Geochemistry and Pb Isotopic Proof for Sources of Heavy Metal(Loid)s in Late Cretaceous Sandstones From Eastern Pontides (NE Turkey)

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Research Article

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Geochemistry and Pb isotopic proof for sources of heavy metal(loid)s in Late Cretaceous sandstones from Eastern Pontides (NE Turkey)

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Abstract

Upper Cretaceous sedimentary rocks are widely exposed around Trabzon, Giresun and Gümüşhane in the eastern Pontides. The sedimentary rocks are mainly composed of sandstones and marls, and the thicknesses of these rocks range from 170 m to 400 m. This paper focused on Late Cretaceous sandstones of Trabzon, Giresun and Gümüşhane regions to identify the concentrations, sources, deposition environment and conditions of certain heavy metal(loid)s (Zn, Pb, Cu, Ni, As, Co, Mo and V). Enrichment factor (EF), geo-accumulation index (*Igeo*), Pollution index (Pi), Pollution load index (Pl_n), Pb isotope and multivariate statistical analysis were performed to elucidate the pollution levels and sources. The mean concentrations of Zn, Pb, Cu, Ni, As, Co, Mo and V were 16.5, 10.8, 9.4, 13.2, 2.1, 4.4, 0.2 and 21 mg/kg, respectively in the Trabzon area, 35, 5.8,18.8, 102, 3.2, 18.6, 0.5 and 109 mg/kg, respectively in the Giresun area, and 36, 8.9, 14.7, 82, 3.9, 16.9, 0.3 and 106 mg/kg, respectively in the Gümüşhane area. In general, the evaluation indices exhibited that the sandstones were moderately polluted by As in the Trabzon area, and strongly polluted by Ni and As, moderately polluted by Co and V in the Giresun and Gümüşhane areas. The results of multivariate statistical analyses indicated that As and partly Pb might be originated from anthropogenic sources, whereas other metals were derived from geogenic origin. Lead isotopic analysis demonstrated two characterized signatures of the pollution sources in the sandstones, one related to geogenic origin and the other to coal, gasoline and pesticides. The sandstones were deposited in transition – marine environment under oxic – weak oxic conditions and paleoclimatic conditions ranged from arid to moist during Late Cretaceous period.

Key word NE Turkey, Late Cretaceous, Pollution indices, Pb isotope, Paleoclimate, Redox condition

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Introduction

Sediments are commonly considered as a sink for most heavy metal(loid)s (Singh et al., 2002; Çevik et al., 2009; Saydam Eker and Demirkol Kiliç, 2018; Saydam Eker and Arı 2020a) and they can be a storage for both geogenic and anthropogenic heavy metal(loid)s (Jiao et al., 2015; Wu and Probst 2021). The spread of heavy metal(loid)s to the environment consists of generally through volcanoes, geological weathering, erosion, vehicles exhausts, fertilizers, mining areas, pesticides and industrial activities (Islam et al., 2015, 2018; Tokatlı et al., 2015; Ustaoğlu and Islam, 2020; Ustaoğlu, 2020). Therefore, geochemical features of sediments are usually used to define the sources of pollution owing to heavy metal(loid)s. The accumulation of heavy metal(loid)s is sediments controlled

by several processes according as the features of the sediments such as organic matter, carbonate and clay mineral contents, pH and redox conditions (Ghrefat and Yusuf, 2006; Du Laing et al., 2009). In additional, grain size distribution of the sediments essentially influences the heavy metal(loid)s concentrations. Some researchers (Ip et al., 2007; Chakraborty et al., 2015; Simonetti et al., 2017; Saydam Eker and Arı, 2020a, Saydam Eker, 2020a) have recommended that fine grained sediments, such as clay-silt, have higher concentrations of heavy metal(loid)s than coarse-grained sediments. The heavy metal(loid)s distribution in the sediments is controlled by climatic and geomorphologic conditions geochemistry of parent rock, sediments texture, time of weathering, living organism and anthropogenic inputs, such as gasoline combustion, mining, agricultural activities, vehicle exhausts, burning coal and industrial and residential emission (Pinto et al., 2017; Seifi et al., 2019). In general, the high heavy metal(loid) contents in sediments can be good indicator anthropogenic pollution, for high substance heavy metal(loid)s are commonly attributed on terrigenous input and anthropogenic, rather than geogenic sources (Goher, 2014; Saydam Eker and Arı, 2020a). Environmental pollution by heavy metals, due to a reality of anthropogenic activities such as industrialization, mining, agriculture, urbanization, energy generation and transportation, has increased importantly global and a critical environmental attention that has been menace ecosystem and human health (Vural, 2015; Yousaf et al., 2016a, b; Cheema et al., 2020). For instance, the heavy metal(loid)s like Cd, Cr, As, Pb and Hg are known systematic toxicants, that can cause a critical threat to environment health and ecosystem (Yousaf et al., 2018). Among these heavy metals, one of the most significant environmental pollutants is Pb which is fairly toxic even if very little because of its abundance and rapid bioaccumulation (Cheema et al., 2020). Lead in sediments generally originates from many sources such as rocks, gasoline, aerosols, , battery industry and cooler pigment. Additionally, the primary origin of Pb and As pollutant in sediments are related to atmospheric depositional burning coal, vehicle exhausts and gasoline combustions. Many researchers (e.g. Cheng and Hu, 2010; Lin et al., 2016; Potra et al., 2017; Saydam Eker et al., 2017; Orani et al., 2019; Lermi and Sunkari, 2020) have suggested that Pb isotopes are beneficial indicator of Pb contamination sources in sediments/soils and additive ratios of different sources.

In the environment, there are four stable-isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, Rabinowitz, 1995) and relative abundances of the Pb isotopes change as regards their geogenic origin (Patel et al., 2008; Cheema et al., 2020). Among these isotopes, ^{206}Pb, ^{207}Pb, ^{208}Pb are radiogenic, only ^{204}Pb is non-radiogenic and its abundance on earth is nearly stable (Komárek et al., 2008). A complementary examination of Pb and other heavy metal(loid)s substances in sediments that are contaminated by anthropogenic activities is a primary approach to determining the degree of pollution or their natural sources.

Late Cretaceous clastic rocks are broadly exposed in the eastern Pontides significantly in Trabzon, Giresun and Gümüşhane region. These rocks are mainly composed of sandstones and marls, rarely claystone, limestone and felsic tuff. Trabzon, Giresun and Gümüşhane, located in northeast Turkey, are places where intensive agricultural activities (include lettuce, potatoes, beans, onions parsley, walnut and apple trees, thus hazelnut is the most growed product of Trabzon and Giresun) and metallic mining activities (Pb-Cu-Zn-Au ores) are performed out and they are also cities of education. Trabzon and Giresun are coastal cities that's way, a temperate marine climate reigns in these areas, where is called Black Sea climate which has cold and wet winters, warm and wet summers. Climate in the Gümüşhane area is step, summer season is a hot and winter is a cold. Therefore, to warm up in all three fields of study area, up to lately coal was burned. The purpose of this study are to: (1) Define the concentrations and vertical change of 8 heavy metal(loid)s (Zn, Pb, Cu, Ni, As, Co, Mo and V) in the Upper Cretaceous sandstones

from Trabzon, Giresun and Gümüşhane areas, (2) Evaluate the level of pollution of these metal(loid)s in the sandstones using some pollution index, such as EF, *Igeo,* Pi and Pl_n, (3) Examined whether the grain size of the sandstones, paleoclimate, paleo-salinity and redox conditions of the deposition environment affect the abundance of the heavy metal(loid)s, (4) Differentiate the sources of collected Pb in the sandstones using Pb isotopes (5) Define the anthropogenic sources of the heavy metal(loid)s.

Study area and geological setting

Trabzon, Giresun and Gümüşhane areas are located in the northeastern Anatolia within Eastern Pontides orogenic belt which lies within Alpin orogenic belt. The eastern Pontides belt is commonly subdivided into southern and northern parts that change in terms of rock companies The northern part is characterized by Carboniferous to Eocene granitoids and volcanic rocks. The southern part includes metamorphic, volcanic, plutonic and clastic rocks from the Paleozoic to Eocene. The basement rocks of the eastern Pontides are formed of methamorphic rocks of Lower Carboniferous age (Topuz et al, 2004; Ustaömer and Robertson, 2010) and crosscutting Upper Carboniferous granitoids (Topuz et al., 2010; Ustaömer and Robertson, 2010; Dokuz, 2011; Kaygusuz et al., 2012). The Early and Middle Jurassic volcanic volcanoclastic and sedimentary rocks (Conglomerates, sandstones, chert and carbonates) (Saydam Eker et al., 2012; Saydam Eker and Arı 2020a, b) lie unconformably on this basement. Upper Jurassic magmatic rocks show an extensive lithological range. Late Jurassic to Middle Cretaceous pelagic and neritic carbonates lie comformably on the Jurassic rocks. Late Cretaceous aged rocks are characterized by turbidites containing mainly sandstones and marls (Saydam, 2002; Saydam and Korkmaz, 2008; Saydam Eker and Korkmaz 2011) and volcanic, granitoids (Sipahi et al., 2018) in the eastern Pontides. Eocene rocks are represented by turbidites (Conglomerates, sandstones and mudstones) (Saydam Eker, 2012; 2013), volcanoclastic and volcanic rocks (Kaygusuz et al., 2011; Aydınçakır, 2014; Akaryalı and Akbulut, 2016) in this region. Quternary units are characterized by alluvium and terraces (Saydam Eker, 2017; 2020 a, b) (Fig. 1).

Materials and methods

Sampling and preparation

In this study, a total of six stratigraphic section were measured from Dağbaşı (Trabzon), Çamlıyayla and Evliyatepesi (Giresun), and Musalla, Pirahmet and Mescitli (Gümüşhane) fields. The thickness of the upper Cretaceous sequences was measured as 170 m in the Dağbaşı (Trabzon) section, 315 m in the Çamlıyayla section, 400 m in the Evliyatepesi section(Giresun), 210 m in the Musalla section, 288 m in the Pirahmet section and 304 m in the Mescitli section (Gümüşhane) (Saydam, 2002; Saydam Eker and Korkmaz, 2011). While measuring stratigraphic sections, a total of 33 sandstone samples (six samples for Dağbaşı section (Trabzon), four samples for Çamlıyayla and six samples for Evliyatepesi section (Giresun), seven samples for Musalla, six samples for Pirahmet and four samples for Mescitli section (Gümüşhane) were gathered for geochemistry analysis (Fig. 2). The sandstone sample was about 2000-2500 g. These sandstones were air dried in the laboratory previous to analysis. Additionally, the sandstone samples were homogenized split into sub-samples and crushed to roughly 200 mesh (0.075 mm) size using an agate mill.

Laboratory Analysis

Grain size analysis

For the well-cemented sandstones, thin sections have to be used and several hundred grain sizes measured with an eyepiece graticule and point counter, as detailed is in McManus (1988).

Physicochemical analysis

The total organic carbon (TOC) content of the sandstone samples was defined by oxidation with acidified $K_2Cr_2O_7$ and back titration with ferrous ammonium sulphate. They were soaked in water with an aliquot of 10% sodium hexamtaphosphate solution and lightly agitated for about 1 h to increase disaggregation. The samples were then washed over an 80 µm sieve and oven-dired at a temperature 0f 60 ºC. The percent mud of the samples was calculated by multiplying the mass of the 80 µm fraction and the initial sample mass minus water content. The TOC content of sandstones was determined by Bernard calcimeter method (Guitián and Carballas, 1976).

Geochemical analysis

Major and trace elements were determined on the 33 sandstone samples (6 samples for Trabzon, 10 samples for Giresun and 17 samples for Gümüşhane), at the commercial Acme Analytical Laboratories Ltd (now Bureau Veritas Minerals) in Vancouver, Canada. Major and element (Al2O3, Zn, Pb, Cu, Ni, As, Co, Mo and V) compositions were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) using 0.2 g of sediment fused with 1.5 g of $LiBO_2$ and dissolved in 100 ml of 5% HNO_3. Loss on ignition (LOI) was determined using dried samples heated to a temperature of 1.000 °C for 15 min. The detection limits were in the range of 0.001 wt% to 0.1 wt% for major element oxides and 0.1 ppm to 10 ppm for trace elements and 0.01 ppm for Hg. Calibration and verification standards together with reagent blanks were added to the sample batches. STD SO-18 was certified in-house against 38 certified reference materials, including CANMET SY-4 and USGS AGV-1, G-2, GSP-2, and W-2 as known external standards. The analytical accuracy is better than 4%.

Pb isotope analysis

Isotopic analysis of Pb was performed at the commercial Acme Analytical Laboratories Ltd. in Vancouver, Canada. The prepared sample is digested with a modified aqua regia solution of equal parts concentrated HCl, HNO_3, and DI H_2O for 1 h in a heating block or a hot water bath. The sample is made up to volume with dilute HCl. Sample splits of 0.5, 15, or 30 g were analyzed. Pb isotope add-ons (+ISO) Pb_{204}, Pb_{206}, Pb_{207}, and Pb_{208} are suitable for geochemical exploration of U and other commodities where gross differences in natural to radiogenic Pb ratios are beneficial. Isotope values can be obtained from the concentrations and intensities. Sample splits of 0.5, 15, or 30 g were analyzed. Pb isotopic analyses were performed on three samples (D1, D17, D21) from

Trabzon area, five samples (C11, C18, A14, A28, A36) from Giresun area and six samples (N17, N37, N40, R34, M30) from Gümüşhane area.

Assessment of the pollution index

Enrichment factor (EF)

EF is commonly used to assist the determination of the level heavy metal(loid) pollution. Furthermore, Thang et al. (2018) suggested that this index is useful in evaluation the anthropogenically introduced heavy metal(loid) and the equation is:

$$\mathrm{EF} = \frac{\left(\frac{Ci}{Cref}\right)Sediment\ sample}{\left(\frac{Bn}{Bref}\right)UCC} \qquad 1$$

Where, *Ci* is the ingredient of the studied element in the sandstone; *Cref* is the concentration of a reference element (Sc) for normalization objectives, Bn is the background concentration of the heavy metal(loid) in the upper continental crust (UCC), and *Bref* is the background concentration of the reference element (Sc) in the UCC (Taylor and McLennan, 1985).

Geo-accumulation index (Igeo)

Igeo, used initially by Müller (1969; 1981), has been generally used to define the pollution level of heavy metal(loid) in sediments and the equation is:

$$Igeo = log2\left[\frac{(Cn)}{(1.5)(Bn)}\right], \qquad 2$$

Where C_n indicates the concentrations of heavy metal(loid) n in the analyzed sample, B_n is the reference concentration of the element in the background sample (Wedepohl, 1995) and the factor (1.5) is used to minimize the influence likely changes in the background values, as a result of lithogenic input.

Pollution index (Pi) and Pollution load index (Pl_n)

Pi is the ratio of single heavy metal(loid) contents in sediments and the background value. Pi is calculated with the following equation (Cheng et al., 2007):

$$\mathrm{Pi} = \frac{C_n}{C_{ref}}, \qquad 3$$

Where C_n is the concentration of the studied heavy metal(loid), Cref is the reference value.

Pl_n is used for definition of total heavy metal(loid) pollution in sediments certain site and mean of Pi of all the distinct heavy metal(loid)s present in the study areas (Tomlinson et al., 1980; Rana et al., 2016; Raj et al., 2019). Pl_n is calculated with the following formula (Cheng et al., 2007):

$$PI_n = \sqrt{\frac{(Pi)^2 max + (\frac{1}{n}\sum_{i=1}^{n} Pi)^2}{2}}, \qquad 4$$

Where Pi is the monomial pollution index of heavy metal(loid), (Pi)max is the maximum value of the monomial pollution indices of all heavy metal(loid)s.

Multivariate statistical analysis

Pearson's correlation matrix (PCM) and principial component (PCA) was used to decode the interrelations among heavy metal(loid)s and physicochemical parameters. These analyses were applied with a statistical software SPSS 22.0. PMC analysis commonly determined the relation among the heavy metal(loid)s and verified the conclusions of multivariate analysis (Tahri et al., 2005; Liao et al., 2017). In addition, this analysis as used to understand pollution sources (anthropogenic and geogenic).

Results

Heavy metal/metalloid concentrations in the sandstones

Concentrations of the some major, trace elements, heavy metal (loid) and TOC and Mz values were presented in the Table 1. Grain size average of the studied samples range from 0.5 – 2 ϕ in the Trabzon area, 1.2 – 2.2 ϕ in the Giresun area and 0.78 – 2.51 ϕ in the Gümüşhane area (Saydam 2002; Saydam Eker and Korkmaz 2011). The sandstones are coarse to medium-grained using the Wentworth scale in the Trabzon area, medium to fine-grained in the Giresun and coarse to fine grained in the Gümüşhane.

The mean concentrations of heavy metal(loid) (mg/kg) varied in the order of V (21) > Zn (16.5) > Ni (13.2) > Pb (10.8) > Cu (9.4) > Co (4.4) > As (2.1) > Mo (0.2) in the Trabzon region, V (109.1) > Ni (102.3) > Zn (34.5) > Cu (18.8) > Co (18.6) > Pb (5.8) > As (3.2) > Mo (0.5) in the Giresun region and V (106) > Ni (81.7) > Zn (36.1) > Co (16.9) > Cu (14.7) >Pb (8.9) > As (3.9) > Mo (0.3) in the Gümüşhane region. The highest mean of TOC value (7.7%) was found in the Trabzon region, followed by Gümüşhane region (2.7%) and Giresun region (2.6%). The heavy metal(loid) concentrations in sediments from Trabzon, Giresun and Gümüşhane areas were summarized in Table 1, Fig. 3. The highest V (155 mg/kg), Zn (76 mg/kg), Pb (29.5 mg/kg), Cu (20.7 mg/kg), Ni (140.9 mg/kg), As (8.7 mg/kg), Co (29.2) values were measured in the Gümüşhane area, and the highest Mo (0.8) value was measured in the Giresun and Gümüşhane areas. The lowest Zn (4.5 mg/kg), Pb (3.5 mg/kg), Cu (2.7 mg/kg) values were measured in the Gümüşhane, the lowest Ni (8.8 mg/kg), As (0.4 mg/kg) and Co (2.3 mg/kg) values were measured in the Trabzon area. The Cu, Zn, Pb and Mn in the Gümüşhane region showed a wide variation range owing to low and high values, whereas all the heavy metal(loid) in the Giresun showed a narrow variation range. Figure 4 indicated the vertical distributions of the heavy metal(loid)s normalized to the UCC (Taylor and McLennan, 1985). The result indicated that three samples (D12, D16 and D21) of the Dağbaşı (Trabzon) section

were enriched in As, one sample (D21) was slightly enriched in Pb, depleted in other heavy metals. All of the Çamlıyayla (Giresun) samples were enriched in Ni, As and V, and depleted in other metals; Evliyatepesi (Giresun) samples were enriched in Ni, As, Co and V, depleted in other metals. All of the Musalla, Mescitli and Pirahmet (Gümüşhane) samples were enriched in Ni (except R34 for Pirahmet), As (except R36 for Pirahmet), V and Co (except R34 for Pirahmet), depleted in other metals. The heavy metal(loid) abundance of the samples was not significant relationship of the thickness of the upper Cretaceous sequences. In addition, the heavy metal(loid) composition of the studied sandstones was not importantly influenced by the grain size of the sandstones (except Zn, Ni, Co, Mo and V in the Trabzon area).

Pollution assessment of heavy metal(loid)s

Enrichment factor (EF)

Table 2 indicated the descriptive statistics of EF for eight heavy metal(loid)s in all studied sandstone samples and average upper continental crust (UCC) values (Taylor and McLennan 1985). The means of EF were in the order of Mo < Zn <V < Cu < Co < Pb = Ni < As in the Trabzon area, Pb < Mo < Zn < Cu < Co = V < As < Ni in the Giresun area and Mo < Zn < Cu = Pb < Co = V < As < Ni in the Gümüşhane area. A threshold of 2 was admitted to descriptive whether a definite metal was enriched in soil. If a local reference element is used to compute EF, this threshold could be decreased to 1.5 (Hernandez et al., 2003; Roussiez et al., 2005; N'guessan et al., 2009; Benabdelkader et al., 2018; Wu and Probst, 2021). The mean EF of the Ni for Giresun area and As, Ni for Gümüşhane area were higher than the threshold of 2. In the Trabzon area, As for D12 and D21 samples was higher than threshold (Fig. 5a). In the Giresun area, As for C18 and A14 samples, Ni for all samples were higher than threshold (Fig. 5b). In the Gümüşhane area, Co for N3 sample, Pb for R34, As for N17, N33, N37, N40, R15, R31, R34, M30 and M33, and Ni for about all samples (except N50, R34, M30 and M33) were higher than threshold (Fig. 5c). The EF values of Mo had been calculated as very low in all the studied samples.

Geo-accumulation index (Igeo)

Table 3 showed the *Igeo* value of six heavy metal(loid)s, average background values, *Igeo* value and class and pollution level. The mean values of *Igeo* were in order of Zn< V<Co<Pb<Cu<Ni<As in the Trabzon area, Pb<Zn<Cu<As<Co<V<Ni in the Giresun area, Pb<Zn<Cu<Co<As<V<Ni in the Gümüşhane area. The values of *Igeo* for all of the heavy metal(loid)s (except max *Igeo* value for As) were negative in the Trabzon area, indicating that the sandstones were unpolluted by these metal(loid)s (Fig. 6a). The mean values of *Igeo* for Zn, Pb, Cu were negative, for Ni (1.66 to 1.87, with a mean of 1.82), V (0.30 to 0.62, with mean of 0.46), As (-0.58 to 0.82, with a mean of 0.08) and Co (-0.26 to 0.26, with a mean of 0.10) were positive in the Giresun area, indicating that the sandstones were polluted by Ni, V, As and Co (unpolluted to moderately polluted by V, As, Co and moderately polluted by Ni), and unpolluted by Zn, Pb, Cu (Fig. 6b). The mean values of *Igeo* for Ni (-0.70 to 2.33, with a mean of 1.51), As (-0.58 to 1.83, with a mean of 0.50) and V (-1.03 to 0.96, with mean of 0.42) were positive, Zn, Pb, Cu and Co were negative in the Gümüşhane area, indicating that the sandstones were polluted by Ni, As and V (unpolluted to moderately polluted by As, V and moderately polluted by Ni), and unpolluted by Zn, Cu, Co and

Pb (Fig. 6c). In additionally, Fig. 5d showed that the sandstones in the Giresun and Gümüşhane areas were polluted by Ni in approximately same amount.

Pollution index (Pi) and Pollution load index (Pl_n)

The Pi rates of the heavy metal(loid) of the sandstones in the Trabzon area exhibited unpolluted to low polluted and varied as: Zn (0.19 to 0.58, with mean of 0.32), Pb (0.35 to 1.23, with mean of 0.63), Cu (0.29 to 1.26, with mean of 0.65), Ni (0.47 to 1.01, with mean of 0.71), As (0.20 to 1.90, with mean of 1.03), Co (0.20 to 0.72, with mean of 0.38) and V (0.15 to 0.92, with mean of 0.40) (Table 4, Fig. 7a). The Pi values of the heavy metal(loid) of the sandstones in the Giresun and Gümüşhane areas indicated unpolluted to strongly polluted and varied as: Zn (0.56 to 0.75 and 0.40 to 1.46, with mean of 0.66 and 0.72, respectively), Pb (0.24 to 0.43 and 0.21 to 1.74, with mean of 0.74 and 0.54, respectively), Cu (1.11 to 1.44 and 0.19 to 1.45, with mean of 1.31 and 1.01, respectively), Ni (4.76 to 6.10 and 1.22 to 7.58, with mean of 5.50 and 4.26, respectively), As (1.20 to 2.65 and 1.00 to 5.35, with mean of 1.59 and 2.12, respectively), Co (1.47 to 1.79 and 0.58 to 2.52, with mean of 1.60 and 1.43, respectively) and V (1.91 to 2.30 and 0.74 to 2.92, with mean of 2.06 and 2.01, respectively (Table 4, Figs. 7b, c).

In the Trabzon area, Pl_n values of Zn, Pb, Ni, Co and V were below 1 (0.47, 0.98, 0.87 and 0.58, respectively), indicating that the sandstones were unpolluted by these metals, and Cu and As were between 1 and 2 (1.0 and 1.53, respectively), indicating that the sandstones were low polluted by Cu and As (Table 5, Fig. 7d). The Pl_n values of the sandstones in the Giresun area varied from 0.39 to 5.81. These sandstones were unpolluted by Zn and Pb (0.71 and 0.39, respectively), low polluted by Cu and Co (1.38 and 1.70, respectively), moderately polluted by As (2.18), V (2.18) and strongly by Ni (5.81) (Table 4, Fig. 7d). In the Gümüşhane area, Pl_n values of Zn, Pb and Cu were between 1 and 2 (1.15, 1.29 and 1.25, respectively), indicating that the sandstones were low polluted by these metals, Co and V were between 2 and 3 (2.05 and 2.51, respectively), indicating that the sandstones were moderately polluted by Co, V, and As and Ni were above 3 (4.07 and 6.15, respectively), indicating that the sandstones were strongly polluted by As and Ni (Table 4 and Fig. 7d).

Lead isotopic tracing in the sandstone

Lead isotopes provide an effective tool for determining the pathways and sources of Pb pollution because the isotopic composition of Pb is not importantly impressed by physico-chemical fractionation processes (Bollhöfer and Rosman 2001; Veysseyre et al., 2001; Komárek et al., 2008). Therefore, Pb isotope analysis is often used to define whether content of metals in sediments of anthropogenic or geogenic. Lead in sediments is possibly a mixture of natural lead from the weathering of host rocks and anthropogenic Pb. Lead is present in widespread various rock kinds range from about 30 mg/kg to 1 mg/kg among igneous rocks, black shale, evaporitic rocks, rhyolite and granitic rocks, respectively (Wedepohl 1995; Cheeme et al., 2020). These rocks included radioactive elements have high concentrations of Pb than sedimentary rock. In same time, sedimentary rocks also include Pb contents ranging from 10 mg/kg to 20 mg/kg (Lovering, 1969; Cheema et al. 2020). Additionaly, the main origin of Pb pollution in sediments is the metal coating, leather whipping, burning coal and fossil fuels, waste pyromania

and paint factories (Kushwaha et al., 2018; Ullah et al., 2017; Yousaf et al., 2017; Cheema et al., 2020). Due to the direct release of Pb from atmospheric deposition or anthropogenic sources Pb enriched in sediment. In this context, anthropogenic enrichment of Pb distributes natural life primary by human activities. Lead isotopes as ratios $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ are commonly used in environmental sciences. $^{206}Pb/^{207}Pb$ is calculated precisely and present abundantly, that's way, it got more significance and scientist attractiveness among them (Komárek et al., 2008).

The Pb isotopic ratios of the sandstones ranged from 18.619 to 19.350, 19.067 to 20.277 and 18.979 to 10.952 for $^{204}Pb/^{206}Pb$, 1.182 to 1.221, 1.167 to 1.237 and 1.191 to 1.231 for $^{206}Pb/^{207}Pb$, 2.069 to 2.099, and 2.062 to 2.076 and 2.042 to 2.080 for $^{208}Pb/^{206}Pb$ in the Trabzon, Giresun and Gümüşhane areas, respectively (Table 5). A plot of the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ compositions indicated that most of the sandstone samples were located in the natural Pb area and three samples in the U.S. gasoline and coal from Central European areas (Fig.8a). In the same way, the bulk Pb content stated as 1/Pb normalized values and the $^{206}Pb/^{207}Pb$ ratios (Lermi and Sunkari, 2020) showed that no Pb pollution of the samples and that present Pb originated from aerosol, gasoline and geogenic sources (Fig. 8b).

Multivariate statistical analyses

Factor analysis (FA) and Pearson's correlation matrix (PCM) using principial component analysis (PCA) were applied in this study. Pearson correlation analysis results were given in the Table 6. In the Trabzon area, the concentrations of Al were negatively correlated with that of the other heavy metal(loid)s at the $p<0.05$ level and with TOC at the $p<0.01$ level. TOC was positively correlated with Zn, Pb, Cu, Ni, Co at the $p<0.05$ level, indicating that the distribution of these elements is controlled by organic matter, Mz was positively correlated with Zn, Ni, Co, Mo and V at the $p<0.05$, exhibiting that distribution of the elements is controlled by grain size. In the Giresun area, Al was positively associated with Zn, Ni at the $p<0.01$ and Cu at the $p<0.05$ level and negatively associated with TOC at the $p<0.05$ and Mz, showing that the distribution of these heavy metals is mainly controlled by clay minerals. TOC and Mz were negatively correlated with Zn, Cu ($p<0.05$), Ni ($Ni<0.05$) and Mo, and Mz exhibited a positive correlated with TOC at the $p<0.05$ level. In the Gümüşhane area, the concentrations of Al showed a positive correlation with Zn at the $p<0.05$ level, but there were no correlations with that of the other heavy metal(loid)s. The concentrations of Ni were a significantly positive correlated with Co, Mo and V at the $p<0.01$ level, and Co exhibited a positive corelated with Mo and V at the $p<0.01$ level. Thus, the concentrations of TOC and Mz were not correlated with that of the other heavy metal(loid)s (Table 6).

The results of PCA by application varimax rotation for heavy metal(loid)s and their component plots in rotated space was exhibited in the Table 7. The first three PCA defined 92.71%, 80.58% and 74.40% of the data's variances in the Trabzon, Giresun and Gümüşhane areas, respectively. The PC1, PC2 and PC3 primary included Zn, Cu, Ni, Co, V, Mz, and Pb, TOC, and Mo, As, respectively in the Trabzon area (49,69%, 28.17% and 14.85% of the total variance, respectively), Al, Cu, Pb, Ni, and Zn, As, Co, and V, respectively in the Giresun area (46.24%, 19.71% and 14.62% of the total variance, respectively), and Ni, Co, Mo, V, and Al, Zn, and Cu, respectively in the Gümüşhane area (37.66%, 22.16% and 14.58% of the total variance, respectively) (Table 7, Figs. 9a, b, c).

Discussion

Source identification

It is known that heavy metal(loid)s originated from both anthropogenic and natural sources. In accordance with, the EF, I*geo*, Pi and Pl_n values and multivariate statistical analyses, the results suggested two main sources of these metals/metalloid: (1) all the heavy metal(loid)s (except As) in the Trabzon area, Zn, Pb, Cu, Co and Mo in the Giresun area, Zn, Pb, Cu and Mo in the Gümüşhane area mainly originated from natural sources, as their EF, I*geo*, Pi and Pl_n values were lower than threshold values; (2) According to the EF, I*geo*, Pi and Pl_n values; the sandstones samples in the Trabzon area were partially polluted by As, in the Giresun area were significantly polluted by Ni, partially polluted by As and V, and in the Gümüşhane area were significantly polluted by Ni and As, partially polluted by V and Co. However, the concentrations of the Ni were significantly correlated with that of the Al, Zn, Cu in the Giresun, and Co, Mo, V in the Gümüşhane area. On account of this, Ni, V and Co were probably originated from natural sources. With respect to Sc/Th vs Co/Th diagram, which is commonly used to separate between the felsic and the mafic sources of the sandstones (Das et al., 2008; Singh, 2010; Peng et al., 2011; Fang et al., 2021), the sandstones samples were mainly plotted in the mafic field (Fig. 10). In this context, Co, V and Ni enrichment may have occurred due to mafic source rocks. (3) The concentrations of As were a positive correlated with Pb and Mo in the Giresun area, and with Pb in the Gümüşhane area, likely indicating that anthropogenic sources, such as coal and gasoline combustion.

When $^{206}Pb/^{207}Pb$ ratio is plotted relative to $^{208}Pb/^{206}Pb$ ratio, it can show general trend that can be used to describe Pb pollution sources (Monna et al., 2000; Potra et al., 2017). In such diagrams, if the data constitutes several groups, multiple Pb sources can be extract and linear inclinations mean mixed Pb sources. However, if the data constitutes a group, only one source of Pb can be invited (Hurst et al., 1996). According to $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ diagram, majority of the samples were located in the natural source field, and one sample each from the Trabzon Giresun and Gümüşhane areas located in the fields of U.S. gasoline (Teutsch et al., 2001) and Central Europe coal (Novak et al. 2003), and one sample each from the Trabzon and Giresun areas located away from the identified Pb sources (Fig. 8a) and these probably originated from other rare sources. The diagram of the 1/Pb normalized values and $^{206}Pb/^{207}Pb$ ratios also confirmed the above (Fig. 8b). In this diagram, all the samples were clustered in geogenic + aerosol + gasoline originated lead field. Additionally, the concentrations of Pb were a positive correlated with As in the Gümüşhane and Giresun areas, indicating that the source of As could be coal burning and gasoline combustion. The study area (Dağbaşı) in Trabzon region is sparsely populated and intensive farming activity. On account of this, besides burning coal unconscious use of fertilizers, insecticide and weed killers during farming activities may have also caused partially As enrichment in this sandstones. The studied areas (Çamlıyayla and Evliyatepesi) in Giresun and (Musalla, Pirahmet and Mescitli) in Gümüşhane were where the human population more intense than Dağbaşı (Trabzon), so the source of As could be burning coal and gasoline combustion. The enrichment of As in these areas was primary about atmospheric deposition of burning coal and gasoline combustion. The As in the atmosphere, likely amalgamated studied sediments with rainwater, and this element was filtered through porous sandstones and gathered in places.

Characteristics of depositional environment of the heavy metal(loid)s

Paleoclimate conditions

The concentrations of some trace and major elements in the sedimentary rocks indicate the paleoclimates changes (Hu et al., 2017). For instance, Ni, Mn, Fe, Cr and V are relatively enriched under moist climate conditions, whereas Mg, Sr, K, Ba, Na and Ca are enriched under arid climate conditions (Cao et al., 2012). C-value as proxy for climatic prosses has been applied in previous studies (C-value = Σ(Fe+Mn+Cr+Ni+V+Co)/ Σ(Ca+Mg+Na+K+Sr+Ba)) (Zhao et al., 2007; Fu et al., 2016; Wang et al., 2017; Vd'ačný et al., 2019; Bal Akkoca et al., 2019; Saydam Eker, 2020b). The C-values for the Trabzon area range from 0.03 and 0.11 (on mean 0.06), for the Giresun area range from 0.34 and 0.61 (on mean 0.50), for Gümüşhane area range from 0.09 and 1.24 (on mean 0.46) (Table 1). The C-values indicated arid paleoclimate conditions for the Trabzon area, semiarid to semimoist paleoclimate conditions for the Giresun area and arid to moist paleoclimate conditions for the Gümüşhane area (Fig. 11). The highest concentrations of heavy metal(loid)s were measured in the Gümüşhane area, followed by Giresun and Trabzon areas (Fig. 11). It is meant that the heavy metal(loid)s deposited more in humid climatic conditions than arid climatic conditions.

Paleo-redox conditions

The content and ratio of some redox-sensitive trace elements (e.g. Ni, Th, Mo, V, Co, U and V/(V+Ni), Ni/Co, Th/U) can determine redox conditions of clastic rocks (Yarincik et al., 2000; Lewan and Maynard, 1982; Jones and Manning, 1994; Algae and Maynard, 2004). In sediments, U is depleted under oxidizing conditions and enriched under reducing conditions, while Th is not influenced by redox conditions (Kimura and Watanabe, 2001). U/Th ratio is lower than 0.75, pointing out an oxidation environment, U/Th ratios are between 0.75 and 1.25, reflecting a weak oxidation environment, and a ratio > 1.25 points to a reducing environment (Jones and Manning, 1994) (Table 8). The U/Th ratios ranged from 0.47 to 0.86 (on mean 0.67) in the samples of Trabzon area, pointing out an oxidation – weak oxidation environment, 0.23 – 0.36 (on mean 0.29) in the samples of Giresun area, pointing out an oxidation environment and 0.24 – 0.83 (on mean 0.33) (Table 1) in the samples of Gümüşhane area, pointing out an oxidation – weak oxidation environment (Table 8). It is known that V is a redox-sensitive chemical element with a trend to be lesser concentrated in sediments principial oxic water (Lewan and Maynard, 1982). Thus, Mo content, Ni/Co and V/(V+Ni) ratios were used as paleo-redox proxies for defining the redox conditions (Vd'ačný et al., 2019). Wang et al. (2017) suggested that Ni/Co ratios < 5 reflect an oxidation environment, range from 5 to 7, pointing out a weak oxidation environment, and > 7 reflect a reducing environment. V/(V+Ni) ratio <0.6 exhibits an oxidation environment, 0.64 – 0.84 indicates a weak oxidation environment, and > 0.84 implies reducing environment (Feng et al., 2017) (Table 8). V/(V+Ni) and Ni/Co ratios of the analyzed samples varied from 0.4 to 0.72 (on mean 0.54) and 2.71 to 5.22 (on mean 3.36), respectively for Trabzon, and 0.49 to 0.56 (on mean 0.52) and 4.83 to 6.67 (on mean5.53), respectively for Giresun, and 0.48 to 0.70 (on mean 0.58) and 2.07 to 6.30 (on mean 4.66) (Table 1), respectively for Gümüşhane area, indicating that samples for each areas also were deposited under oxidation – weak oxidation conditions (Table 8). The bivariate plots of Ni/Co vs Mo and Ni/Co vs V(V+Ni) (Fig. 12a, b) confirmed oxic and weak oxic conditions during deposition for the analyzed samples.

Paleo-salinity

Paleo-salinity is a significant cursor of the depositional environment because the salinity of ancient water is determined by paleo-salinity degree. The ratio and concept of some elements such as Sr/Ba and Log^m ($Log(100x(MgO/Al_2O_3))$) (Jones and Manning, 1994) can define the marine and continental facies of depositional environment and paleo-salinity (Li et al., 2020). Log^m value and Sr/Ba ratio decrease from marine to continental facies. The Log^m value <0 indicates nonmarine facies, while 0-1 represents transition facies, and >1 shows marine facies (Jones and Manning, 1994). Wang et al. (2017) suggested that the Sr/Ba < 0.6 represents nonmarine facies, 0.6 – 1.0 indicates transition facies, and >1.0 represents marine facies (Table 8). The Sr/Ba ratios varied from 0.94 to 10.3 (0n mean 4.9) in the Trabzon area, 0.88 to 1.72 (on mean 1.43) in the Giresun area, and 0.26 and 2.11 (on mean 1.20) (Table 1) in the Gümüşhane area, implying that all three of the study areas were transition – marine facies with brackish – saline water (Table 8). The Log^m values in the Trabzon and Giresun areas ranged from 1.24 to 1.77 (on mean 1.52) and 1.49 to 1.60 (on mean 1.55), respectively, indicating marine facies with saline water for both areas, and in the Gümüşhane area ranged from 0.81 to 1.61 (on mean 1.42) (Table 8), implying transition – marine facies with brackish – saline water (Table 8) for this area.

Conclusions

In this paper, the concentrations of heavy metal(loid)s (Zn, Pb, Cu, Ni, As, Co, Mo and V), mean grain size (Mz) and TOC were analyzed in the Late Cretaceous aged sandstones collected from Trabzon, Giresun and Gümüşhane areas (Eastern Pontides).

The mean concentrations of the heavy metal(loid) followed in the descending order of V>Zn>Ni>Pb>Cu>Co>As>Mo in the Trabzon area, V>Zn>Ni>Cu>Co>Pb>As>Mo in the Giresun area, V>Zn>Ni> Cu>Co>Pb>As>Mo in the Gümüşhane area. According to mean EF values, all heavy metal(loid)s were not enriched in the sandstone samples for Trabzon area, Ni was enriched in the samples for Giresun area and As and Ni for Gümüşhane area. According to *Igeo* values, the sandstones was unpolluted – moderately polluted by As in the studied three sites. Pl_n values indicated that investigated sandstones were low polluted by As and Cu for Trabzon area, low polluted by Cu and Co, moderately polluted by As, and strongly polluted by Ni for Giresun area, and low polluted by Zn, Pb and Cu, moderately polluted by Co and V, strongly polluted by Ni and As for Gümüşhane area.

The results of multivariate statistical analyses in the samples indicated that the accumulation of Zn, Cu, Ni, Co, V, Mo and mostly Pb was derived from geogenic sources, whereas As and partly Pb (for Gümüşhane and Giresun) might be derived from anthropogenic sources (atmospheric deposit for Giresun and Gümüşhane, agriculture for Trabzon). Pb isotopic tracing supported multivariate analysis results. Lead isotopic analysis indicated that two signatures related to the sources of heavy metal(loid); first signature indicated that natural Pb was the main sources and second signature showed that anthropogenic Pb was the minor sources including atmospheric deposits (coal burning, gasoline combustion and aerosol) and may be agriculture activities.

Paleoclimate index showed arid climatic conditions for Trabzon area, semiarid to semimoist climatic conditions for Giresun area and arid to moist climatic conditions for Gümüşhane area during deposition of the studied

sandstones. These sandstones were deposited oxic – weak oxic water column and in the transition – marine environment. According to the data obtained in this study, heavy metal(loid)s accumulated more in moist climatic conditions than arid climatic conditions.

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FIGURE CAPTIONS

Fig. 1 Simplified geological map of the eastern Black Sea Region (simplified from Güven et al. 1993) and location map of the study area, 1- Paleozoic metamorphic basement, 2- Paleozoic granites, 3- Jurassic–Lower Cretaceous sequences 4- Upper Cretaceous sedimentary rocks, 5- Upper Cretaceous volcanic rocks, 6- Paleocene volcano-sedimentary sequences, 6- Paleocene granites, 7- Eocene volcanic, volcano-clastic rocks, sedimentary sequences, 9- thrust fault, 10. (1 Dağbaşı section (Trabzon), 2 and 3 Çamlıyayla and Evliyatepesi sections (Giresun), 4,5 and 6 Musalla, Pirahmet and Mescitli sections (Gümüşhane)

Fig. 2 Stratigraphic sections of late Cretaceous sequences (modified from Saydam Eker and Korkmaz 2011)

Fig. 3 Box and whisker plots of heavy metal(loid) contents fort he studied sandstones

Fig. 4 Vertical change of heavy metal(loid)s in the sandstone samples, data are average values normalized to UCC (Taylor & McLennan, 1985)

Fig. 5 Distribution of EF for heavy metal(loid)s of the sandstone samples

Fig. 6 Distribution of *Igeo* for heavy metal(loid)s of the sandstone samples

Fig.7. Distribution of Pi and PIn for heavy metal(loid)s of the sandstone samples.

Fig. 8. a) Plot of $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ in the sandstones and potential source materials, b) 1/Pb normalized values vs. $^{206}Pb/^{207}Pb$ ratios indicating the sources and levels of pollution of the sandstones.

Fig. 9. Plots of the principial components (PC1, PC2, PC3) showing four groups of physicochemical parameters and heavy metal(loid)s in the sandstones.

Fig. 10. Plot of Sc/Th vs. Co/Th of the sandstone samples.

Fig.11. The C-value of the sandstone samples reflecting the paleoclimate. The distinguishing criteria are after Zhao et al. (2007) and Cao et al. (2012).

Fig.12. Plots of various trace element parameters used as paleo-redox proixes for the sandstone samples. Boundaries for different redox environments are from Jones and Manning (1994) and Xu et al. (2012).

Figures

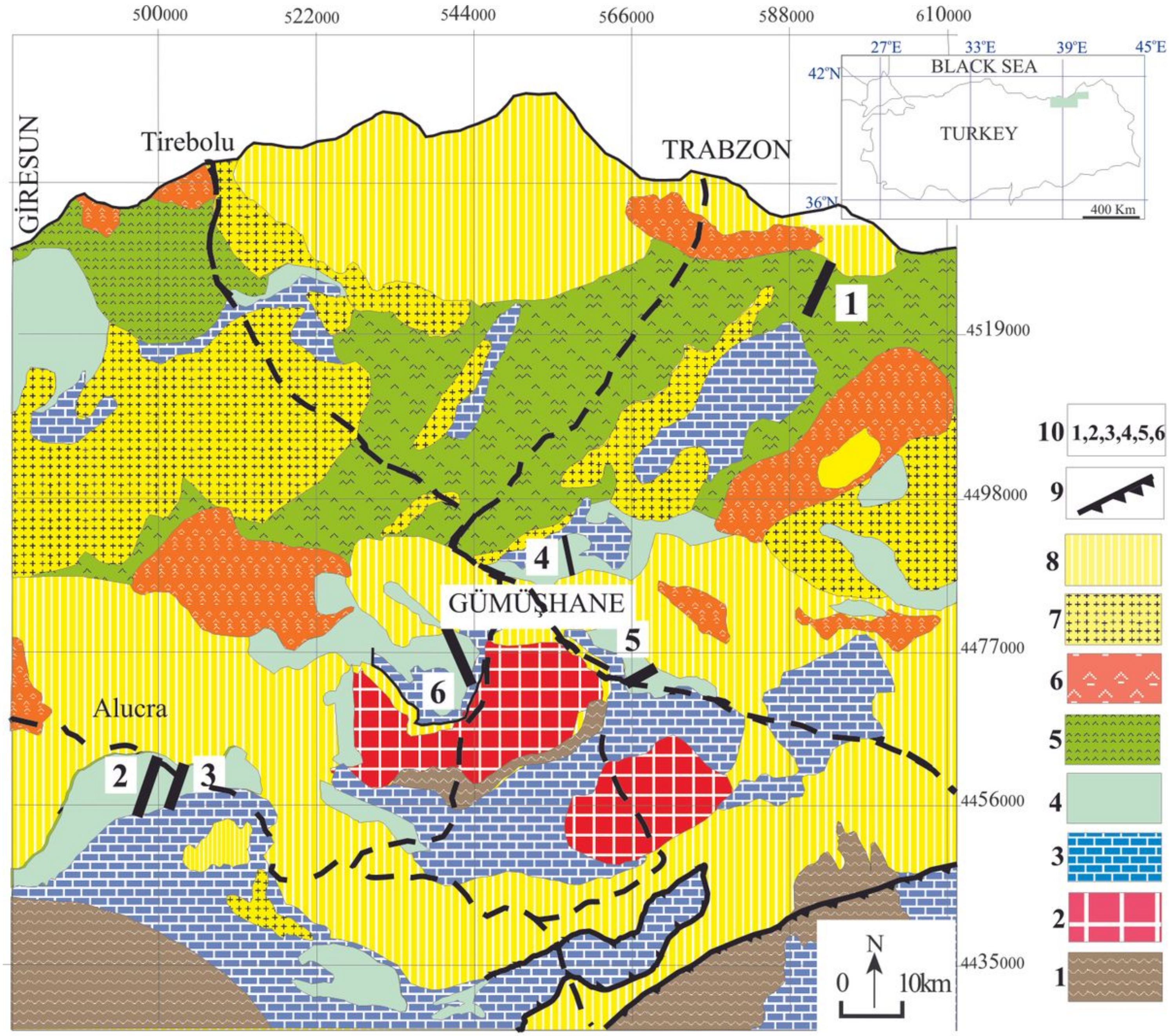

Fig.1

Figure 1

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The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

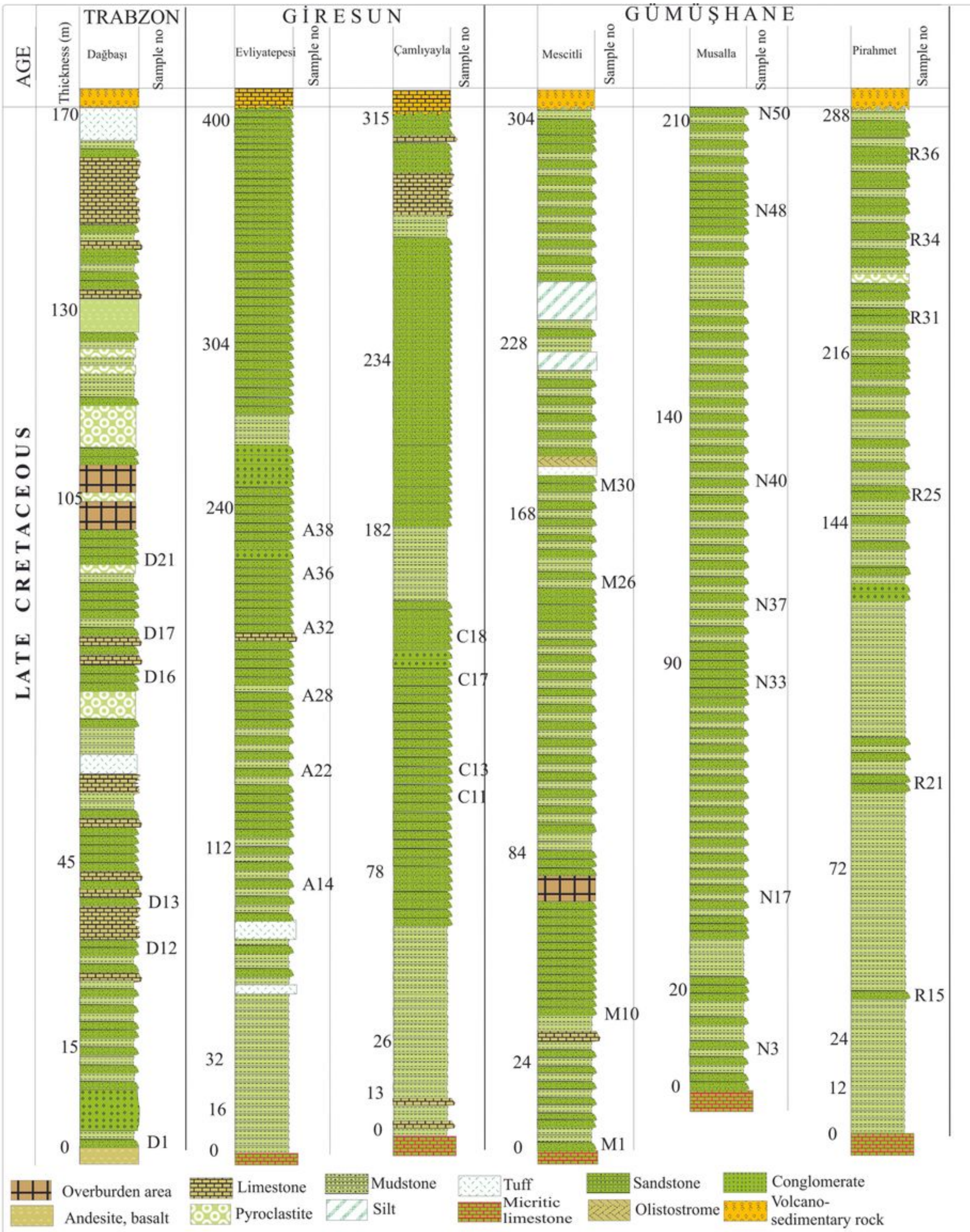

Fig. 2

Figure 2

Stratigraphic sections of late Cretaceous sequences (modified from Saydam Eker and Korkmaz 2011)

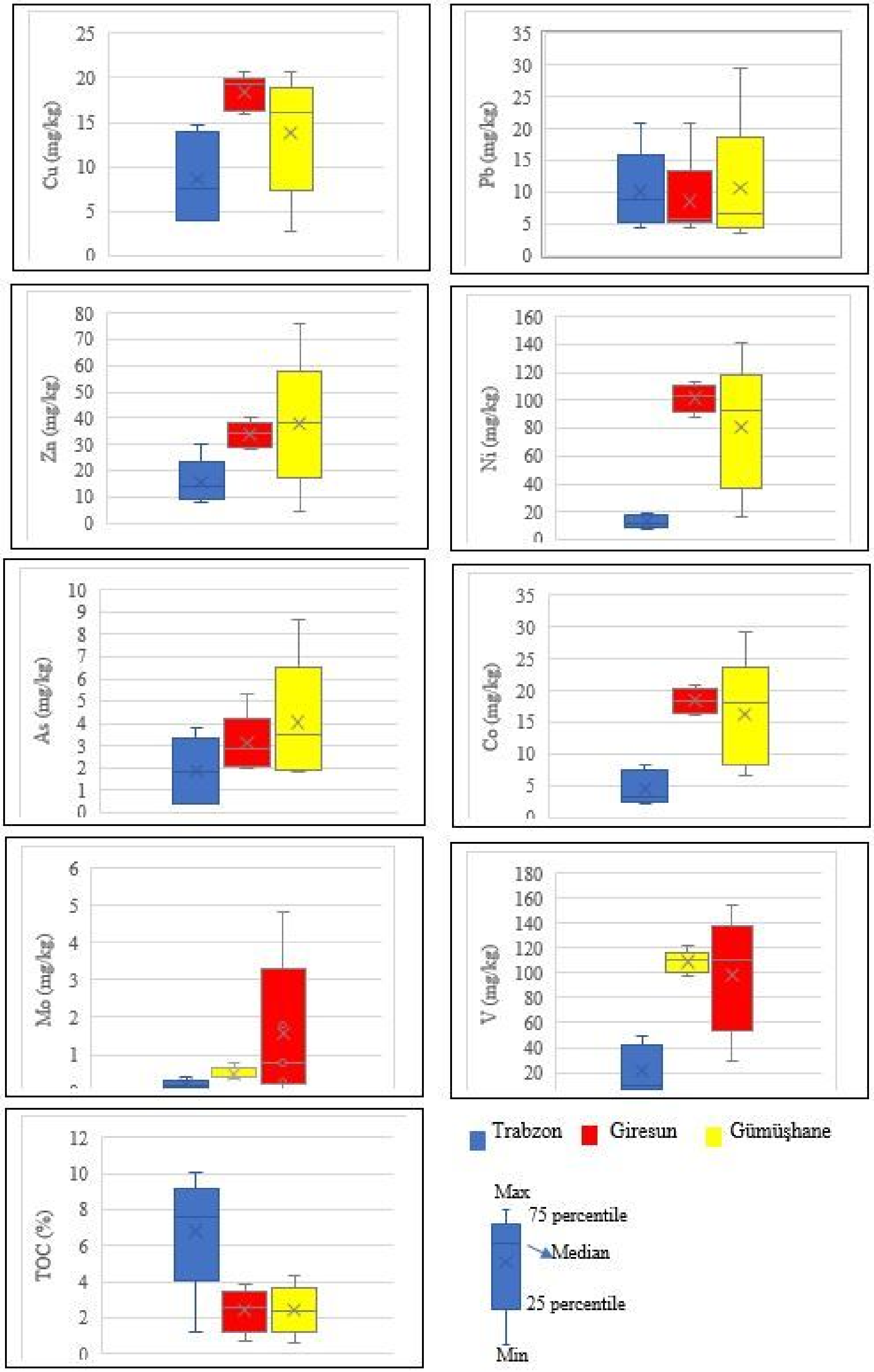

Figure 3

Box and whisker plots of heavy metal(loid) contents fort he studied sandstones

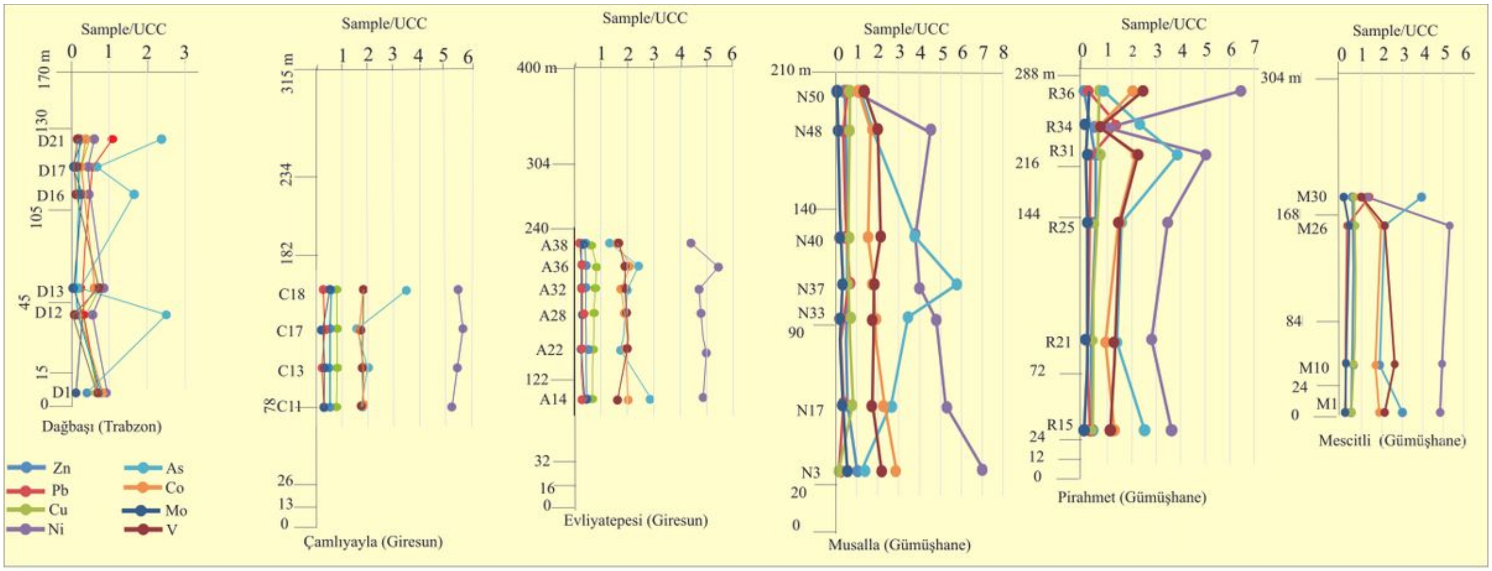

Fig.4

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Figure 4

Vertical change of heavy metal(loid)s in the sandstone samples, data are average values normalized to UCC (Taylor & McLennan, 1985)

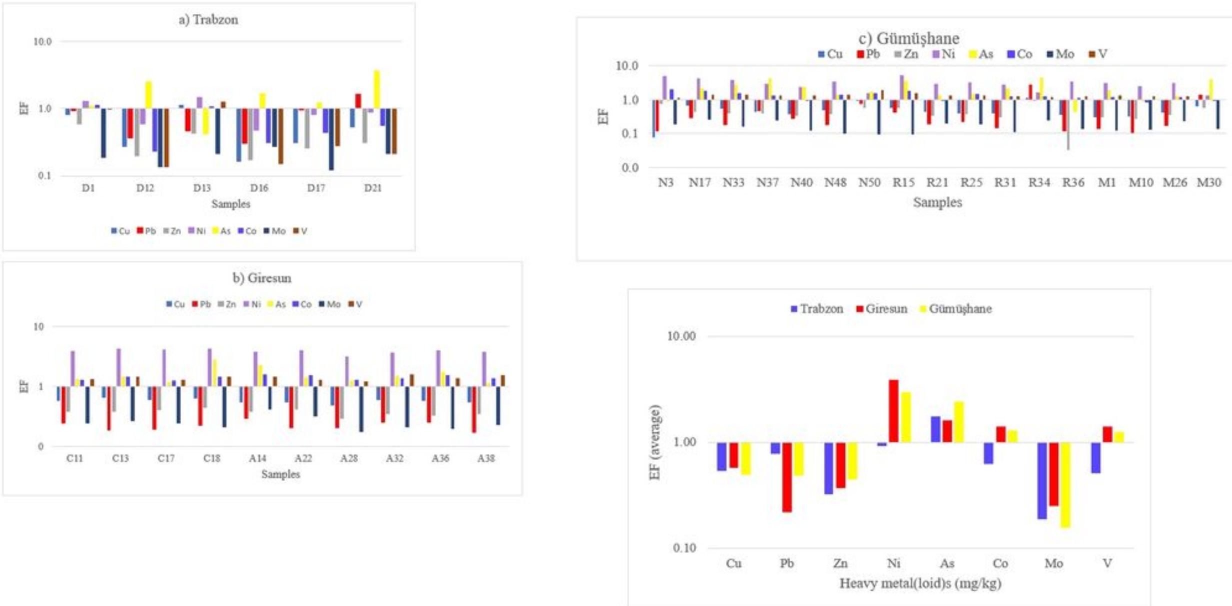

Figure 5

Distribution of EF for heavy metal(loid)s of the sandstone samples

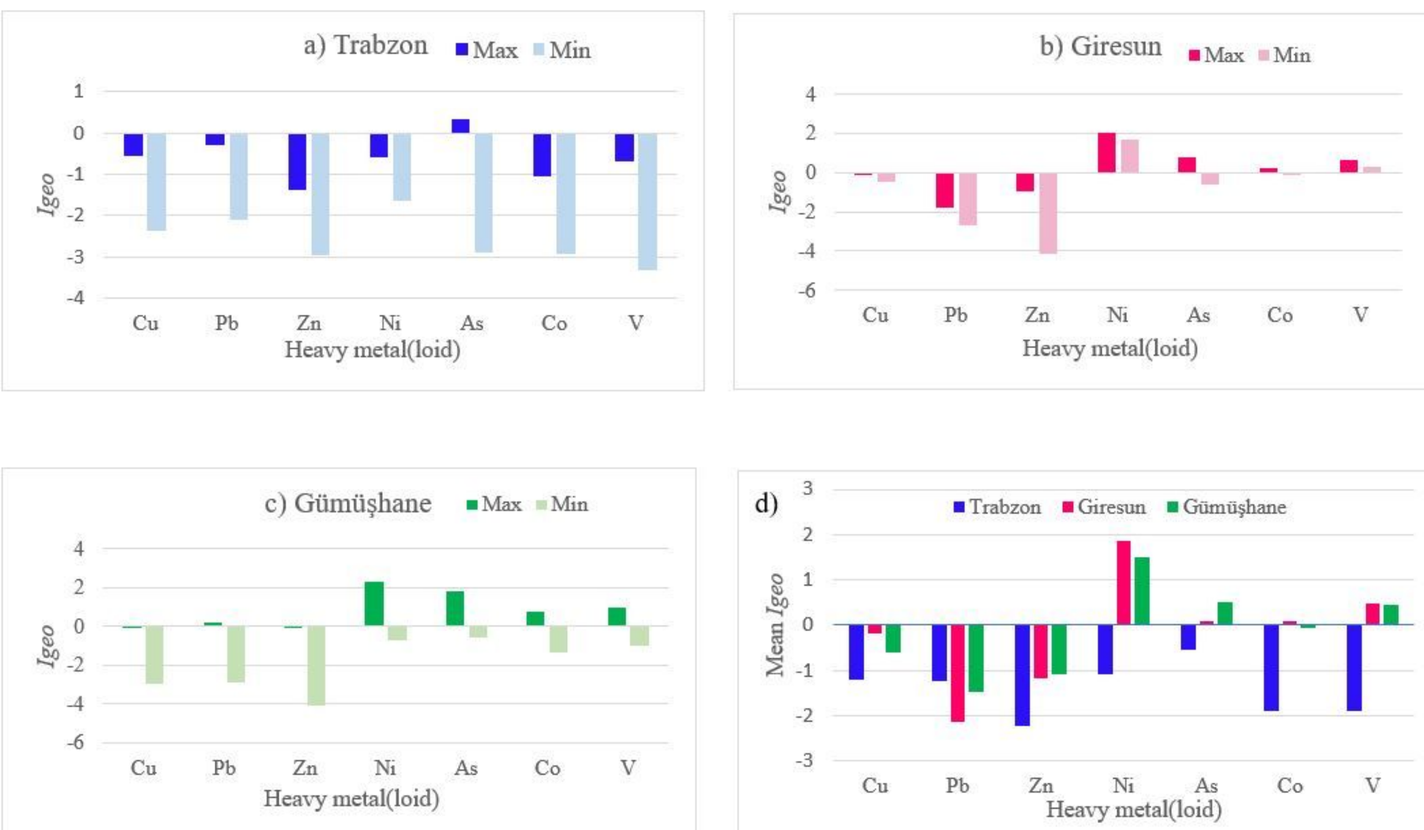

Figure 6

Distribution of Igeo for heavy metal(loid)s of the sandstone samples

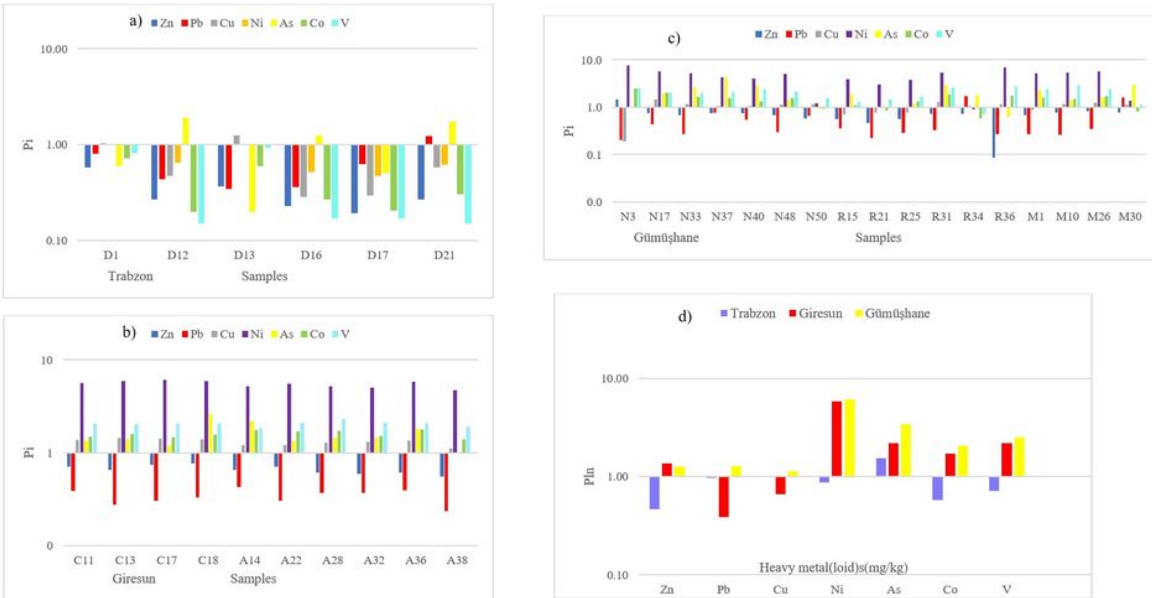

Figure 7

Distribution of Pi and PIn for heavy metal(loid)s of the sandstone samples.

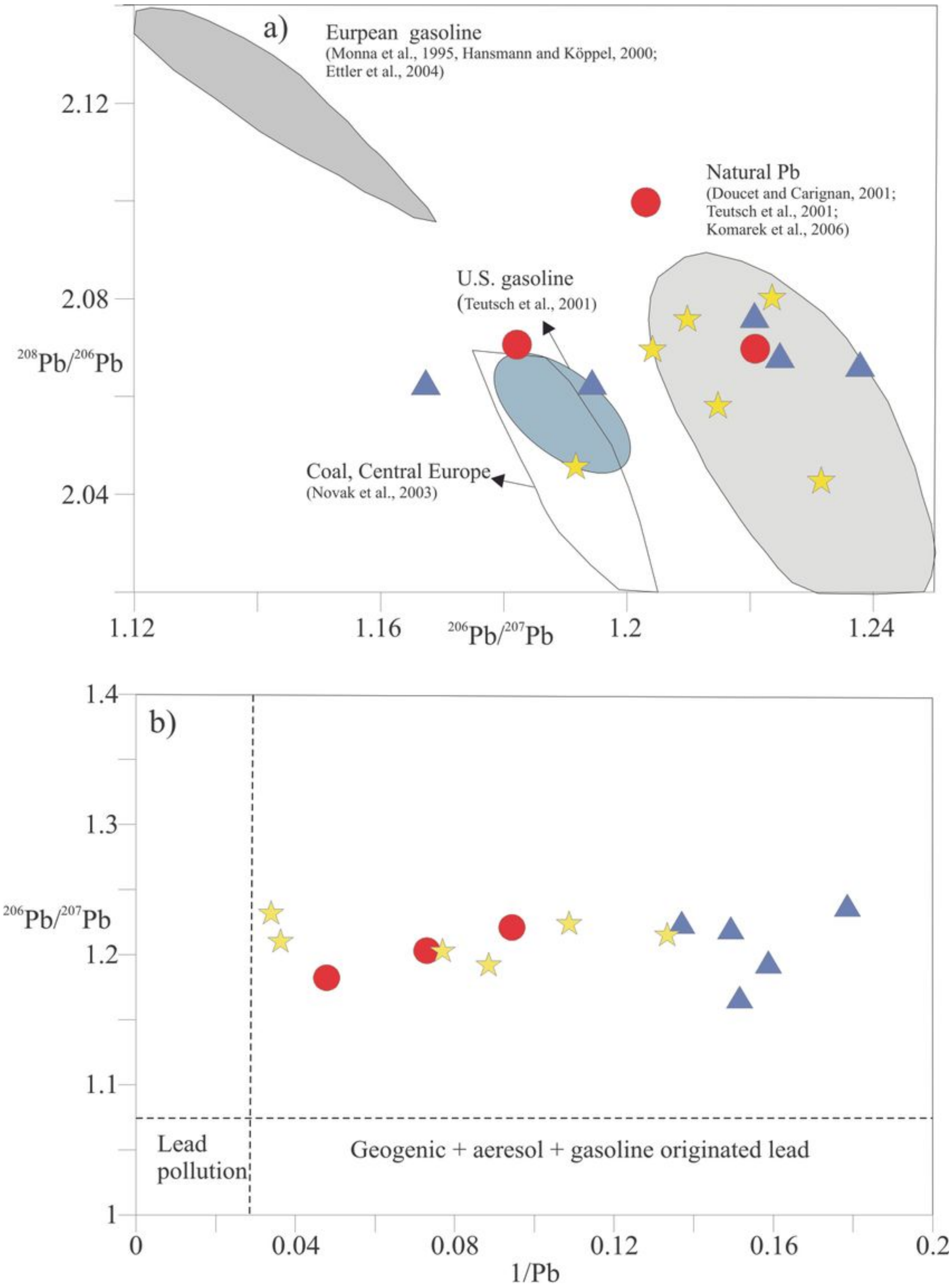

Fig. 8

Figure 8

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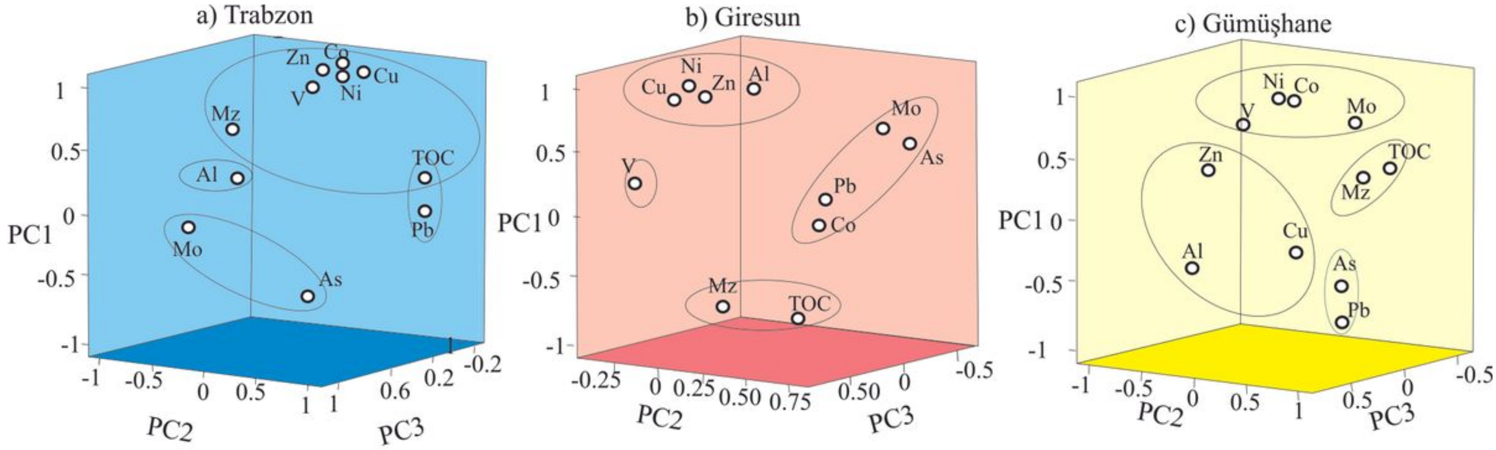

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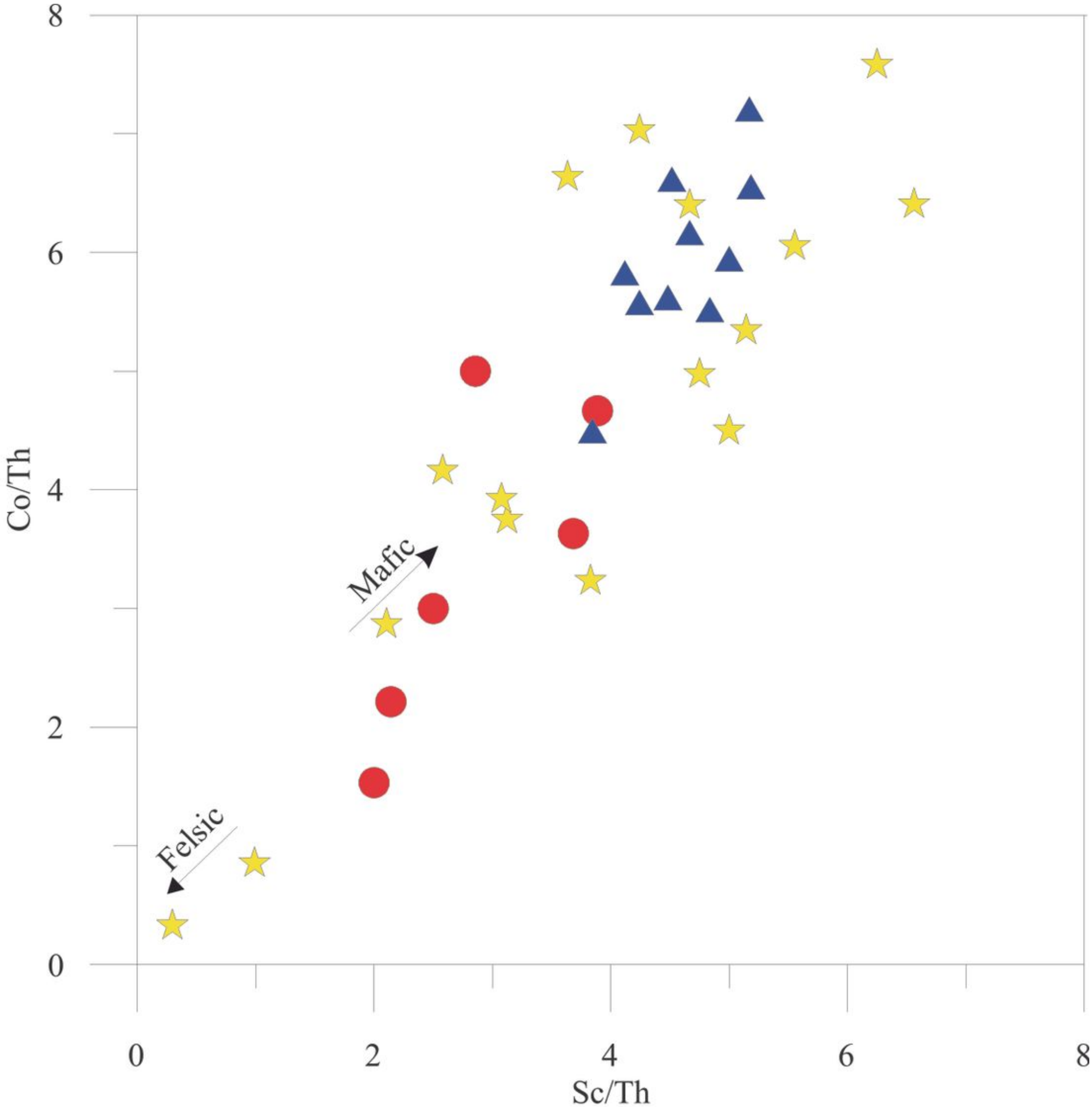

Fig. 10

Figure 10

Plot of Sc/Th vs. Co/Th of the sandstone samples.

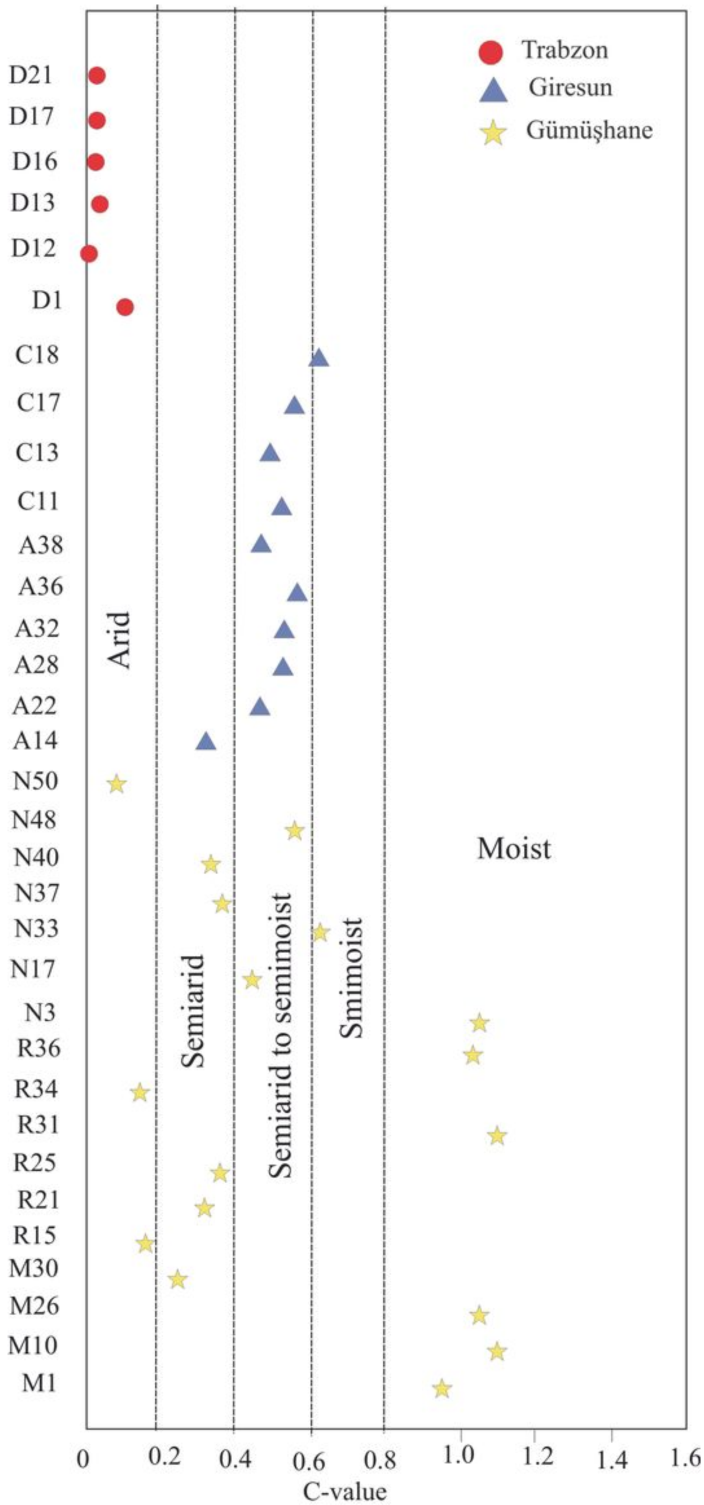

Fig. 11

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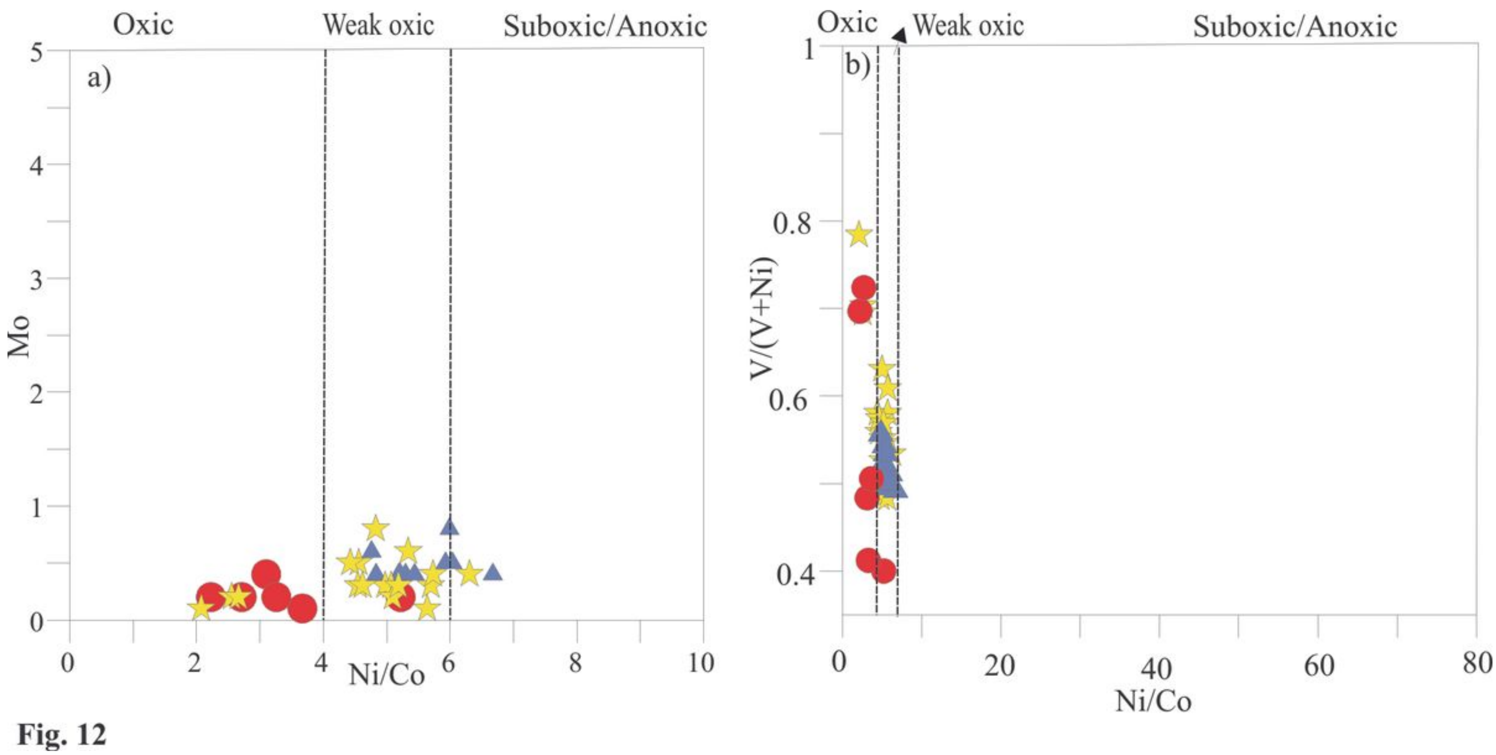
The C-value of the sandstone samples reflecting the paleoclimate. The distinguishing criteria are after Zhao et al. (2007) and Cao et al. (2012).



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Plots of various trace element parameters used as paleo-redox proixes for the sandstone samples. Boundaries for different redox environments are from Jones and Manning (1994) and Xu et al. (2012).