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Major and trace element enrichment in Kızıldere formation (Arsuz-Hatay)

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Abstract

The study area is in the Arsuz - HATAY region and the geochemical properties and deposition environment of the claystones in the Kızıldere Formation (Middle - Upper Miocene) were investigated in this study. Kızıldere Formation, which is common in Arsuz and İskenderun (Hatay) regions, has both bedrock and reservoir rock characteristics. It generally consists of a sequence of medium bedded sandstones and thin to medium bedded claystones. The average concentrations of major and trace elements in the samples taken from ten different points of the Arsuz region were determined (V-1180.65 ppm, Ni-219.83 ppm, Cr-149.26 ppm, Co-19.45 ppm, Cu-22.63 ppm, Rb-42.96 ppm, As-8.40 ppm, Zn-54.47 ppm, Sb- 0.61 ppm, Mo-1.28 ppm, Cd - (- 0.71) ppm, Pb- 5.68 ppm, U-1, It is 35 ppm, Ba-171.15 ppm, Li-24.64 ppm, Cs-3.06 ppm, S-325.48 ppm). V / Ni, Ni / Co, V (V + Ni), V / Cr, (Cu / Mo) / Zn ratios in claystones and increases in concentrations in trace elements (e.g. V, U, Ni) indicates that it precipitated in the marine-anoxic environment. In addition, in the distribution mapping drawn according to the trace elements Ni-U-Cu-Zn in the region, the paleo-environment changes with organic matter conservation were determined.

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Reservoir rock.

1. Introduction

The aim of the research is to determine the environmental conditions in Arsuz (Hatay) region by investigating the units in Kızıldere Formation. The study area includes of İskenderun-Arsuz of Hatay (Figure 1). Generally, field studies, petrography and geochemical analyzes are performed to determine the environmental conditions of a region [1]. Some of the analyzes are done to determine the amount of organic matter and are carried out to determine the cause of trace element enrichment in the environment conditions.

XRF (X-Ray Fluorescence Spectrometer), ICP-MS (Inductively Matched Plasma Mass Spectrometry) and AAS (Atomic Absorption Spectroscopy) analysis methods are used to determine trace elements [2]. The amount of trace elements in the environment, which are present together with the hydrocarbon in the samples in the research area, are determined with the results of trace element analysis, This data used in determining the oxic-anoxic-euxinic state environment is interpreted and concluded that it is suitable / unsuitable for the formation of hydrocarbon.

Trace elements are described as elements that are mostly less than 0.01% in amount in rocks. Interpretation of environmental conditions is determined by the amount of elements with trace element analysis and it is possible to identify new geothermal energy resources, source rocks that produce oil and natural gas, and new mineral deposits. In many published source rock potential studies, it has been observed that trace element enrichments are directly related to the high production of organic matter in the region [1, 2]. Environmental properties can also be determined with trace element analysis [2]. Studies that reveal the reservoir rock characteristics of the region where the Kızıldere Formation is located are related to geological, tectonic and sedimentological areas, but there is no study on the geochemical examination of the elements and determination of the source rock.

The terms oxic, anoxic/suboxic or euxinic are used depending on the amount of O_2 in environmental classifications. Anoxic environment is the most effective in enrichment of organic matter and H_2S is not present in the water column in this environment.

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Researchers investigating the changes of organic matter under reducing conditions proved that the protection of organic matter increases under anoxic conditions where oxygen decreases [3, 4]. There are two approaches regarding the relationship between sedimentation rate or burial rate and the protection of organic matter in their studies by different researchers. The first of these is the increase in the protection of organic matter based on the increase in sedimentation rate. The other is the increase in organic matter due to the slow sedimentation rate [5].

The geochemical conditions of the depositional environment can be determined from the enrichment of trace metals and anoxic/euxinic environment correlations. If there is no Mo enrichment in the environment with U and V enrichment, it is interpreted that the environment is in anoxic/suboxic depositional conditions without free H_2S. Conversely, sediments with enrichments in U, V and Mo indicate euxinic conditions at the sediment-water interface or in the water column. Mo and Zn enrichments are related to TOC (Total Organic Carbon) and can be controlled very strongly by the environmental conditions of sedimentation [6].

It is known that organic matter accumulation does not occur with a single control mechanism. The redox conditions of the depositional environment can be oxic, suboxic, anoxic or euxinic, depending on the amount of oxygen in the environment. Trace element enrichments increase according to organic matter accumulation as a result of the decrease in the amount of oxygen in the environment. Trace elements such as Mo, Ni, Co, Cu, V, U, Th and Cr have been used in many studies to determine the paleo-redox environmental conditions.

The Miocene sequence unconformably deposited on ophiolites started with coarse clastics (Kalecik Formation). Reef limestones (Horu Formation) are lenticularly observed over the Kalecik Formation and the Kızıldere Formation consisting of a later sandstone-shale sequence has been deposited [7, 8, 9, 10].

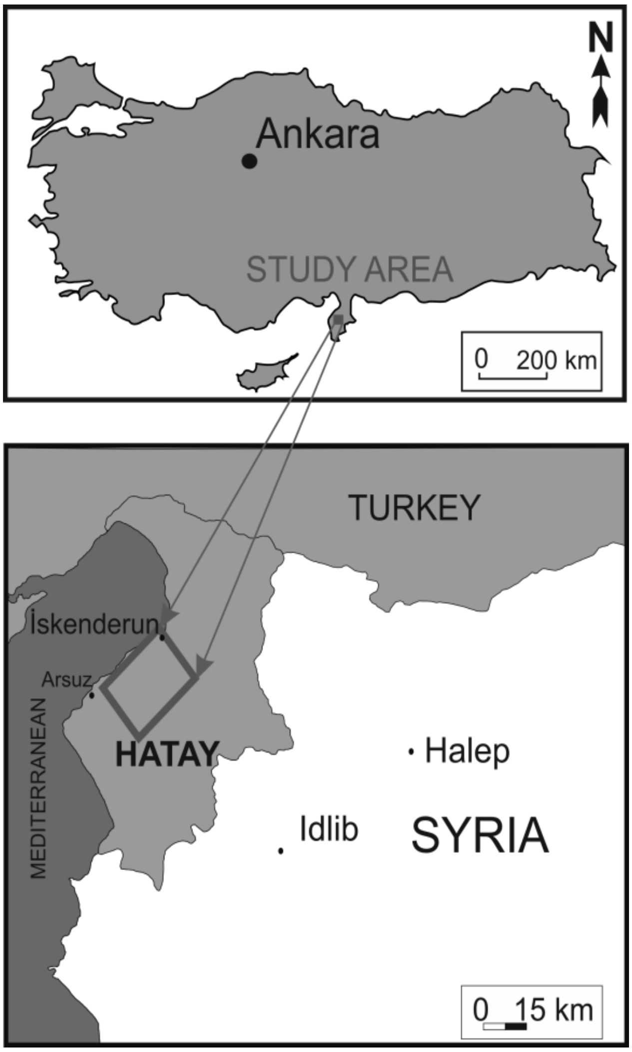

Figure 1. Location map of the study area.

During the Messinian period, evaporitic sediments (Haymaseki Member) were deposited in the Kızıldere Formation due to the sea regression, and then the marine clasts of the Aktepe Formation were deposited in the region with transgression. The stratigraphic section of the region is given in Figure 2. Geological maps and fault lines are not shown since the samples were taken from near the surface.

Kızıldere Formation was named by Schmidt [7]. Kozlu [8] used "the Kızıldere Formation" name by adding the Miocene sequence located in the south of the region. The Kızıldere Formation consists of the sequence of gray-colored medium-thick layered sandstone and shale layers. Carbonized plant origin clastics are observed in almost every layer [11, 14]. It has been determined that the formation shows the source rock feature that can form an oil system in the region according to the total organic carbon and main-trace element contents [12, 13].

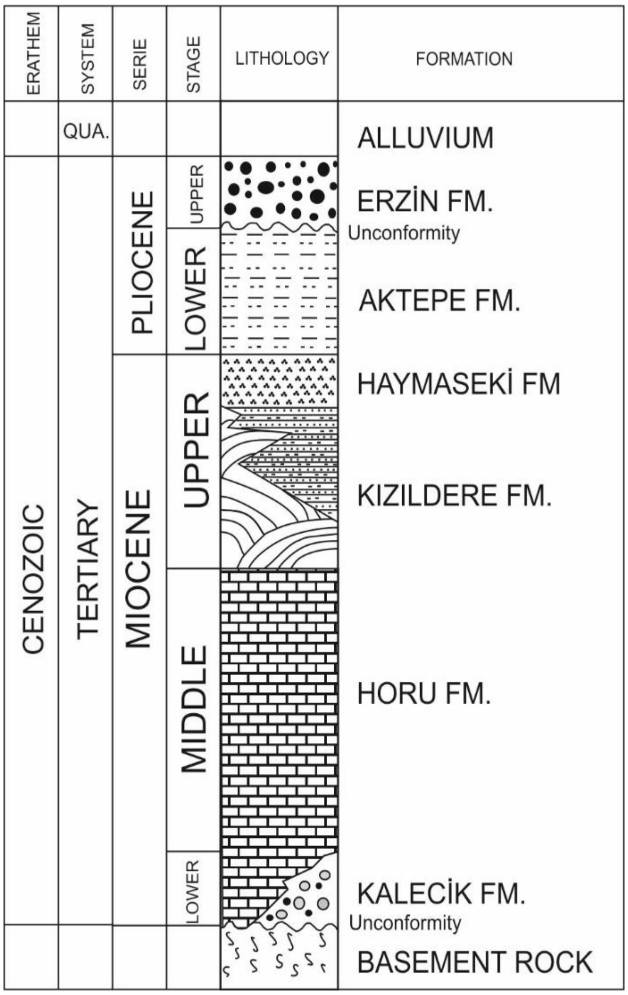

Figure 2. Generalized stratigraphic section of the region [14]

2. Material and Method

2.1. Field description of Kızıldere formation

The study area was deposited in the Neogene period and is located in Konacık, Tülek and Işıklı in Arsuz-İskenderun basin. Kızıldere Formation (Middle-Late Miocene) is typically observed in Konacık (Arsuz-HATAY) region. In the Kızıldere Formation, where sand and clay sequences are common, gray-yellow colored sandstones are medium-thick bedded between 10-50 cm and gray-colored claystones are thin-medium bedded between 2-30 cm (Figure 3A-B). The sequence of sandstone and claystone overlies the layered jibs deposits and the layer thicknesses of the jibs are 5-15 cm. The claystone layers are generally thinning from bottom to top, layer thicknesses on the lower parts of the profiles reach up to 102 cm. Tectonic cracks are commonly observed in the formation due to the effective post-Middle Miocene tectonism (Figure 3-B). Plant residuals can be seen with marls and jibs layers.

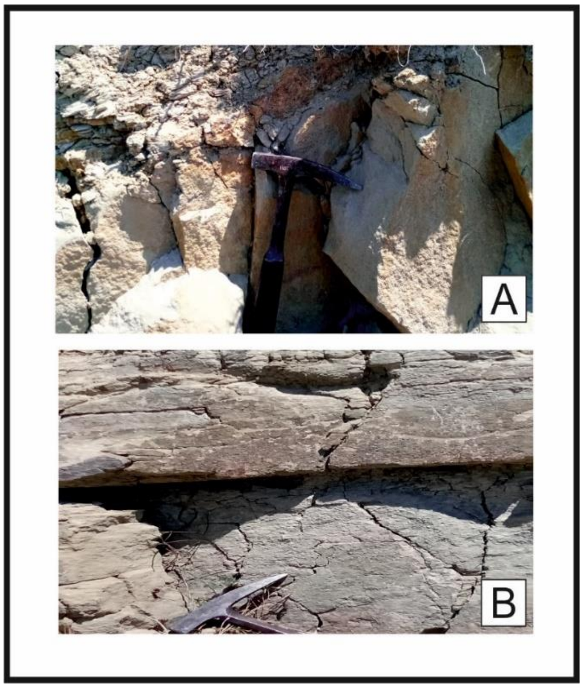

Figure 3. The field descriptions of the Kızıldere Formation, (A) medium-thick bedded, cracked sandstone layers sequenced claystone (B) cracks formed by tectonism in claystone-sandstone.

2.2. Trace elements and environmental descriptions of Kızıldere formation

Trace element concentrations in organic material rich sediments have been studied by many researchers [13, 15, 16, 17]. Consumption and enrichment of some elements such as V, Mo, Ni, Ba in sediments depend on environmental conditions. Changes in Ni, Co, Cu, U and V elements in Kızıldere Formation claystones have similarities.

Trace elements such as U, Zn, Ni and Cu and TOC (Total Organic Carbon) are enriched in the formation. Table 1 shows the main and trace elements in Kızıldere sandstones. The enrichment of U, V, Zn, Ni, Mo and Cu in claystones is an indication of anoxic conditions. It is known that the elements sensitive to redox are U, V and Mo, and other enriched elements depend on organic matters. U and Mo enrichments are indicators of oxygen consumption according to some researchers [15].

The U (Uranium) average values of the Kızıldere Formation are 1.224 ppm. Soua [15] compared the values in different claystone samples and indicated the trend of these values to an anoxic environment at the water-sediment interface of the formation. Pedersen and Calvert's [16] “productivity” model fits these Kızıldere Formation claystone data, and the increase in redox sensitive (U and V) and productivity (Ba, Cu and Ni) elements form the basis of the model.

Table 1. Main (Ca, K, Mg, Na) and trace (Rb,Cu, Cr, As, Zn, Sb, Co, Mo, Cd, Pb, U, Ba, Li, Cs, S, Ni, V) element contents of Kızıldere Formation claystones [17].

Sample	KD 1	KD 6	KD 7	KD 8	KD 9	KD 11	KD 13	KD 14	KD 15	KD 16	Mean
Ca (ppm)	18830	62870	69480	72410	93540	95290	102900	59510	54130	63110	74804.4
K (ppm)	48.23	8987	8658	7541	6832	7617	7492	7220	11070	7992	8156.56
Mg (ppm)	71630	29110	61290	36500	32670	33990	34350	23040	49580	42690	38135.6
Na (ppm)	407.2	12960	8186	7680	5221	7873	6959	17890	6500	11480	9416.56
Rb (ppm)	0.52	40.89	31.53	58.65	42.81	43.76	46.13	42.58	38.49	41.77	42.96
Cu (ppm)	134.49	20.91	13.09	34	26.43	31.31	21.66	21.65	17.01	17.56	22.63
Cr (ppm)	140.78	151.17	149.68	186.63	173.52	135.47	138.6	142.16	124.53	141.61	149.26
As (ppm)	1.68	7.43	9.19	8.25	12.02	10.46	7.91	8.61	5.13	6.56	8.4
Zn (ppm)	61.24	49.51	36.57	70.16	54.47	65.32	63.01	53.35	50.68	47.22	54.47
Sb (ppm)	0.21	0.62	0.57	0.67	0.78	0.9	0.5	0.49	0.41	0.52	0.61
Co(ppm)	189.24	22.18	15.02	17.63	18.23	19.27	19.56	25.67	23.02	14.46	19.45
Mo(ppm)	0.8	3.33	0.36	2	0.61	1.53	0.29	0.37	0.96	2.07	1.28
Cd(ppm)	-0.66	-0.68	-0.8	-0.61	-0.75	-0.55	-0.73	-0.78	-0.76	-0.7	-0.71
Pb(ppm)	-2.34	3.43	4.08	7.91	11.25	8.75	4.22	4.47	3.15	3.82	5.68
U(ppm)	0.12	1.61	0.94	2.13	1.11	1.24	1.2	1.07	1.33	1.49	1.35
Ba(ppm)	8.17	158.96	213.78	172.3	218.72	199.73	134.54	126.45	138.56	177.3	171.15
Li(ppm)	6.25	24.63	18.35	31	25.52	25	25.98	24.8	23.14	23.37	24.64
Cs(ppm)	0.08	3.26	1.63	4.47	2.95	2.76	3.34	2.57	3.18	3.34	3.06
S(ppm)	-67.19	341.38	34.6	354.48	377.16	403.41	280.05	269.35	272.77	286.1	325.48
Ni(ppm)	1809.05	212.41	149.79	249.63	185.84	235.56	249.36	292.49	200.15	203.21	219.83
V(ppm)	2482.95	1116.18	1104.31	1285.95	1175.41	1237.89	1222.9	1343.68	976.89	1162.63	1180.65

The average value of Cd (cadmium) in claystones is -0.70 ppm. This amount is below the Cd threshold. According to Pattan and Pearce [18], the negative result of Cd amounts in the measurements in the samples taken from the study area indicates that the environment is not oxic.

Many researchers have used Ni/Co, V/Cr and V/(V+Ni) indices to determine paleo-redox conditions. Jones and Manning [19] suggested that Ni/Co ratios <5 indicate oxic conditions, 5-7 disoxic conditions and> 7 anoxic-suboxic conditions. V/Cr ratios were determined to be <2 for oxic conditions, 2–4.25 for disoxic conditions, and> 4.25 for suboxic to anoxic conditions. Lewan (1984) noted that the V/(V+Ni) value should be greater than 0.5 for organic matter deposited under euxinic conditions. The average of Ni / Co, V/Cr and V/(V+Ni) ratios in Kızıldere Formation claystones are 11.45, 7.44 and 0.84, respectively, and all values indicate anoxic conditions. Kızıldere claystones were formed in anoxic environment according to the graph of Ni /Co and /(V+Ni) values [20, 21].

Ni/Co ratio is widely used to determine paleoredox conditions [19]. The average of Ni/Co ratios in Kızıldere claystone is 11.25 and indicates anoxic conditions (Figure 4.A-B).

Molybdenum (Mo), used as a indicator for depositional conditions, is associated with humic acids in organic matter. Mo concentrations increase with increasing anoxic conditions and the enrichment of Mo depends on the amount of organic matter and sulfidic conditions of the environment. According to Wedepohl [22], the average Mo value in claystones deposited under anoxic conditions is 2.6 ppm, and there is a Mo concentration close to this value in the Kızıldere Formation claystones and changes between 0.29-3.33 ppm (Figure 4.A).

Similarity is observed in Kızıldere claystones in concentrations measured from whole rock analyzes and enrichments in elements (Ni-Zn-Cu-U-V) which are the indicator of redox environment. The environmental sensitivities of these elements are compatible in all samples in terms of increase and decrease. Figure 4.C-D shows the variation of these elements.

There is usually a relationship between V/(V-Ni) and Ni/Co, indicating environmental properties [20]. In the graph shown in Figure 4.E, it is observed that Kızıldere claystones were deposited in anoxic environment.

Hallberg [23] noted that the Cu/Zn and (Cu+Mo)/Zn ratios are redox parameters. According to Hallberg [23], low Cu/Zn ratios indicate oxidizing conditions and high values indicate reduction conditions in sedimentation basins. Wedepohl [22] stated that the mean values of claystones are shallow marine sediments accumulated under oxidizing conditions.

The average Cu/Zn ratio in the Kızıldere Formation is 0.58, while the (Cu+Mo)/Zn ratio is 0.83.

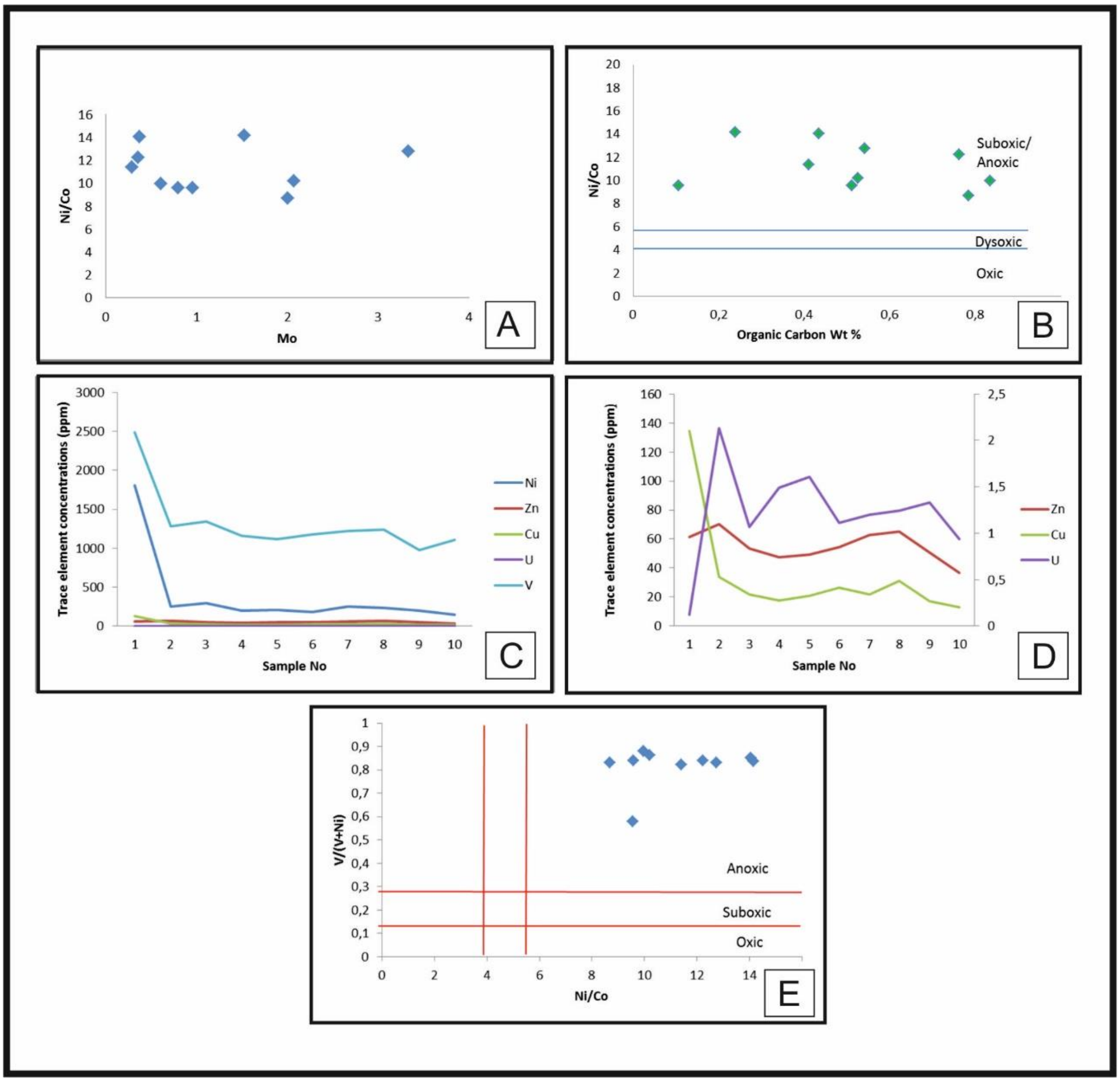

Figure 4. Environment indicators of trace elements A) Ni/Co –Mo plot, B) TOC-Ni/Co graph, C-D) comparison of similar environmental indicator elements, E) V/(V + Ni) -Ni /Co plot.

2.3. Regional distributions of elements

The regional distributions of the elements used in the environment interpretation in the region are shown in Figure 5. The distribution maps of these elements indicating the anoxic environment are similar and match with the TOC (Total Organic Carbon) distribution map. It is observed that the enrichments indicating anoxic values increase in the northeast direction of the region on the Ni-U-Cu-Zn distribution maps.

In Figure 5, the variations of the elements in the same coordinates are shown with contour maps depending on their quantities.

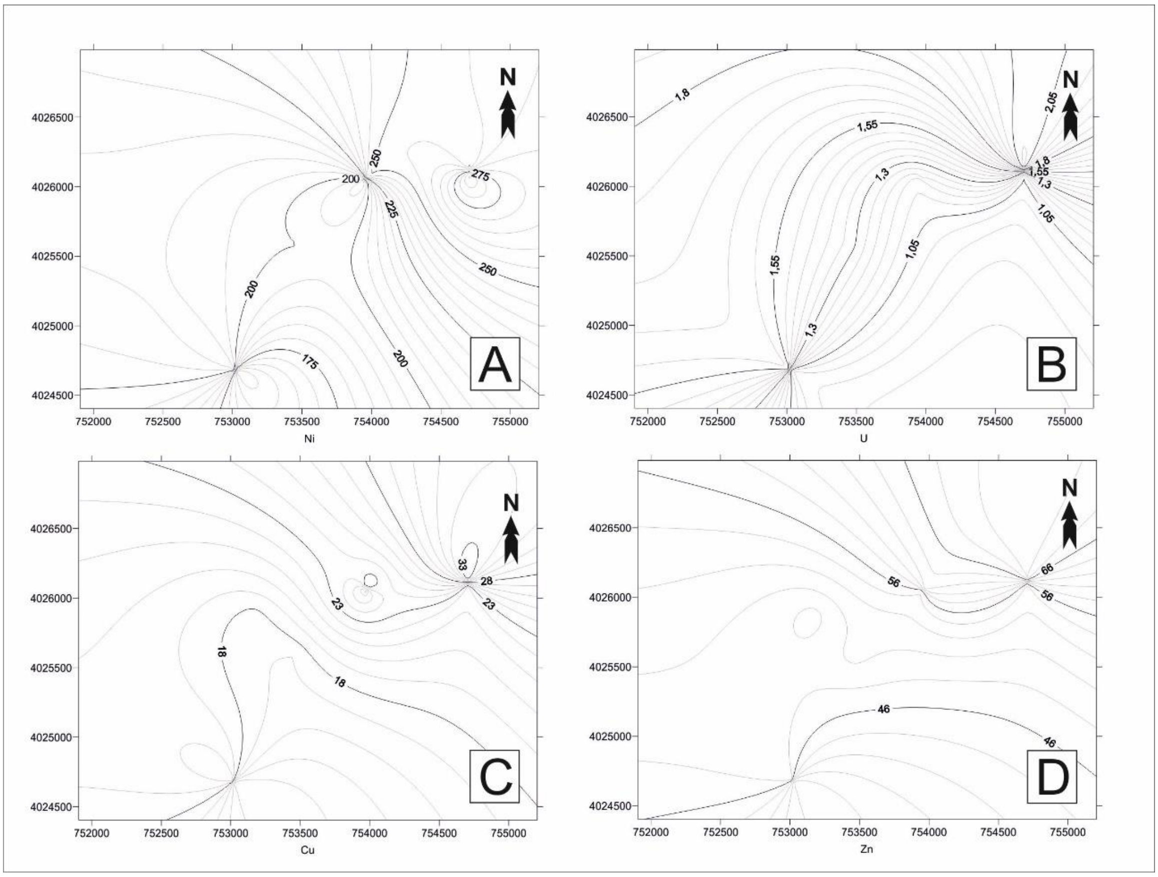

Figure 5. Contour maps of elements used as environmental indicator, A) Ni (nickel) contour map, B) U (uranium) contour map, C) Cu (copper) contour map, D) Zn (zinc) contour map.

3. Conslusions

It is important to determine the environmental conditions, especially the characteristics of claystones in hidrocarbon exploration areas. The Kızıldere Formation is important in the petroleum system as it has both reservoir and source rock properties, and trace element concentrations and environmental properties are revealed in this study. Increases in Ni-Zn-Cu-U-V elements, which are anoxic environment indicators, have been observed in Kızıldere Formation claystones, and Ni/Co -Mo, TOC-Ni / Co, V/(V + Ni) -Ni/Co values used as environment indicators proves that it precipitated in the environment. The similarities of the regional concentration distributions of these elements are also evidence of environmental changes. The similarities of the regional concentration distributions of these elements are also evidence of environmental changes. In addition, enrichment of trace elements that support the protection of organic matter content indicates that claystones may be source rock.

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Conflicts of interest

The authors state that did not have conflict of interest.

References

[1] Schneider S., Hornung J., Hinderer M., Garzanti E., Petrography and Geochemistry of Modern River Sediments in an Equatorial Environment (Rwenzori Mountains and Albertine Rift, Uganda) Implications for Weathering and Provenance, *Sedimentary Geology*, 336 (2016) 106-119.

[2] Rollinson H. R., Using Geochemical Data: Evaluation, Presentation, Interpretation, Routledge, 2014.

[3] Gélinas Y., Baldock J.A., Hedges, J.I., Organic Carbon Composition of Marine Sediments: Effects of Oxygen Exposure on Oil Generation Potential, *Science*, 294 (2001) 145-148.

[4] Xie X., Borjigin T., Zhang Q., Zhang Z., Qin J., Bian L., Volkman, J. K., Intact Microbial Fossils in the Permian Lucaogou Formation Oil Shale, Junggar Basin, NW China, *International Journal of Coal Geology*, 146 (2015) 166-178.

[5] Kätz B.J., Controlling Factors on Source Rock Development a Review of Productivity, Preservation, and Sedimentation Rate, In: Harris, N.B. (eds), The Deposition of Organic Carbon Rich Sediments: Models, Mechanisms, and Consequences, *SEPM*, (2005) 282.

[6] Koca D., Sarı A., Koç Ş., Yavuz B., Koralay D.B., Denizel Kaynak Kayalarda Ana ve İz Element Zenginleşmelerine Türkiye'den Bir Örnek: Akkuyu Formasyonu (Orta Toroslar), Ankara, *Gazi Üniv. Müh. Mim. Fak. Der*., 25(2) (2010) 243-256.

[7] Schmidt G.C., Stratigraphic Nomenclature for the Adana Region Petroleum District VII, Ankara, *Petroleum Administration Bull.*, 6 (1961) 47-63.

[8] Kozlu H., İskenderun Basen Jeolojisi ve Petrol Olanakları, TPAO Rapor no:1921, 1982.

[9] Kozlu H., Misis Andırın Dolaylarının Stratigrafisi ve Yapısal Evrimi. Ankara: Türkiye 7. Petrol Kongresi, (1987) 104-113.

[10] Yaşar E., Assessment of Petroleum geology of Iskenderun Basin, (2018) 200-206.

[11] Kozlu H., Doğu Akdeniz Bölgesinde Yer Alan Neojen Basenlerinin (İskenderun, Misis-Andırın) Tektono-stratigrafi Birimleri ve Bunların Tektonik Gelişimi. Adana: Yayınlanmamış Doktora Tezi, Çukurova Üniversitesi, Fen Bilimleri Enstitüsü, (1997) 189.

[12] Kılınç E., Yeşilot Kaplan M., Source Rock Characterictic of The Kızıldere Clays (ARSUZ-HATAY), *Cumhuriyet Sci. J.*, 39(2) (2018) 524-530.

[13] Kilinc E., Kaplan M.Y., Paleoenvironmental Conditions, Geochemistry and Hydrocarbon Potential of Kızıldere Formation (Hatay-Turkey), *Fresenius Environmental Bulletin*, 28(4A), (2019) 3516-3526.

[14] Tekin E., Varol B., Ayyıldız T., Kozlu H., İskenderun Havzası Messiniyen (Üst Miyosen) Evaporitlerinin Sedimantolojisi. Ankara: MTA 59. Türkiye Jeoloji Kurultayı, (2006) 191-192.

[15] Soua M., Productivity and bottom water redox conditions at the Cenomanian-Turonian Oceanic Anoxic Event in the southern Tethyan margin, Tunisia, *Revue Mediterraneenne de l'Environement*, 4 (2010) 653-664

[16] Pedersen T.F., Calvert S.E., Anoxia vs. productivity: what controls the formation of organic-carbon-rich sediments and sedimentary rocks, *American Association of Petroleum Geologists Bulletin*, 74 (1990) 454-466.

[17] Kılınç, E., Arsuz (Hatay) yöresi Kızıldere formasyonunun hidrokarbon potansiyelinin araştırılması, MS Thesis, İskenderun Teknik Üniversitesi, Mühendislik ve Fen Bilimleri Enstitüsü (2018) 96.

[18] Pattan J.N., Pearce N.J.C., Bottom water oxygenation history in southeastern Arabian Sea during the past 140 ka: Results from redox-sensitive elements, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 280 (2009) 396-405.

[19] Jones B., Manning D.A.C., Comparison of geological indices used for the interpretation of palaeoredox conditions in ancient mudstones, *Chemical Geology*, 111 (1994) 111-129.

[20] Goldberg K., Humayun M., Geochemical paleoredox indicators in organic-rich shales of the Irati Formation, Permian of the Paraná Basin, southern Brazil, *Brazilian Journal of Geology*, 46(3) (2016) 377-393.

[21] Lewan M.D., Factors controlling the proportionality of vanadium and nickelin crude oils, *Geochimica et Cosmochimica Acta.*, 48 (1984) 2231-2238.

[22] Wedepohl K.H., Environmental influences on the chemical composition of shales and clays, In: Ahrens, L.H., Press, F.,Runcorn, S.K., Urey, H.C. (Eds.), *Physics and Chemistry of the Earth*, 8 (1971) 307-331.

[23] Hallberg R., Халлберг Р., A Geochemical Method for Investigation of Paleoredox Conditions in Sediments, *Ambio Special Report*, (4) (1976) 139-147.