry (Hillaire-Marcel et al., 1990) and that the uranium contents of seawater (such as through foraminiferal tests, Russell et al., 1990) may prove to be useful indicators of paleoredox conditions.

"A total of 53 cores from the southern part of the Black Sea were used to investigate the geochemical distribution of uranium in three units of late Pleistocene-Holocene sediments. Vertical and areal distribution of U, together with selective extraction studies, suggest that in the reduced sediments of units 1 and 2, deposited on the abyssal plain, U is mainly associated with organic matter. High U contents (>5 ppm) appear in sediments with C_{org} values greater than 2%. This threshold value for C_{org} appears to provide the essential reducing capacity for U fixation in these sediments" (Cağatay et al., 1990).

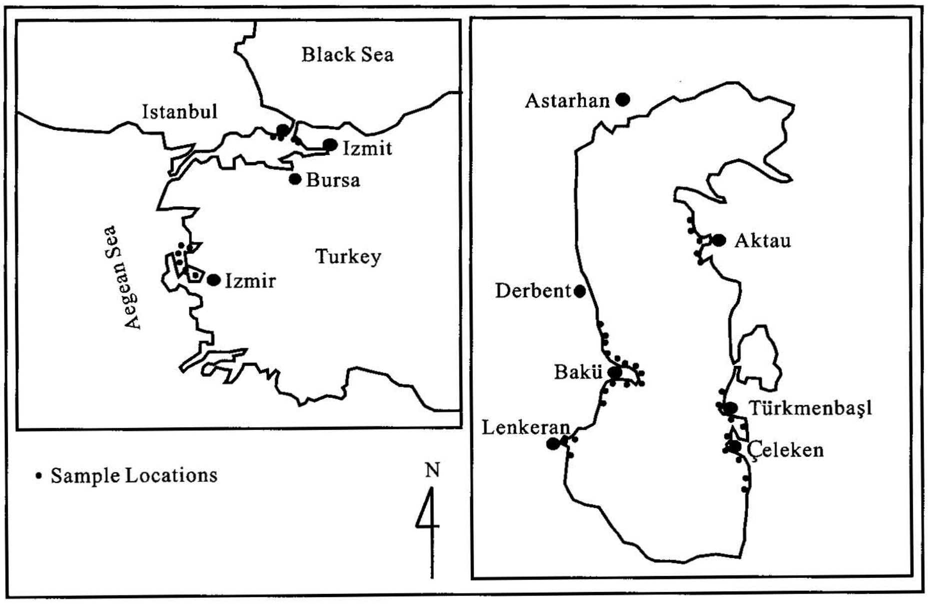

Fig. 1. Sampling map and study area.

Data in this report support the results from these more recent pore-water studies (Santschi et al., 1988; Anderson et al., 1989; Barnes and Cochran, 1990; Thomson et al., 1990) indicating that marine sediments are a substantial sink for the uranium dissolved in seawater and that this removal process affects the sedimentary record. This paper adds details to what we know about the behavior of dissolved uranium at the sediment-water interface, which makes it possible to refine our estimate of the rate of uptake into sediments and further constrain the geochemical processes important in the marine cycle of uranium.

In this study, detailed investigations are carried out on recent and fossil mollusc shells from the Caspian Sea, Sea of Japan, Sea of Marmara, Aegean Sea, Black Sea, Mediterranean Sea, and Baltic Sea, and Indian Ocean, which differ from each other in terms of physical, chemical, and geochemical characteristics. Nine Gastropoda and fifty-four Pelecipoda shells of different species are analyzed (Fig. 1). Necessary internal and external factors influencing the U distributions are discussed and the related parameters are determined. In addition, the BAR of U of molluscs is determined. The analytical results of U values for Pelecypoda and Gastropoda shells are given in Table 1. Also, the BAR values for different mollusc species relative to the average U value in seawater are calculated. As shown in Table 1, U percentages in recent mollusc shells vary between 0.034 ppm and 0.65 ppm. The lowest U values are found in molluscs from the Sea of Japan (0.034 ppm) and the Baltic Sea (0.05 ppm), whereas the shells with highest U contents are confined to the molluscs of the Indian Ocean (0.42 ppm to 0.65 ppm), the Caspian Sea (0.25 ppm to 0.58 ppm) and the Sea of Marmara (0.18 ppm to 0.36 ppm).

On the basis of U values in mollusc shells, the BAR levels for various basins are as follows: 24 for the Sea of Japan, 33 for the Baltic Sea, 61 for the Caspian Sea, 80 for the Mediterranean Sea, 110 for the Sea of Marmara, 130 for the Indian Ocean, and 152 for the Black Sea. Thus, the BAR values are quite different from various basins.

2 Materials and Methods

The samples of this study comprise more than 60 mollusc (9 gastropod and 54 mollusc) shells and the surrounding sediments obtained from basins with varying environmental conditions. U and C_{org} determinations are carried out on 300 samples including whole shells and seasonal growth layers.

The percentage of uranium in mollusc shells was determined using the perlovo (uranium)-luminescence method which is based on the fluorescence of uranium under the influence of ultraviolet light. The separation of U^{4+} from the associative elements was carried out through the precipitation using zirconium chloroxide in an acidic environment. The error of the method is no more than ± 5% of the values measured. The sensitivity of the method is $n\times10^{-7}$% (Volkov, 1982).

Table 1 Uranium values in modern mollusc shells and water and the relation to each other

Mollusc species	Basin	U, Seawater (ppm)*	U, Shell (ppm)	U_{shell}/U_{water}
Mactra corallina	Indian Ocean	0.003	0.65	216
Anadara dilivii	"	"	0.42	140
Pectunculus	Mediterranean	"	0.264	88
Cerithium	"	"	0.23	76.6
Mytilus edulis	Sea of Marmara	"	0.34	113.3
Donax variegatus	"	"	0.36	120
Cardium edule	"	"	0.31	103.3
Venus dysepa	"	"	0.21	70
Cardium edule	Aegean Sea	"	0.11	36.6
Mactra corallina	"	"	0.11	36.6
Patella pectinata	"	"	0.12	40
Cerithium	"	"	0.10	33.3
Mytilus edulis	Black Sea	0.002	0.25	125
Chione galline	"	"	0.23	115
Ostrea edulis	"	"	0.3	150
Mytilus galloprovincialis	Baltıc Sea	0.0015	0.048	32
Macoma baltica	"	"	0..05	33.3
Mya arenaria	"	"	0.05	33.3
Theodoxus pallasi	Caspian Sea	0.006	0.38	63.3
Micromelania caspia	"		0.42	70
Micromelania meneghiniana	"	"	0.46	76.6
Cardium edule	"	"	0.33	55
Monodacna caspia	"	"	0.25	41.6
Monodacna edentula	"	"	0.45	75
Didacna trigonoides	"	"	0.33	55
Didacna protracta	"	"	0.31	51.6
Didacna piramidata	"	"	0.58	96.6
Didacna baeri	"	"	0.36	60
Abra ovata	"	"	0.27	45
Mytilaster	Caspian Sea	0.006	0.34	56.6
Dreissena distincta	"	"	0.46	76.6
Dreissena polymorpha	"	"	0.32	53.3
Dreissena caspia	"	"	0.38	63.3
Dreissena elata	"	"	0.5	83.3
Mercenaria stimpsoni	Sea of Japan	0.0021	0.05	23.8
Saxidomus purpuratus	"	"	0.043	20.5
Venerupis japonica	"	"	0.08	38.1
Crenomytilus grayanus	"	"	0.034	16.2
Anadara broughtoni	"	"	0.072	34.3

Note: * after Krauskopf, 1982; Baturin, 1975.

To determine the characteristics of U distribution in shell, average values and their biological accumulation rates relative to percentages in seawater and sediments are calculated. The determination of C_{org} in shell was made using chromic acid to oxidize C_{org} in shell.

3 Factors Controlling the Distribution of Uranium in Shells

The marine environment is a particular system where a variety of conditions, such as physical, chemical, biogeochemical, geochemical, geographic, biological and tectonic conditions, are effective. In this system, the organisms are always faced to abiotic factors. These play important role in their life and growth. In this study, the effects of biotic and abiotic factors, which can constrain concentrations in mollusc shells, are investigated in detail.

4 External Factors

4.1 The factor of uranium in seawater

Uranium is removed from the oceans by diffusion across the sediment-water interface of organic-rich sediments. This pathway is the largest single sink in the global budget of this element. Metallo-organics play an important role in the diagenetic behavior of this element as some uranium is released into solution when labile organics are consumed at the sediment-water interface. Uranium behavior in suboxic sediments is characterized by a mirror-image relationship between pore-water profiles and sediment distributions (Klinkhammer and Palmer, 1991). It is clear from these profiles that diffusion from overlying seawater results in significant shifts in the distribution of uranium within the sediment column.

Uranium is thought to be conservative in oxygenated seawater (Ku et al., 1977) because of the formation of stable and soluble U^{6+} carbonate complexes (Langmuir, 1978). Thermodynamics predicts, however, that soluble U^{6+} is capable of being reduced to insoluble U^{4+} at conditions found in natural waters. Its conservative behavior in oxygenated seawater and capacity for reduction has focused attention on anoxic basins (Degens et al., 1977; Anderson, 1987; Todd et al., 1988), and pelagic sediments (Wallace et al., 1988).

Based on experimental studies, U concentration in the algae *Lemna minor* increases to 5000 ppm in water of 10 ppm U and 10.000 ppm C_{org} (U/C_{org} ratio 100, Guskova, 1972).

The U concentration in the algae depending on the U concentration of the seawater varies between 0.65 ppm (in water 0.003 ppm; Baturin, 1975) and 23.5 ppm (in water 0.03 ppm, Issik-Kul Basin; Kovalski and Vorotnitskaya, 1965).

The U distributions in the fishes are more diverse. The fin, scale, bone, and skin parts of the fish contain 99% of U present in the organism. The remaining percentage of U belongs to the soft tissues of the fishes. The normal U concentration in the water is 0.003 ppm (Krauskopf, 1982) and 0.05 ppm in bone parts of fish. But, this can reach much higher values because of U enrichment in water. For example, in an environment containing 0.03 ppm of U (Issik-Kul Basin), U concentration is 0.64 ppm in the bone part. In the water with 10 ppm, U concentration is found to be 500 ppm in the bone (Guskova, 1972).

When the U concentrations in the organic-carbonate phase of shells of modern molluscs are considered, the average U concentration in the mollusc shells under normal marine water condition is 0.11 ppm (Baturin, 1975). However, the U percentages in the carbonate-organic phases of molluscs change significantly together with the change of U concentration in the water. While the U concentration is as low as 0.03 ppm in the seawater, it is 1.83 ppm in the shells, which is much higher than that of seawater (Neruchev, 1982). As shown in Table 1, the U content of mollusc shells collected from the Baltic Sea is 0.049 ppm whereas it is 0.38 ppm in the mollusc shells of the Hazar Sea.

Organisms, living in a high-U environment, have more uranium regarding to those in the low-U environment. Works indicate that the U content in the organisms is in

Table 2 Uranium concentrations in mollusc shells and the surrounding sediments and $U_{shell}/U_{sediment}$

Mollusc species, Biocoenosis	Sample location (Caspian Sea)	Age	Sediment type	U (ppm)		$U_{shell}/U_{sedim.}$
				Shell (mean)	Sediment (mean)	
Biocoenosis 1	Location 19	Recent	Medium grain sand	0.325	0.39	0.830
Biocoenosis 2	Location 22	"	Medium grain sand	0.37	0.4	0.925
Biocoenosis 3	Location 22	"	Medium grain sand	0.27	0.34	0.794
Biocoenosis 4	Location 23	"	Carbonate mud	0.45	0.53	0.850
Biocoenosis 5	Location 24	"	Sandstone	0.44	0.51	0.863
Biocoenosis 6	Location 25	"	Carbonate mud	0.28	0.42	0.666
Biocoenosis 7	Location 26	"	Medium grain sand	0.33	0.37	0.892
Dreissena distincta	Tazabat	Holocene	Carbonate mudstone	0.8	0.78	1.025
Dreissena distincta	Karagöl	"	Carbonate mudstone	0.85	0.77	1.104
Didacna kovalevskii	"	Pleistocene	Clayey	0.41	0.34	1.206
Dreissena polymorpha	"	"	Sandstone	0.2	0.34	0.666
Monodacna beibatica	Yasamal	"	Clayey Sandstone	0.27	0.22	1.227
Dreissena distincta	"	"	Clayey	0.31	0.23	1.348
Monodacna laevigata	Dağüstüpark	"	Clayey sand	0.56	0.28	2.000
Monodacna minor	"	"	Clayey sand	0.44	0.42	1.047
Apscheronia propinqua	"	"	Clayey sand	0.61	0.47	1.298
Dreissena distincta	"	"	Clayey sand	0.45	0.49	0.918
Dreissena polymorpha	"	"	"	0.52	0.42	1.238
Dreissena distincta	Atbulak-2	"	Sandy clayey	0.32	0.23	1.391
Dreissena distincta	Atbulak-3	"	Clay	0.36	0.4	0.900
Monodacna bakuana	Gözdek-4	"	"	0.32	0.25	1.280
Monodacna bakuana	Sabuncu	"	Sandy clayey	0.44	0.4	1.100
Apscheroria propinqua	Sabuncu	Pleistocene	Clay	0.58	0.5	1.160
Dreissena distincta	"	"	Clay	0.48	0.5	0.960
Dreissena distincta	Bibiheybet	"	Sandy clayey	0.5	0.41	1.219
Dreissena eichwaldi	"	"	Sandy clayey	0.49	0.41	1.195
Cardium dombra	Şuduk	"	Sandy clayey	0.68	0.42	1.620
Dreissena rostriformis	Duzdağ	Pontian	Sandy clayey	1.17	0.46	2.540
Prosoducna schirvanica	Sündü	"	Sandy clayey	1.51	0.46	3.280
Dreissena anisoconcha	Nabur	Pontian	Sandy clayey	1.2	0.41	2.920
Melanopsis mitraeformis	Sündü	"	Sandy clayey	0.9	0.46	1.950

good relation with that in depositional environments. However, the species of organisms are also important. The organisms, living in the same uranium environment, may have different U contents according to the taxonomic evolution of different species.

4.2 Uranium distribution in sediments

The average U percentage in sediments of earth's crust is 3.5 ppm (Krauskopf, 1982), but U varies in different sediment types in a wide range. For example, the average U values in recent and older geological materials are given in Table 2. The table shows that U values in recent sands range between 0.34 ppm to 0.53 ppm, and in calcareous mud 0.77 ppm to 0.78 ppm of U is determined. In older sediments: 0.22 ppm to 0.49 ppm of U in clayey sands, 0.23 ppm to 0.46 ppm of U in sandy clays, and 0.23 ppm to 0.5 ppm in clays is found.

The differences in U values between fossilized mollusc shells and surrounding sedimentary rocks are evaluated to be the results of diagenetic and catagenetic processes (Sultanov and Isayev, 1982).

When sediments were carried to depositional basins under warm and moist climate, they mostly formed dark gray or gray muddy and muddy sand strata that are rich in organism. The sedimentary strata are usually U-bearing formations because clay minerals and organisms absorb uranium quite a lot. Moreover, their organisms are also necessary reductants for forming hydrogenic uranium deposits (Li and Pang 2000).

Experimental studies and thermodynamic calculations (Agamirov, 1963; Andreev and Chumachenko, 1964; Kochenov et al., 1977; Langmuir, 1978) show that the Eh-pH conditions at the sediment-seawater interface in the Black Sea are suitable for the precipitation of uraninite. More recent experimental work by Nakashima et al. (1984), carried out under acidic conditions, indicates that fixation of uranyl species on lignite begins by the formation of stable organo-metallic compounds at 45°C and that the reduction of uranyl species to uraninite does not start until 120°C. These results and the fact that no uranium mineral has been reported from the Black Sea sediments suggest that the U phase dissolved by the hydrogen peroxide extraction (U_{org}) occurs as stable organo-uranium compounds.

4.3 Organic matter content in sediments

"The areal distribution of U in the Pleistocene-Holocene sediments from the southern part of the Black Sea is similar to the distributions of C_{org} and sedimentation rates. The concentration of U increases from 2 ppm on the shelves and continental slope up to 24 ppm on the abyssal plain, where the sedimentation rate is low (<10 cm ka^{-1}) and C_{org} contents are high (up to 14.3%). Vertical distributions of C_{org} show a strong correlation with those of U whereas $CaCO_3$ appears to have a dilution effect on U" (Çağatay et al., 1990).

The U/C_{org} ratio increases due to the decrease of C_{org} masses with a transition from reduction to oxidation environment. The bitumen content also increases in the mass of organic matter (Vassoyevich, 1973; Neruchev, 1982; Akyüz and Bassarı, 1998). The organic matter mass in the sediments decreases during the diagenetic oxidation while the concentrations of more stable bitumen and hydrocarbon components increase in the oxidation environment. Increases also occur in the percentages of U, V, Mo, P, and other trace elements in organic matter. It is important to note that the uranium content of the material being doposited and the depth to which seawater uranium is diffusing are not completely independent variables. This dependency arises from the direct relationship between organic carbon and uranium. The reason for this general correlation is somewhat controversial, but there is no doubt that such a relationship exists over a wide range of sediment types and sedimentation rates (Anderson et al., 1989; Çağatay et al., 1990). The detailed investigations are carried out on recent sediments to check the accuracy of these results. The results of these studies are shown in Fig. 2 (Baturin, 1975). Figure 2 shows that organic matter

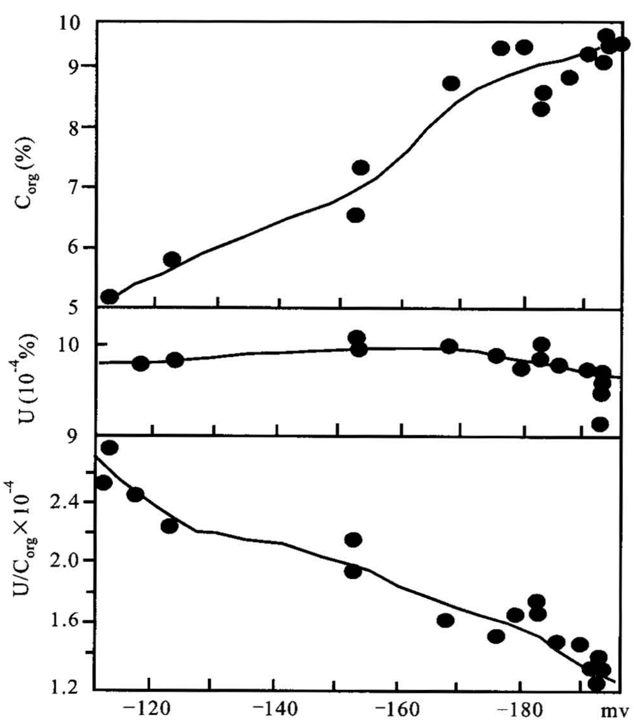

Fig. 2. The dependence of organic carbon and uranium concentrations and U/C_{org} ratios on oxidation-reduction potential (Baturin, 1975).

percentage decreases from 10% in anoxic environment to 5% in less reducing oxic environment due to bacterial oxidation. The U concentration in sediments does not change significantly prior and post diagenesis. However, U/C_{org} values can increase 50% along the diagenesis process.

The U concentration in sediments occurs before biological oxidation, until the diagenetic stage, even depending on the physiological environment of organisms when alive. Later in time, various geochemical factors affect the U values. During diagenetic oxidation processes of organic matter, the remaining organic matter is enriched with stable bitumen and hydrocarbons. Thus, the primary cause of U concentration in sediments can be related to the organic matter enrichment in sediments (Neruchev, 1976). Black shale refers to marine sedimentary rocks composed of argillaceous, silty and siliceous substances with high contents of organic materials and disseminated pyrite and uranium. Uraniferous black shale has uranium content of more than 20 ppm (Zhang, 2000). When black shale is eroded, especially in the Meso-Cenozoic, it can become one of uranium sources for younger epigenetic roll-type uranium deposits. It is worth pointing out that the uraniferous black shale could not be formed in considerable amount in the Precambrian, because there were very few organisms then (Chen et al., 2000).

Table 3 Uranium and organic carbon and concentrations in modern mollusc skeletons and U_{shell}/U_{sedim} ratios

Mollusc species	Sample location	U (ppm)	C_{org} (ppm)	U/C_{org} ($\times10^{-5}$)
	Caspian Sea			
Adacna laeviuscula	Bilgeh	0.36	2000	18.00
Dreissena polymorpha	Astara	0.4	2200	18.10
Monodacna edentula	Sangaçal	0.42	2800	15.00
Dreissena polymorpha	Şıkov	0.44	2700	16.30
Cardium edule	Lenkeran	0.46	2800	16.40
Cardium edule	Sangaçal	0.45	2900	15.50
Didacna trigonoides	"	0.5	2900	17.20
Mytilaster lineatus	Sumgayıt	0.54	3500	15.40
Didacna trigonoides	"	0.62	3700	16.70
Dreissena distincta	"	0.7	3900	18.00
Mean		0.49	2940	16.63
Venus dysepa	Sea of Marmara	0.21	1500	14.00
Cardium edule	"	0.31	2100	14.70
Mytilus edulis	"	0.34	2400	14.10
Mean		0.286	2000	14.3
	Sea of Japan			
Acmae polida	Sea of Japan	0.04	2100	1.90
Anadara broughtoni	"	0.07	5400	1.30
Mean		0.055	3750	1.46
	Black Sea			
Ostrea edulis	Odessa	0.28	4200	6.60
Mytilus galloprovincialis	"	0.32	5900	5.40
Mean		0.31	5000	6.20

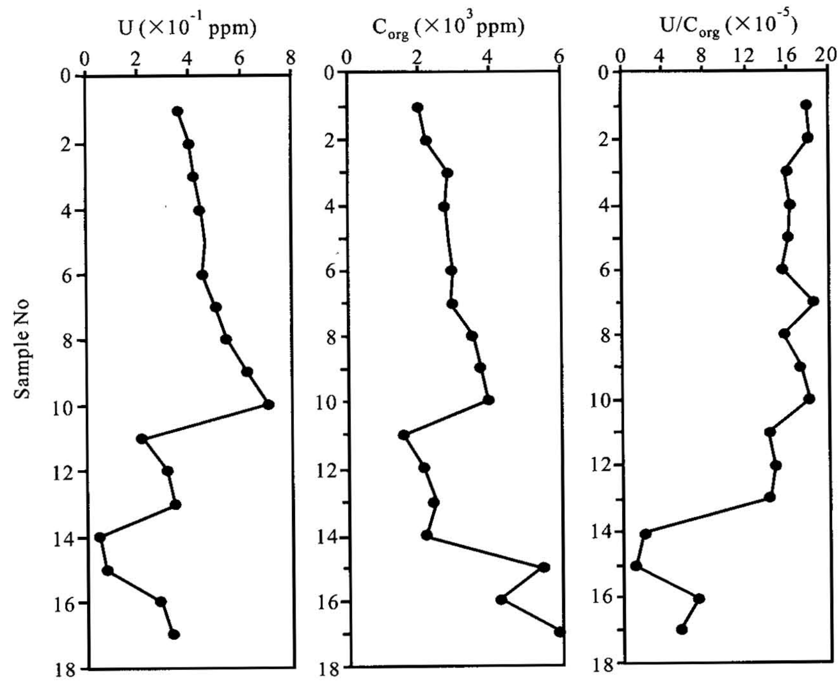

Fig. 3. Uranium and organic carbon correlations in modern mollusc shells.
1–10. Samples of the Caspian Sea; 11–13. samples of the Sea of Marmara; 14–15. samples of the Sea of Japan; 16–17. samples of the Black Sea.

5 Internal factors

5.1 Organic carbon concentration in mollusc shells

In this study, detailed investigations are carried out on organic carbon of various mollusc shells from the Sea of Marmara, Caspian Sea, and Sea of Japan having different environmental conditions (Tables 3 and 4, Fig. 3).

The U and C_{org} values in Tables 3 and 4 and Fig. 3 display differences among the various molluscs. For example, the lowest U and C_{org} distributions (0.36 ppm U and 2×10^3 ppm C_{org}) in mollusc shells of the Caspian Sea belong to the mollusc species *Adacna laeviuscula.* The highest U and C_{org} concentrations

(0.7 ppm U and 3.9×10^3 ppm C_{org}) belong to the mollusc species *Dreissena distincta*. The high U and C_{org} concentrations are determined in the mollusc species from the Shikov region that has the same biotope characteristics, *Dreissena polymorpha* (0.44 ppm U and 2.7×10^3 ppm C_{org}), *Didacna trigonoides* (0.62 ppm U and 3.7×10^3 ppm C_{org}), and *Didacna distincta* species (0.7 ppm U and 3.9×10^3 ppm C_{org}) (Table 3). Therefore, there is a good agreement between the U and C_{org} concentrations (Aliyev and Sarı, 2001).

To determine the concentration of U with respect to organic phase in shells, U/C_{org} ratios are also determined. The U/C_{org} ratios are different for molluscs from various basins. For example, the highest U/C_{org} ratio for the Caspian Sea molluscs is 15.40×10^{-5} to 18.1×10^{-5} ppm while lower U/C_{org} ratio values (1.30×10^{-5} to 1.90×10^{-5} ppm) belong to the Sea of Japan molluscs. The highest enrichment factor of U belongs to molluscs of the Caspian Sea and Sea of Marmara (1.40 and 1.47 ppm, respectively). The average values related to U/C_{org} ratios are in good agreement in the Caspian Sea and Sea of Marmara (16.63×10^{-5} and 14.30×10^{-5} ppm, respectively) (Table 3). The U/C_{org} ratio values for mollusc shells of the Sea of Japan are 1.35×10^{-5} ppm (Table 4).

The differences are found in C_{org} values from various mollusc species in the same basin. For example, *Adacna laeviuscula* 2×10^3 ppm, *Didacna trigonoides* 2.9×10^3 ppm, and *Dreissena distincta* 3.9×10^3 ppm in Caspian Sea; *Venus dysepa* 1.5×10^3 ppm and *Mytilus edulis* 2.4×10^3ppm in the Sea of Marmara; *Acmaea polida* 2.1×10^3 ppm and *Anadara broughtoni* 5.4×10^3 in the Sea of Japan. It is thought that these differences are based on taxonomic characteristics of organisms (Aliyev et al., 2000).

5.2 Uranium accumulation during the ontogenesis evolution of molluscs

The U concentrations in the seasonal layers of the mollusc shells that are formed through their entire lives are shown in Table 4 and Fig. 4. The shells used in this study principally comprise three layers; upper (outer) prismatic, middle prismatic and inner (mother-of- pearl) layers. In addition, when possible, the head, the middle, and the lower parts of the shells are used for analysis. A clear similarity has been observed between the distributions of U and C_{org} values in lifetime layers of molluscs. In all cases, the U values increase from inner to outer layers. The increase of C_{org} in the layers also contributes to the enrichment of U. The konkiolin-bearing upper layer is rich in both U and C_{org} values. We also studied the head, the middle, and the lower parts of shells and observed that the U and C_{org}

Table 4 The change of organic carbon and uranium values in shells of modern molluscs during the ontogenesis

Mollusc species	Living layers in shell	U (ppm)	C_{org} (ppm)	U/C_{org} ($\times10^{-5}$)
Sea of Japan: East Bay. *Mercenaria stimpsoni*	Whole shell	0.05	3100	1.61
	Outer prismatic layer	0.075	3800	1.97
	Middle prismatic layer	0.031	2900	1.06
	Inner layer (mother-of-pearl)	0.028	2400	1.16
Saxidomus purpuratus	Whole shell	0.043	3900	1.1
	Outer prismatic layer	0.076	4700	1.61
	Middle prismatic layer	0.028	3800	0.73
	Inner layer (mother-of-pearl)	0.026	2600	1.10
Venerupis japonica	Whole shell	0.080	5200	1.53
	Outer prismatic layer	0.1	5800	1.72
	Middle prismatic layer	0.055	3900	1.41
	Inner layer (mother-of-pearl)	0.045	3700	1.22
Crenomytilus grayanus	Whole shell	0.034	2900	1.17
	Outer prismatic layer	0.04	3600	1.11
	Middle prismatic layer	0.032	2800	1.14
	Inner layer (mother-of-pearl)	0.028	2500	1.12
	Head of shell	0.028	2100	1.33
	Middle part of shell	0.033	2900	1.13
	Lower part of shell	0.042	3800	1.10
Anadara broughtoni	Whole shell	0.072	5400	1.33
	Outer prismatic layer	0.08	6100	1.31
	Middle prismatic layer	0.067	5000	1.34
	Inner layer (mother-of-pearl)	0.055	3900	1.41
	Head of shell	0.049	3900	1.25
	Middle part of shell	0.065	5500	1.18
	Lower part of shell	0.079	6800	1.16
Caspian Sea: *Didacna trigonoides*	Whole shell	0.29	3700	7.83
	Outer prismatic layer	0.31	4300	7.21
	Middle prismatic layer	0.16	3000	5.33
	Inner layer (mother-of-pearl)	0.175	3400	5.14
	Head of shell	0.153	2700	5.66
	Middle part of shell	0.219	3900	5.61
	Lower part of shell	0.335	4500	7.44

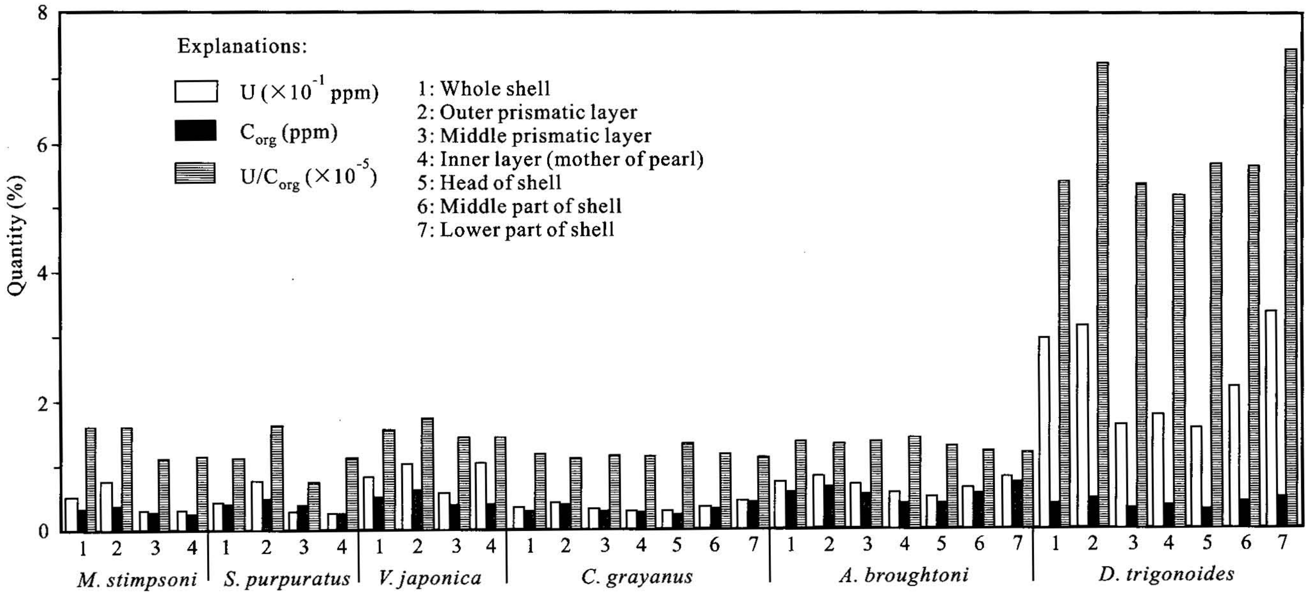

Fig. 4. Uranium and organic carbon correlations in shells related to the ontogenesis of molluscs (living layers).

concentrations gradually decrease towards the head.

In conclusion, the concentrations of both U and C_{org} in the layers are determined by organisms. Also, as the molluscs build their shells, they accumulate U in their shell structure. There exists a clear positive correlation between the U and C_{org} concentrations in mollusc shells (Aliyev and Sarı, 2001). Good correlation between the uranium content in shells of organisms and C_{org} values indicates their genetic associations. Uranium and C_{org} concentrations in the organisms depend, first of all, on the biologic processes. The environmental influences are also important for the evolution of C_{org} and U quantities.

5.2.1 Uranium concentrations in mollusc shells in relation to their ages

To study the uranium concentration in mollusc shells in relation to their ages, the molluscs are used from various areas of the Caspian Sea (*Cardium edule* and *Didacna trigonoides*), the Black Sea (*Mytilus galloprovincialis*), and the Indian Ocean (*Anadara dilivii*) (Table 5, Fig. 5). The species *Cardium edule* shown in this table represents the western and eastern Caspian Sea. In general, the U percentages in modern mollusc shells are slightly higher compared to those in older ones. This characteristic is

Table 5 Uranium and organic carbon concentrations in shells of modern molluscs in relation to their lifespan time and U/C_{org} ratios

Mollusc species	Location	Year	U (ppm)	C_{org} (ppm)	U/C_{org}, ($\times10^{-5}$)
	Caspian sea				
Cardium edule	Çeleken Area	2	0.45	3000	11.66
Cardium edule	"	2	0.42	2800	11.78
Cardium edule	Ulsk (Aktau) Area	2	0.46	2900	15.86
Cardium edule	"	2	0.44	–	–
Cardium edule	Lenkeran	2	0.46	3100	23.00
Cardium edule	"	2	0.44	–	–
Cardium edule	Sumgayıt	3	0.31	1800	26.36
Cardium edule	"	3	0.31	1700	16.47
Cardium edule	Kobustan	3	0.31	–	–
Cardium edule	"	3	0.31	–	–
Cardium edule	Bayandovan	4	0.255	1300	19.61
Cardium edule	"	4	0.265	1400	18.92
	Indian Ocean				
Anadara dilivii		2	0.54	–	–
Anadara dilivii	"	4	0.38	–	–
Anadara dilivii	"	6	0.31	–	–
	Black Sea				
Mytilus galloprovincialis	Odessa Area	3	0.39	9700	4.02
Mytilus galloprovincialis	"	3.5	0.32	9200	3.47
Mytilus galloprovincialis	"	4	0.30	9200	3.36
Didacna trigonoides	Caspian Sea	3	0.45	–	–

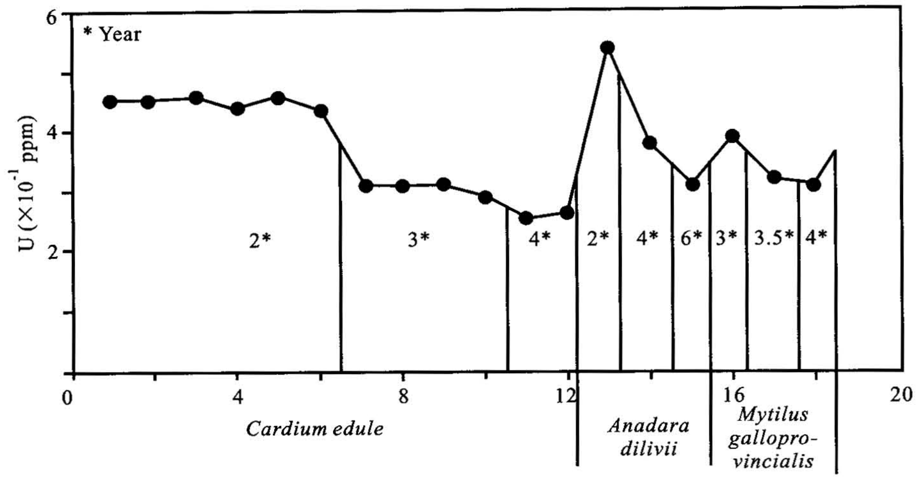

Fig. 5. Uranium concentration in shells related to the ages of modern molluscs.

clearer as the age differences among the molluscs increase (Table 5, Fig. 5). For example, the difference of U concentrations between two older species of *Cardium edule* from the Ulsk region (0.44 ppm to 0.46 ppm) and four older ones from the Bayandovan region (0.23 ppm to 0.26 ppm) is approximately 2.

The reasons for varying U values in the same and different taxons, which are under different circumstances during their lifetime, are not only the ages of molluscs but also the C_{org} values. Also, the C_{org} values determined in some mollusc samples support this conception (Table 5). The high C_{org} values in recent molluscs also reflect their enrichment in U.

According to Waskowiak (1962), the $CaCO_3$ content in modern mollusc shells is lower than that in older mollusc shells. In other words, the carbonization degree in modern molluscs is lower than that in older ones, hence, the $CaCO_3/C_{org}$ ratio is also low.

In conclusion, the occurrence of a positive correlation between U and C_{org} is shown.

6 Conclusions

Uranium is a toxic radioactive metal and is found in all living materials. The U levels in various marine organisms are quite different (from 0.11 ppm to 0.39 ppm). On the basis of the U values in mollusc shells, the BAR values for various basins are as follows: 24 for the Sea of Japan, 33 for the Baltic Sea, 61 for the Caspian Sea, 80 for the Mediterranean Sea, 110 for the Sea of Marmara, 130 for the Indian Ocean, and 152 for the Black Sea. Thus, the BAR values are quite different for various basins.

The U concentrations of mollusc shells are higher in basins with high U concentration. For example, the mollusc shells of the Baltic Sea contain 0.05 ppm of U where seawater has on average 0.15 ppm of U. In the Caspian Sea, U has a concentration of 0.38 ppm in seawater and 0.6 ppm in molluscs. The concentration of U in shells is related to the taxonomic characteristic of organisms and to the U concentration in the basin.

The average U values in recent mollusc shells and sediments show similar characteristics. The increase and decrease in U in sediments also resulted in U variations in shells. In both cases, the U variations are generally associated with U concentrations in the environment. In other words, the U concentrations in both sediments and the mollusc shells seem to be derived from the same source.

There is a proportional relationship between the values of organic matter and U in the mollusc shells. Namely, the gradual increases of C_{org} in shells parallel to the increases of U in shells. The U/C_{org} ratios are different for molluscs from various basins. For example, the highest U/C_{org} ratios for the Caspian Sea molluscs are 15.4×10^{-5} to 18.1×10^{-5} ppm while the lower U/C_{org} ratio values (0.73×10^{-5} to 1.97×10^{-5}) belong to the Sea of Japan molluscs. As can be seen, the highest enrichment factor of U belongs to the molluscs of the Caspian Sea and the Sea of Marmara (14.0×10^{-5} to 14.7×10^{-5}). A clear similarity can be observed between the distributions of U and C_{org} in the lifetime layers of molluscs. In all cases, both parameter values show a parallel increase from inner to outer layers. The increase of C_{org} in the layers also contributes to the enrichment of U.

The reasons for varying U values in the same and different taxons, which are under different circumstances during their lifetime, are not only the ages of molluscs but also the C_{org} values. The U concentration in recent mollusc shells is higher compared to that in older shells. The carbonization degree is quite low in modern molluscs relative to that in older molluscs, while the organic phase during the formation of shell is more abundant in modern than in older ones.

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