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Biogeochemical interrelations between the Çayırhan oil shales and some plants growing on them (Turkey)

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Abstract: Oil shales are exposed in wide areas around the town of Çayırhan (Beypazarı-Ankara). It is known that some elements are enriched in oil shales and similar organic-material rich rocks. The purpose of this study was to understand the possible relations between the element abundances found at the Çayırhan oil shales (ÇOS) and those of some plant types growing on these rocks. The results of chemical analysis of selected plants (8 species) were compared with each other and with element abundances from the ÇOS. The plant types examined were divided into 2 groups with respect to enrichment factors. The first group contained 6 plant species: *Eryngium campestre* L. var. *virens* Link, *Echinophora tournefortii* Jaub. & Spach, *Sideritis gulendamiae* H.Duman & Karavel., *Euphorbia macroclada* Boiss., *Reichardia glauca* V.A.Matthews, and *Centaurea virgata* Lam. In this group of plant types, almost all of the same elements (Na, Si, V, Cr, Rb, Y, Zr, Mo, Sn, Sb, Tl, Bi, Th, and U) were found to be enriched. The second group was represented by *Echinops pungens* Trautv. var. *pungens* and *Reseda lutea* L. var. *lutea*. In these plants, only 6 elements (U, Zr, Si, V, Cr, and As) were enriched. Some elements (e.g., Si, V, Rb, Y, Cr, Zr, Mo, Sb, Bi, and U) were enriched in both groups. Among these 10 elements, Si, Cr, Zr, and U showed enrichment in all plant species. Considering the enrichments of world oil shale averages, all of the major elements and the trace elements of Co, Ni, Cu, As, Rb, Sr, Zr, Mo, Cd, Ba, Pb, and U were found to be enriched in the ÇOS to varying extents. The data indicate that element enrichments in the plants are not related to the enrichments in rocks. Out of several elements enriched in the ÇOS, only 6 of them (Si, V, Cr, Zr, U, and Mo) showed enrichment in all of the studied plants. Although major elements Mg, P, S, K, Ca, Fe, and Mn and trace elements Ni, Cu, Zn, Sr, Ba, and Pb were enriched in the ÇOS, they were not seen to be enriched in any of the plants. The elements Tl, Sb, Rb, and Na, not enriched in world oil shale averages, were determined to be enriched in the first group of plants. Results reveal that, in addition to rock geochemistry, biologic factors are still more dominant behind the observed element accumulations in plants.

Key words: Çayırhan oil shales, major element contents, trace element contents, biogeochemistry, plants

Introduction

In the area examined in the present study, a lignite-based power plant has been established. The deposits of the Çayırhan oil shales (ÇOS) have been the subject of intense study in the fields of organic geochemistry (Özçelik, 2002; Kara Gülbay & Korkmaz, 2005; Yavuz et al., 2009a, 2009b), inorganic geochemistry (Yavuz et al., 2009a, 2009b, 2010b, 2010c), and plant geochemistry (Ergin et al., 2009; Yavuz et al., 2010a, 2010c) over the last decade. The association of oil

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shales and similar organic material-rich rocks with some trace elements (particularly U, P, S, Mo, V, Cu, Zn, Ni, Cr, Co, Pb, Au, Ag, As, Re, La, Ce, Pr, Nd, Sm, and Y) has been studied by Levanthal and Hosterman (1982), Ruskeeniemi (1991), Mossman et al. (1993a, 1993b), Alberdi-Genolet and Tocco (1999), Mossman (1999), Nameroff et al. (2001), Schatzel and Stewart (2002), Paradis (2004), and Lipinski et al. (2003). As the organic carbon content of these rocks increases, their inorganic element concentrations also increase. Considering that the element potential of the ÇOS may result in geologic and environmental contamination, in this study we carried out a new type of investigation which focuses on a possible biogeochemical relation between element abundances of the ÇOS deposits and some plants growing on the ÇOS. Plant geochemistry is very effective and has been investigated for a variety of purposes. For the last 40 years, for example, the environmental impacts of plants have been the subject of notable studies (Epstein, 1972; Hewitt & Smith, 1975; Bowen, 1979; Lepp, 1981; Robb & Pierpoint, 1983; Fergusson, 1990; Markert, 1993; Farago, 1994; Marschner, 1995, Bishehkolaei et al., 2011, Gunathilaka et al., 2011). Multidirectional investigations on the element contents of plants include the toxic effects of some elements with an anthropogenic character and their use as a tracer for atmospheric pollution and biomonitoring. The aim of this study was to examine the role of the ÇOS elements rich in organic compounds, to determine very common plant species growing on this rock, and to analyse the major and trace element contents of the plant species. In addition, the element contents and concentrations of the plant species were compared with element concentrations from the ÇOS. Enrichments were specified by comparing element contents with the average values of world oil shales and plants and, accordingly, plants were categorised with respect to their element enrichments. Although the enrichment trends of rocks and plants and their contributing processes are quite difficult to explain, some significant biogeochemical relations were determined and discussed.

Materials and methods

The Çayırhan area, 100 km northwest of Ankara, is noted for its lignite and oil shale deposits (Figure 1). Plant and rock samples collected from the Hırka Formation were the material used in this investigation. Samples were collected in August 2008. Plant samples were taken from a very narrow area. In the study area, 8 different plant species were determined, only 1 of which was a local endemic species. For plant identifications and descriptions, *Flora of Turkey* (Davis, 1965-1985; Güner et al., 2000) was utilised.

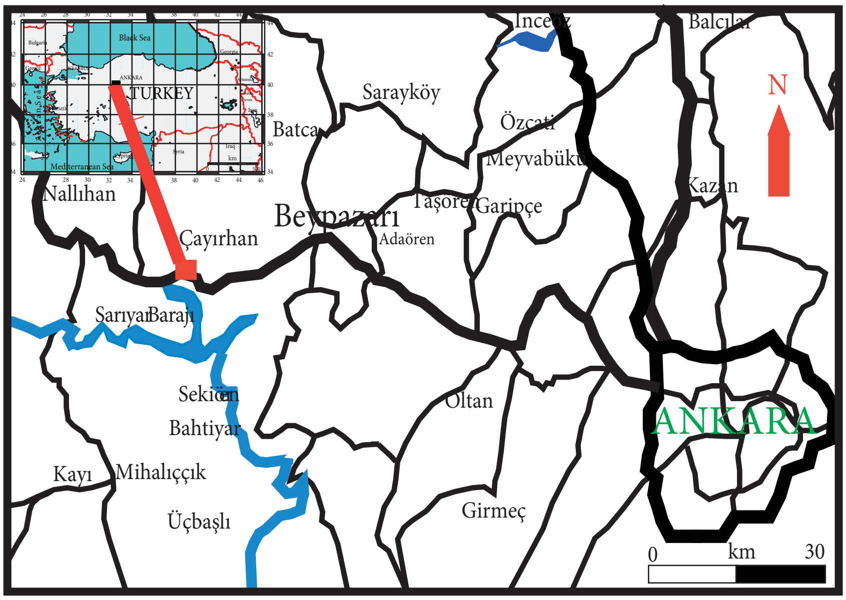

Figure 1. Location of the study area.

Rock samples were powdered while plant samples were washed in deionised water, dried, and then powdered for analysis. Trace element analysis of rock and plant samples was conducted at the Geochemistry Laboratories of Ankara University with an XLAB 2000 polarised energy dispersive x-ray fluorescence device (PEDXRF) and at ACME Laboratories in Canada using the inductively coupled plasma mass spectrometry (ICP-MS) method. The computed averages and enrichment factors of elements of the rock samples are displayed in the relevant tables and figures. Enrichments for rock and plant samples were calculated with respect to average shale (Turekian & Wedepohl, 1961; Wedepohl, 1971) and world plant average values (Reimann et al., 2001), respectively.

Geologic setting and stratigraphy

The Paleocene Kızılbayır Formation is the oldest unit in the study area. It is unconformably overlain by middle Miocene sedimentary units which consist of, from bottom to top: the Boyalı, Hırka, Karadoruk, and Sarıağıl formations. These units are cut by Teke volcanites. The Pliocene Softa Formation and alluvium cover all of these units (Figures 2 and 3).

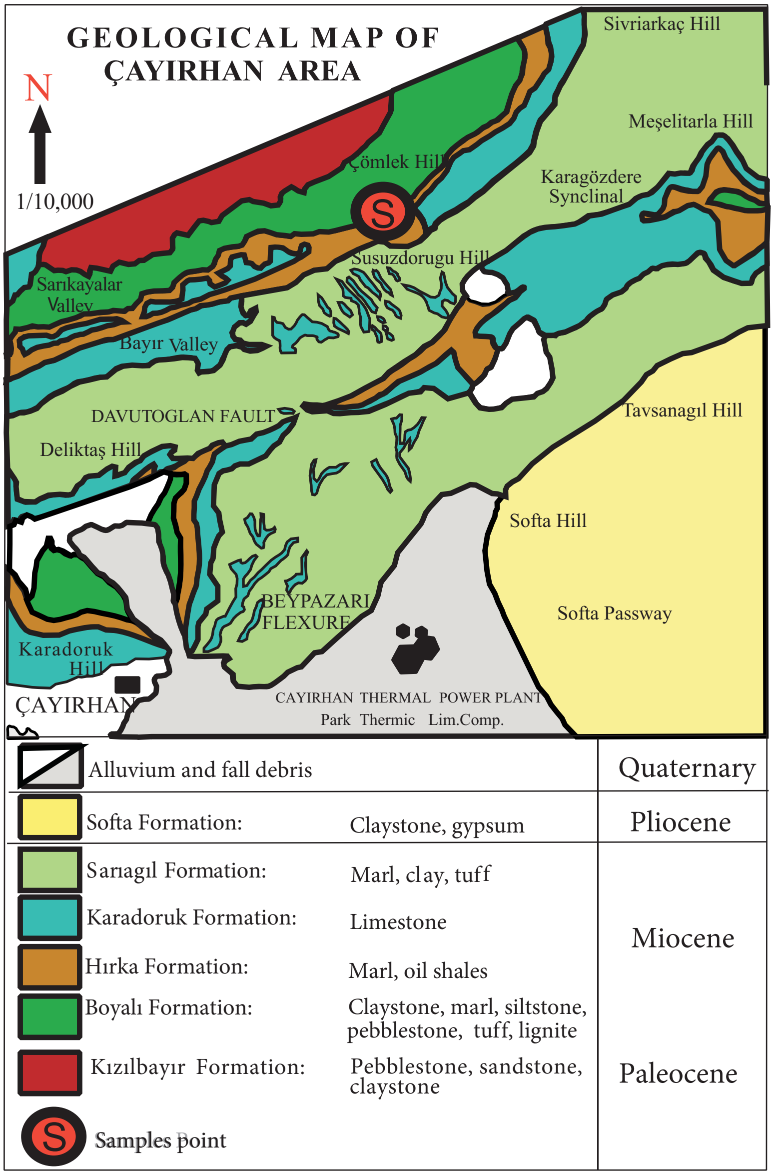

Figure 2. Geological map of the study area.

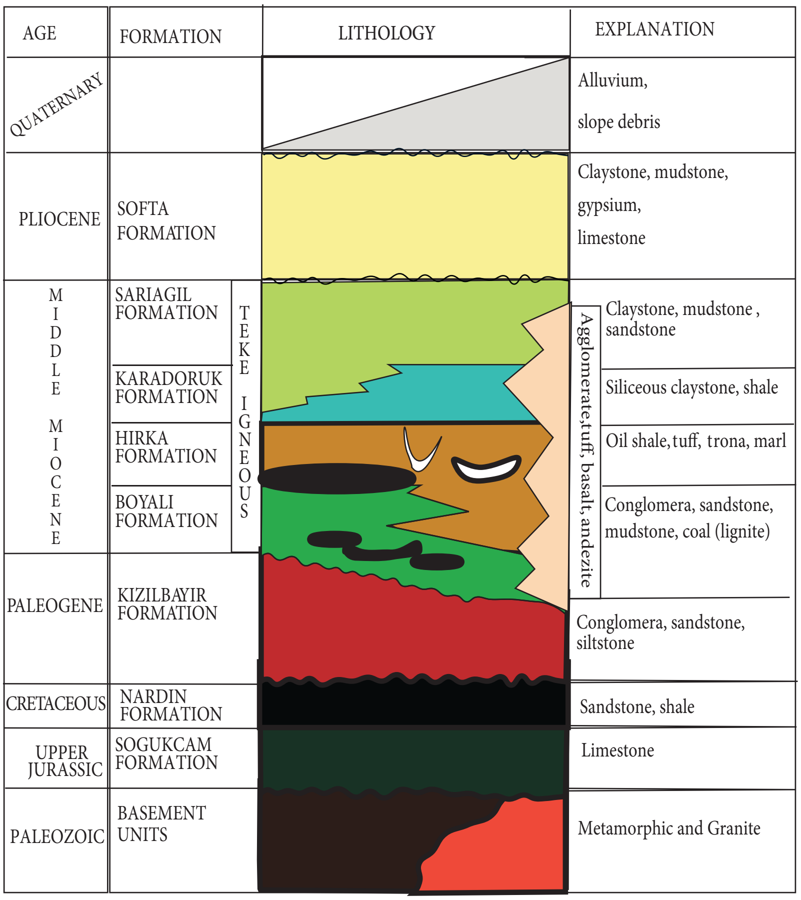

Figure 3. The stratigraphy of the study area.

The ÇOS under investigation were formed within the Hırka Formation, which conformably overlies the Boyalı Formation with lateral and vertical transitions. A typical section of the formation is around the village of Hırka, where laminated sandstone, claystone, oil shale, carbonaceous shale, dolomitic limestone, tuff, trona, and local intraformational breccia occur. The oil shales of the Hırka Formation are in colours changing from grey to light-dark brown and are very thin-bedded. Oil shales of 8-22 m in thickness are interlayered with dolomitic limestone and tuffs. This unit contains leaf fossils, trunk pieces, and gastropod and ostracode fossil fragments.

Results

Element concentrations of plants and rocks

The ÇOS within the Hırka Formation are of middle Miocene age and have a thickness of 8-22 m. The total organic carbon (TOC) values of these rocks are between 3.43% and 18.12%. It is known that the organic material content of rocks is positively correlated with inorganic element content. This is also supported by the element contents of these rocks, which were enriched in TOC (3.43%-18.12%). A total of 13 major elements (V, Mn, Cr, Ti, Fe, Na, P, S, Mg, Ca, Al, K, Si) and 29 trace elements (Se, Bi, Tl, Hg, Cd, Pb, Ta, Ga, U, Th, Hf, Sn, Y, Co, Mo, Ni, Nb, Cs, W, Cu, As, Sb, Zn, Rb, La, Ba, Zr, Ce, Sr) were analysed from the plant and rock samples using the X-ray fluorescence (XRF) and ICP-MS methods (Table 1). As a result, notable biogeochemical relations were found between the element contents of the ÇOS and the elements accumulated in plants growing on them.

When compared with other formations, the Hırka Formation is striking with regard to its plant population (Figure 4). Therefore, oil shales with high organic-material content and 8 different plant species growing on them were investigated. These species are

Table 1. The main and trace element concentrations of ÇOS (rocks) and plant species from the study area (nd = not determined).

Elements	*Eryngium campestre*	*Echinophora tournefortii*	*Sideritis gulendamiae*	*Euphorbia macroclada*	*Echinops pungens*	*Reseda*	*Reichardia glauca*	*Centaurea virgata*	Çayırhan oil shales	World shale averages (Brumsack, 2006)	World plant averages (Reimann et al., 2001)
Na (%)	0.11	0.03	0.03	0.05	0.20	0.11	0.06	0.05	0.36	1.19	0.00
Mg (%)	0.53	0.17	0.24	0.18	3.20	1.69	0.91	0.58	6.23	1.56	0.14
Al (%)	0.24	0.08	0.10	0.07	1.73	0.90	0.12	0.11	3.37	8.83	0.01
Si (%)	0.61	0.22	0.28	0.17	7.41	3.82	0.67	0.48	14.60	27.09	0.02
P (%)	0.06	0.05	0.09	0.04	0.04	0.04	0.11	0.10	0.04	0.07	0.14
S (%)	0.25	0.07	0.21	0.07	0.53	0.30	0.49	0.35	0.99	0.20	0.13
K (%)	2.91	1.39	1.65	1.74	1.86	1.63	2.13	1.89	2.33	2.99	0.60
Ca (%)	1.16	0.78	2.27	0.86	4.79	2.79	1.80	2.04	8.80	1.57	0.52
Ti (%)	0.00431	0.00073	0.00209	0.00076	0.087122	0.043926	0.006635	0.004363	0.173515	0.467	nd
V (%)	0.000285	0.00024	0.00024	0.00018	0.003163	0.001701	0.000755	0.000498	0.006086	0.013	0.000015
Cr (%)	0.000495	0.00024	0.00039	0.00028	0.004284	0.002262	0.000375	0.000383	0.008328	0.009	0.000019
Mn (%)	0.002245	0.00111	0.00315	0.00146	0.018036	0.009573	0.002645	0.002898	0.034961	0.085	0.0585
Fe (%)	0.03825	0.00581	0.01423	0.00505	1.048657	0.527234	0.0498	0.032015	2.091505	4.823	0.0075
Co (ppm)	2.80	0.60	1.30	1.00	6.26	3.43	2.85	2.08	11.92	19.00	0.17
Ni (ppm)	21.25	2.70	3.80	3.50	45.17	23.93	5.35	4.58	87.63	68.00	1.97
Cu (ppm)	16.95	5.30	11.50	11.60	16.31	10.80	14.65	13.08	27.31	45.00	4.98
Zn (ppm)	41.90	21.20	33.00	27.00	24.70	22.95	57.15	45.08	28.20	95.00	32.00
Ga (ppm)	0.40	0.30	0.40	0.40	3.67	1.99	0.65	0.53	7.05	nd	nd
As (ppm)	0.45	0.20	0.30	0.20	7.21	3.71	0.55	0.43	14.23	10.00	0.04
Se (ppm)	0.30	0.20	0.20	0.20	0.51	0.36	0.25	0.23	0.82	nd	0.49
Rb (ppm)	47.85	33.80	75.30	41.30	43.37	38.59	19.75	47.53	52.94	140.00	0.35
Sr (ppm)	62.70	69.70	75.10	34.50	215.75	142.73	94.70	84.90	361.81	300.00	11.30
Y (ppm)	0.65	0.60	0.70	0.60	3.58	2.09	0.60	0.65	6.56	nd	0.02
Zr (ppm)	3.20	3.00	4.80	2.60	46.33	24.66	3.20	4.00	89.65	160.00	0.05
Nb (ppm)	2.25	2.10	2.20	4.20	4.84	3.47	2.25	2.23	7.58	nd	nd
Mo (ppm)	4.70	2.30	2.40	2.30	6.07	4.19	7.10	4.75	9.85	1.00	0.05
Cd (ppm)	0.80	1.00	1.00	1.00	0.57	0.79	0.95	0.98	0.15	0.13	0.08
Sn (ppm)	1.20	1.00	1.30	1.10	1.04	1.02	1.15	1.23	1.09	nd	0.02
Sb (ppm)	1.30	1.20	1.20	1.20	0.72	0.96	1.25	1.23	0.24	1.50	0.01
Cs (ppm)	12.30	5.70	5.80	5.80	4.37	5.04	10.60	8.20	3.05	nd	nd
Ba (ppm)	22.80	43.00	39.50	27.20	130.63	86.81	24.10	31.80	218.26	580.00	29.00
La (ppm)	29.35	63.60	13.00	26.80	36.85	50.23	17.45	15.23	10.10	nd	nd
Ce (ppm)	18.00	55.00	57.00	18.00	36.99	45.99	21.00	39.00	18.97	nd	nd
Hf (ppm)	2.05	1.00	1.80	1.60	1.57	1.29	2.10	1.95	2.15	nd	nd
Ta (ppm)	2.50	1.40	2.10	1.90	0.90	1.15	2.40	2.25	0.41	nd	nd
W (ppm)	2.30	1.50	1.80	1.60	5.02	3.26	6.20	4.00	8.55	nd	nd
Hg (ppm)	0.40	0.30	0.40	0.40	0.17	0.23	0.50	0.45	0.04	nd	nd
Tl (ppm)	0.40	0.30	0.40	0.30	0.23	0.26	0.45	0.43	0.15	0.68	0.01
Pb (ppm)	0.95	0.50	0.90	0.70	6.54	3.52	0.85	0.88	12.57	22.00	15.60
Bi (ppm)	0.40	0.30	0.40	0.40	0.28	0.29	0.40	0.40	0.26	nd	0.00
Th (ppm)	0.55	0.50	0.60	0.60	2.09	1.30	0.85	0.73	3.68	nd	0.02
U (ppm)	2.25	7.30	5.40	4.10	5.07	6.18	2.85	4.13	2.84	3.70	0.01

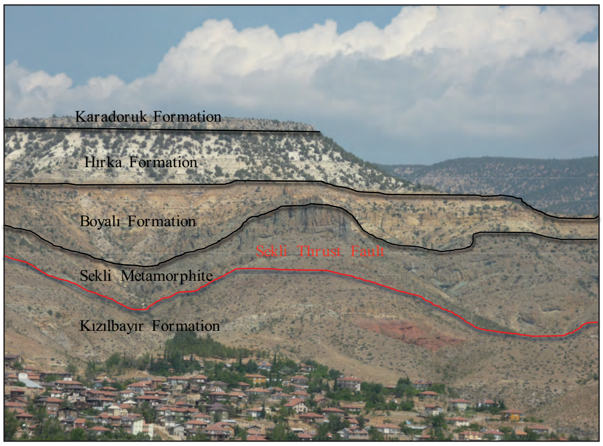

Figure 4. An image of the vegetation on the Hırka Formation.

Sideritis gulendamiae (local endemic), *Centaurea virgata* Lam., *Euphorbia macroclada* Jaub. & Spach, *Echinops pungens* Trautv. var. *pungens*, *Reseda lutea* L. var. *lutea*, *Eryngium campestre* L. var. *virens*, *Reichardia glauca* L., and *Echinophora tournefortii* Jaub. & Spach (Figure 5).

Correlation of element abundances

Comparison with world oil shale averages (WOSAs) and world plant averages (WPAs) revealed that concentrations of several of the elements under investigation reached high values in the selected plant species and the rocks on which they grew. Concentrations of Mg, S, Ca, Ni, As, Sr, Mo, and Cd in the ÇOS were higher than the WOSA while Ga, Se, Y, Nb, Sn, Cs, La, Ce, Hf, Ta, W, Hg, Bi, and Th, which are absent from the WOSA, had significantly accumulated in the ÇOS deposits. Concentrations of Na, Al, Si, P, K, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Rb, Zr, Sb, Ba, Tl, Pb, and U, however, were lower than those of the WOSA.

Due to the different affinities of elements to plants and their different accumulation rates in plants, element concentrations of the 8 selected plants were found to be different from the world averages. For example, with the exception of P, Mn, Se, and Pb, the concentrations of Na, Mg, Al, Si, K, Ca, V, Cr, Co, Ni, Cu, As, Rb, Sr, Y, Zr, Mo, Cd, Sn, Sb, Tl, Bi, Th, and U were greater in all of the studied plants than those of the WPA. Concentrations of S and Fe were lower than the WPA in only 2 samples (*Echinophora tournefortii* and *Euphorbia macroclada*), while Zn was lower

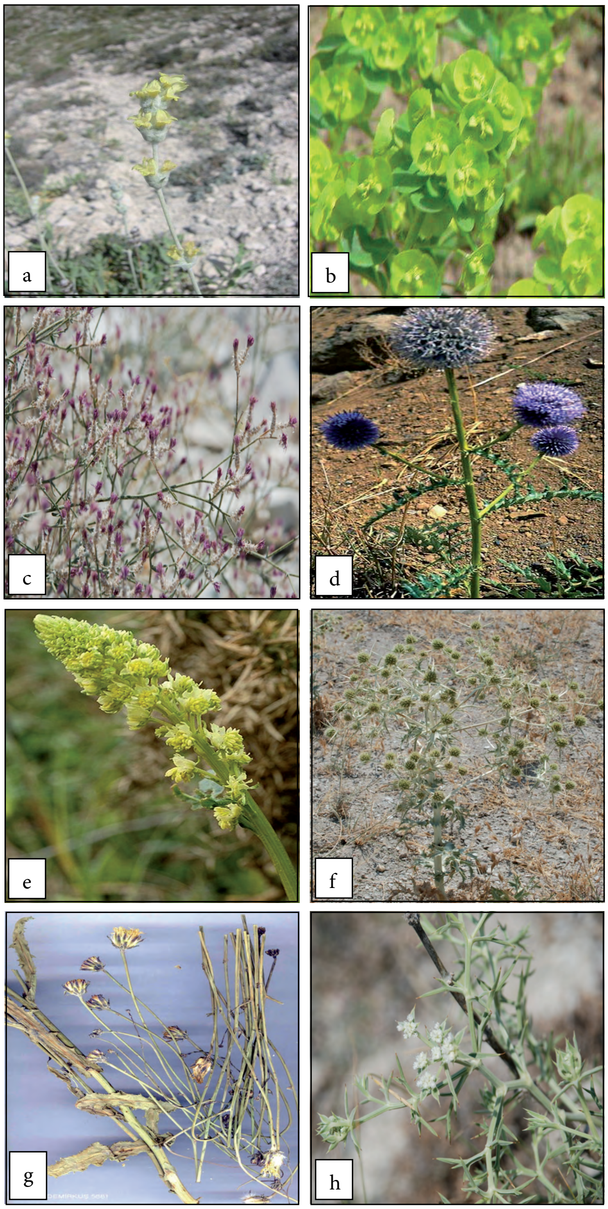

Figure 5. Plants evaluated in this study: a) *Sideritis gulendamiae*, b) *Euphorbia macroclada*, c) *Centaurea virgata*, d) *Echinops pungens* var. *pungens*, e) *Reseda lutea* var. *lutea*, f) *Eryngium campestre* var. *virens*, g) *Reichardia glauca*, h) *Echinophora tournefortii*.

in 4 samples (*Echinophora tournefortii*, *Euphorbia macroclada*, *Echinops pungens*, and *Reseda lutea*) and Ba was lower in 3 samples (*Eryngium campestre*, *Euphorbia macroclada*, and *Reichardia glauca*). Furthermore, Ti, Ga, Nb, Cs, La, Ce, Hf, Ta, W, and Hg, all of which are absent from the WPA, were detected in the studied plant samples (Table 1). Following, the plant groups selected herein are examined in more detail with enrichment coefficients.

A comparison of major trace element contents indicates that concentrations of V, S, Mg, Mn, Ti, Cr, Cu, Si, Na, Se, Ca, Sr, Al, As, Sr, Ga, Co, Ni, Fe, Hf, Ba, Mo, Nb, Zr, Y, Rb, K, Pb, Th, and W were much higher in the oil shales than in plants (Figures 6 and 7). On the contrary, concentrations of La, Cs, Sb, Cd, P, Bi, Tl, Hg, and Ta were greater in all of the plants than in the rocks (Figure 8). In addition, except for *Eryngium campestre* var. *virens*, the U content was very low in the plants. Finally, Zn, Sn, and Ce concentrations in the ÇOS may be lower or higher than the element contents in some of the plants (Figure 9).

Element enrichments in rock and plant samples

In order to determine major and trace element enrichments, the concentration of each element was normalised with respect to Al, which is resistant to the alteration, and an enrichment factor was computed. In calculations, the following formula was used: enrichment factor $_{\text{element X}}$ = $(X/Al)_{\text{sample}}$ / $(X/Al)_{\text{average sample}}$ (Brumsack, 2006). For the average value, WOSAs (Brumsack, 2006) and WPAs (Reimann et al., 2001) were used (Table 1). Results from this computation were evaluated as enriched if ≥1 and as depleted if <1 (Table 2; Figures 10 and 11).

The 8 examined plant species growing on these rocks were divided into 2 groups with respect to the enrichment factors indicated in Table 2.

The first group comprised plant species *Eryngium campestre* var. *virens*, *Echinophora tournefortii*, *Sideritis gulendamiae*, *Euphorbia macroclada*, *Reichardia glauca*, and *Centaurea virgata* (Figure 10). In these 6 plant species almost all of the same elements were

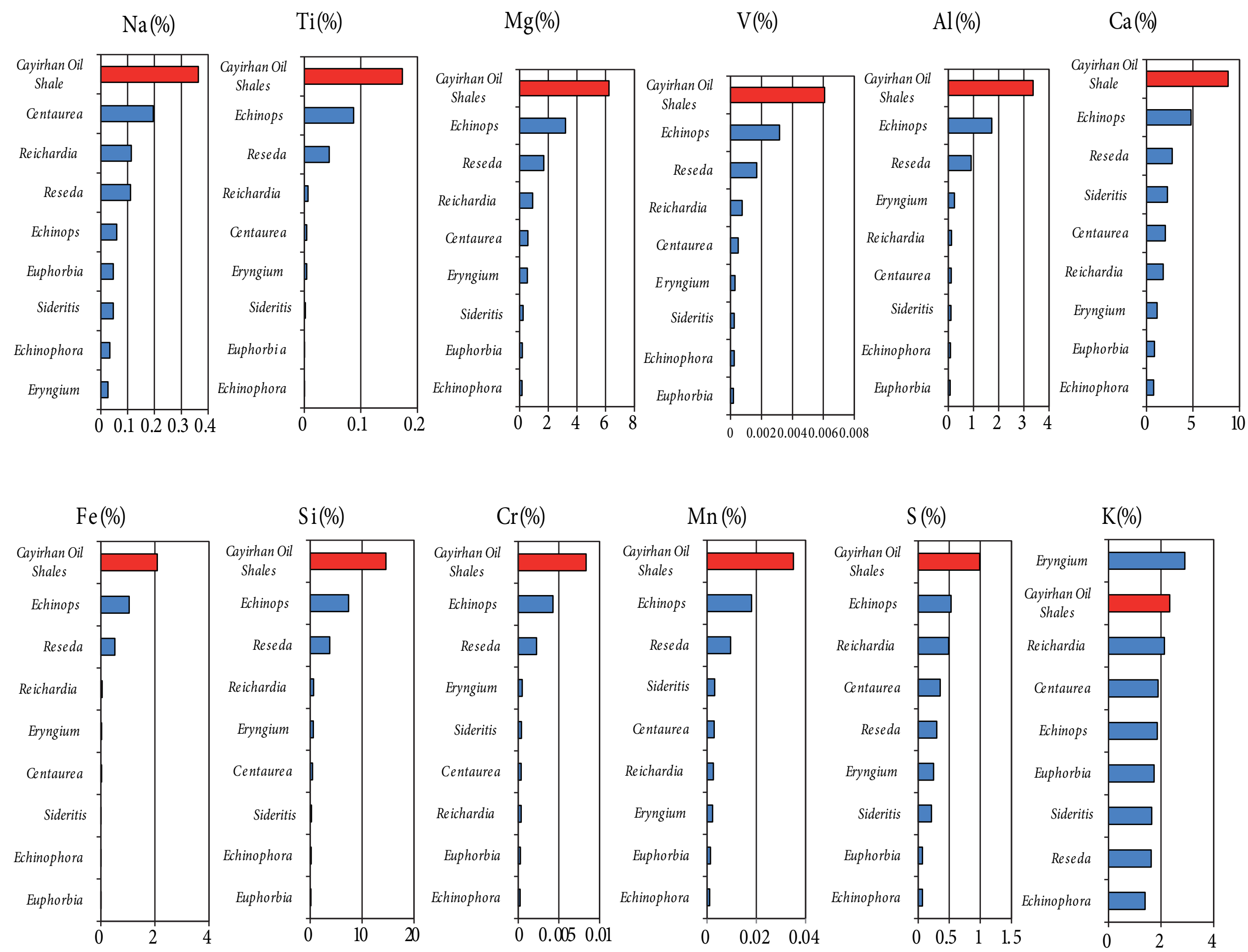

Figure 6. Comparison of main elements (%) of the plant and rock samples (ÇOS > any of the plants examined).

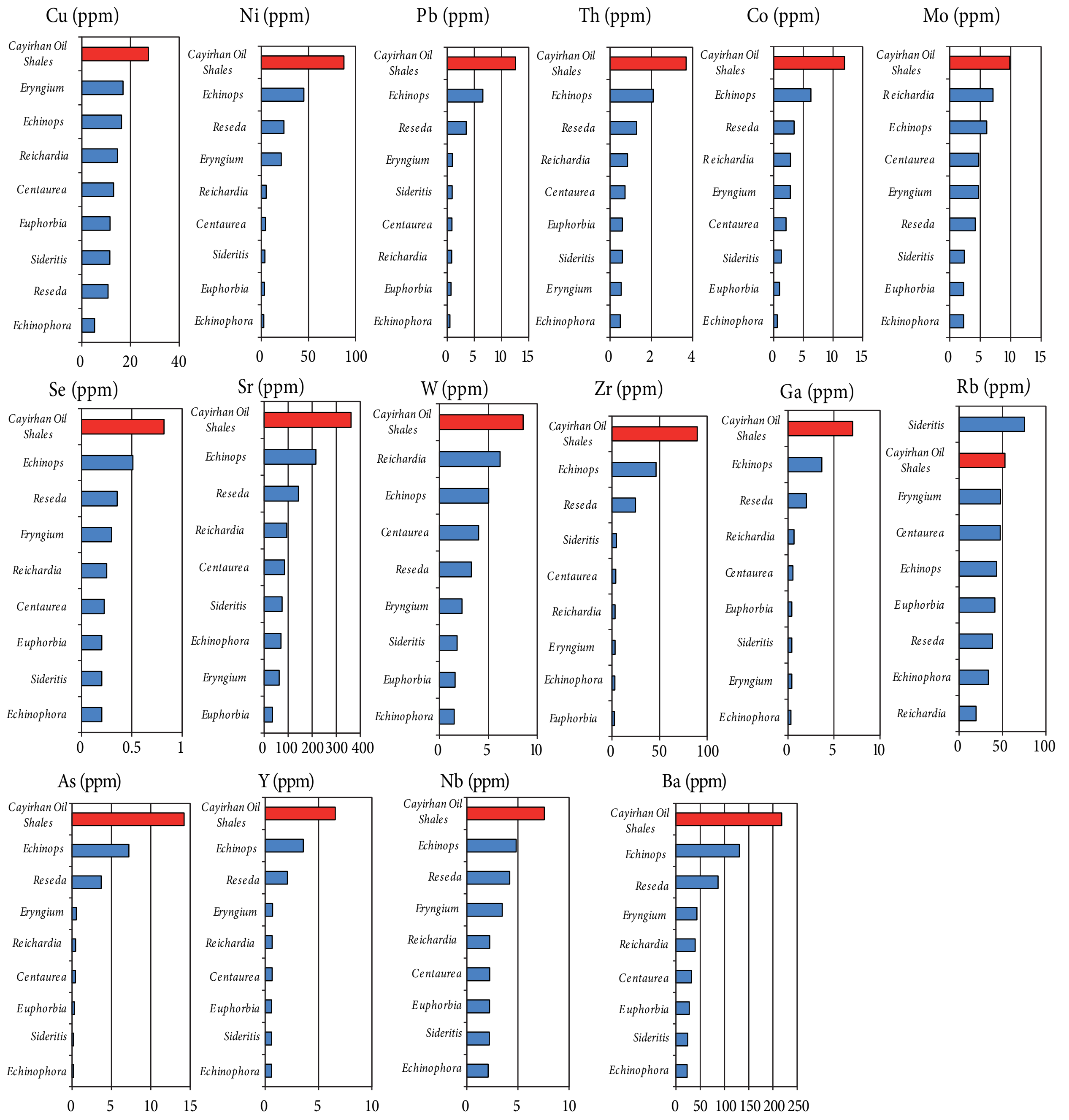

Figure 7. Comparison of trace elements (ppm) of the plant and rock samples (ÇOS > any of the plants examined).

enriched (Na, Si, V, Cr, Rb, Y, Zr, Mo, Sn, Sb, Tl, Bi, Th, and U). Among these elements, with the exception of Na and Cr, the remaining 12 elements were the least enriched in *Eryngium campestre* var. *virens*.

U was the most enriched element in this group, with enrichments of 20-fold in *Eryngium campestre* var. *virens*, 192-fold in *Echinophora tournefortii*, 111-fold in *Sideritis gulendamiae*, 126-fold in *Euphorbia macroclada*, 50-fold in *Reichardia glauca*, and 78-fold in *Centaurea virgata*. In terms of the magnitude of the increase coefficient, U was followed by Bi, Rb, Sb, Sn, Tl, Mo, Zr, Y, and Th. In contrast, Na, Si, V, Cr, and Cd were represented by low increase coefficients varying from 1.2 to 2.8.

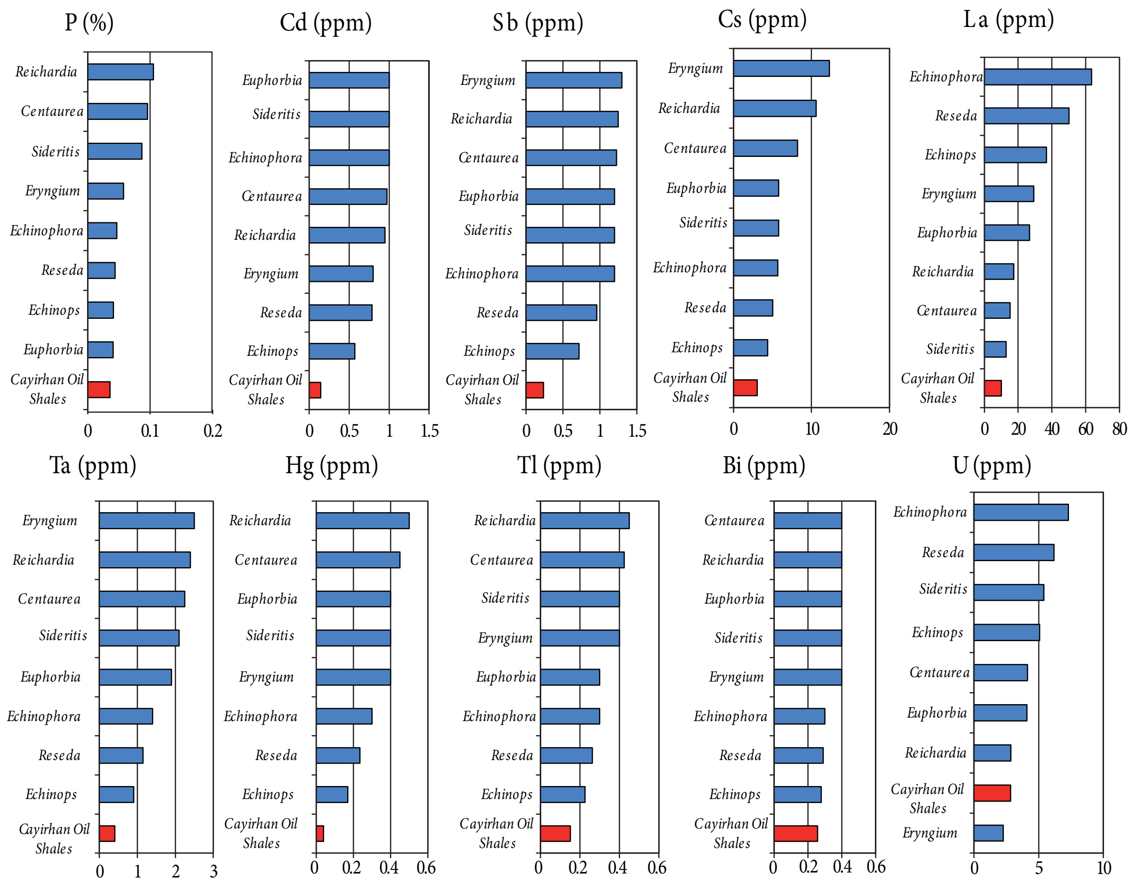

Figure 8. Comparison of elements in plant and rock samples in the study area (ÇOS < any of the plants examined).

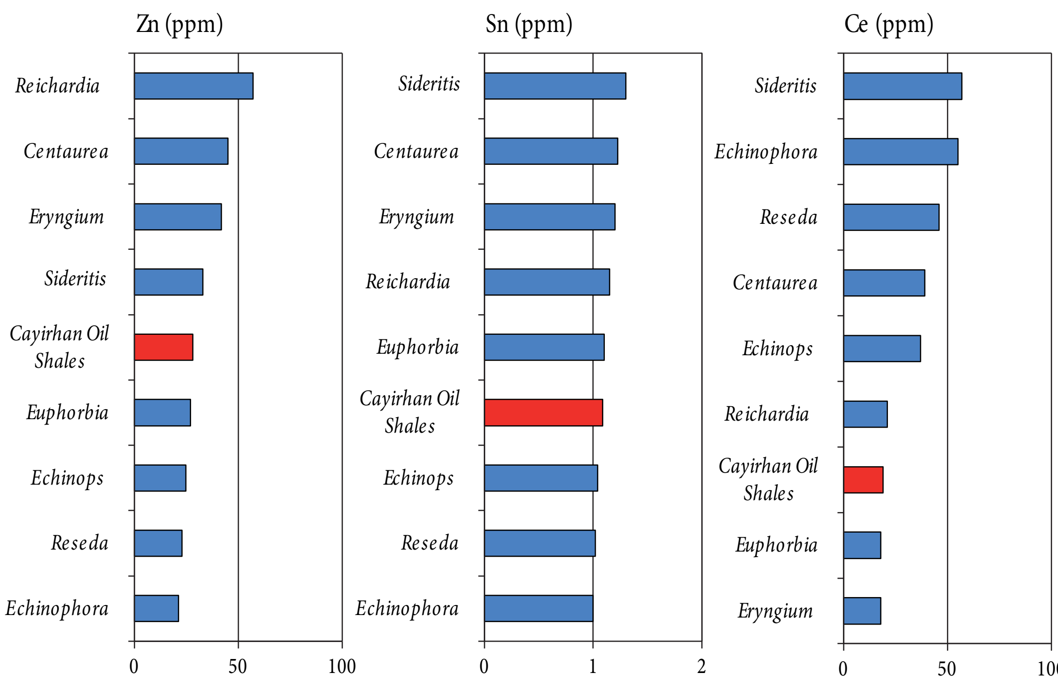

Figure 9. Comparison of element abundances of Zn, Sn, and Ce in plant and rock samples from the study area.

Table 2. The major and trace element enrichment coefficients of ÇOS and plant species (nd = not determined).

Elements	*Eryngium campestre*	*Echinophora tournefortii*	*Sideritis gulendamiae*	*Euphorbia macroclada*	*Reichardia glauca*	*Centaurea virgata*	*Echinops pungens*	*Reseda lutea*	Çayırhan oil shales
Na (%)	1.95	1.37	1.35	2.78	2.00	1.70	0.46	0.50	0.80
Mg (%)	0.16	0.16	0.17	0.19	0.56	0.38	0.14	0.14	10.47
Si (%)	1.38	1.48	1.48	1.33	2.99	2.30	2.32	2.29	1.41
P (%)	0.02	0.04	0.07	0.05	0.07	0.07	0.00	0.00	1.34
S (%)	0.08	0.07	0.17	0.08	0.33	0.26	0.03	0.03	12.96
K (%)	0.22	0.31	0.28	0.45	0.31	0.30	0.02	0.03	2.05
Ca (%)	0.10	0.20	0.45	0.25	0.30	0.37	0.06	0.06	14.68
V (%)	0.84	2.11	1.65	1.85	4.40	3.14	1.30	1.33	1.23
Cr (%)	1.16	1.66	2.12	2.27	1.73	1.91	1.38	1.40	2.42
Mn (%)	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	1.08
Fe (%)	0.23	0.10	0.20	0.10	0.58	0.40	0.86	0.83	1.14
Co (ppm)	0.73	0.46	0.79	0.90	1.47	1.16	0.23	0.24	1.64
Ni (ppm)	0.48	0.18	0.20	0.27	0.24	0.22	0.14	0.14	3.38
Cu (ppm)	0.15	0.14	0.24	0.36	0.26	0.25	0.02	0.03	1.59
Zn (ppm)	0.06	0.09	0.11	0.13	0.16	0.13	0.00	0.01	0.78
As (ppm)	0.48	0.63	0.74	0.73	1.15	0.96	1.05	1.04	3.73
Se (ppm)	0.03	0.05	0.04	0.06	0.04	0.04	0.01	0.01	nd
Rb (ppm)	6.08	12.72	22.18	18.15	4.94	12.85	0.76	1.29	0.99
Sr (ppm)	0.25	0.81	0.69	0.47	0.73	0.71	0.12	0.15	3.16
Y (ppm)	1.26	3.44	3.14	4.01	2.28	2.68	0.96	1.07	nd
Zr (ppm)	2.63	7.32	9.17	7.41	5.18	7.01	5.27	5.36	1.47
Mo (ppm)	4.54	6.58	5.38	7.69	13.50	9.78	0.81	1.07	25.80
Cd (ppm)	0.46	1.71	1.34	2.00	1.08	1.20	0.05	0.12	2.94
Sn (ppm)	2.96	7.32	7.45	9.40	5.59	6.44	0.36	0.67	nd
Sb (ppm)	5.78	15.80	12.37	18.46	10.94	11.60	0.44	1.13	0.41
Ba (ppm)	0.03	0.20	0.14	0.14	0.07	0.10	0.03	0.04	0.99
Tl (ppm)	2.96	6.58	6.87	7.69	6.56	6.71	0.23	0.51	0.58
Pb (ppm)	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	1.50
Bi (ppm)	8.89	19.75	20.62	30.77	17.50	18.93	0.86	1.70	nd
Th (ppm)	1.29	3.47	3.26	4.86	3.91	3.61	0.68	0.80	nd
U (ppm)	20.00	192.25	111.36	126.15	49.87	78.10	6.23	14.52	2.01

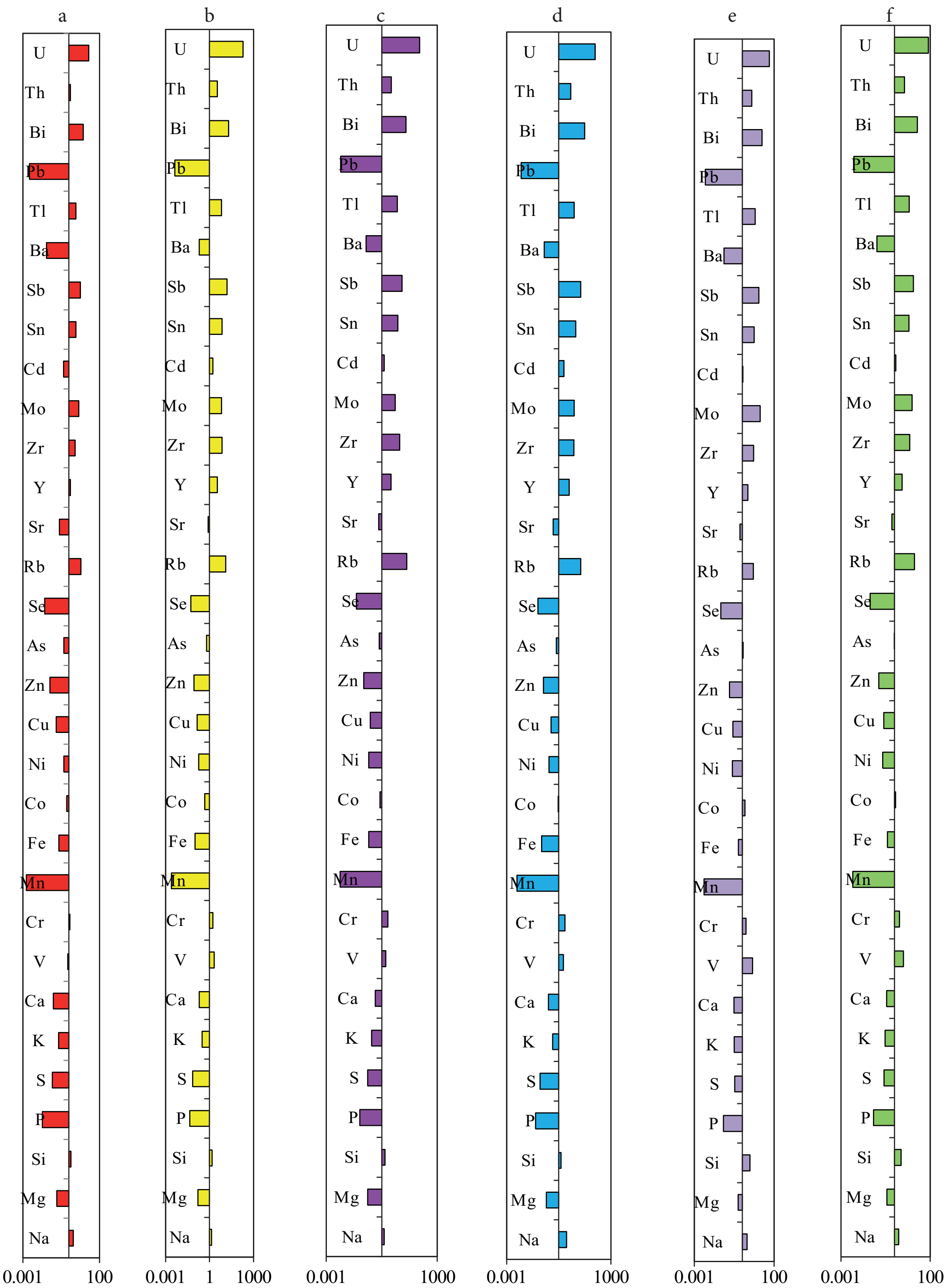

Figure 10. Element enrichment graphics of plants: a) *Eryngium campestre* var. *virens*, b) *Echinophora tournefortii*, c) *Sideritis gulendamiae,* d) *Euphorbia macroclada*, e) *Reichardia glauca*, f) *Centaurea virgata*.

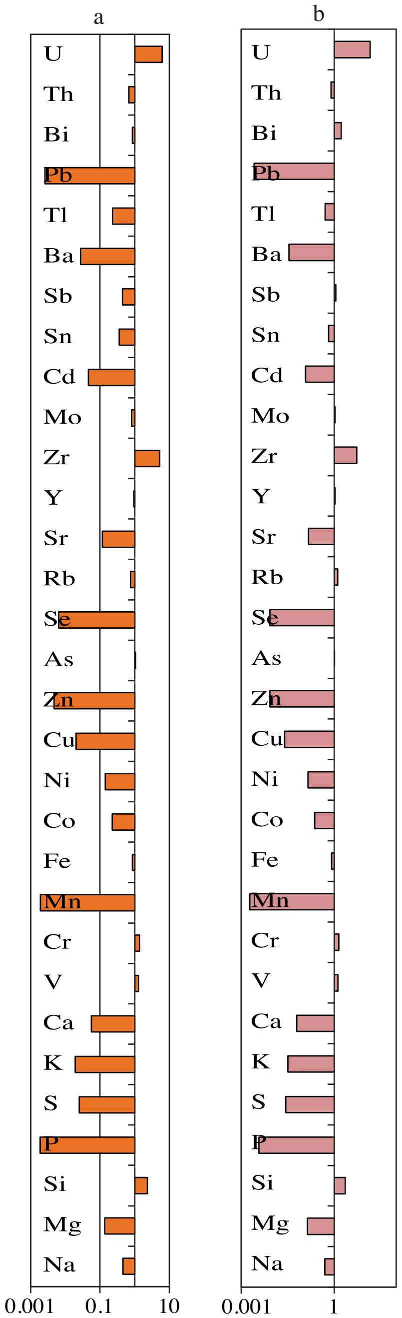

Figure 11. Element enrichment graphics of plants: a) *Echinops pungens* var. *pungens*, b) *Reseda lutea* var. *lutea*.

The second group comprised the plant species *Echinops pungens* var. *pungens* and *Reseda lutea* var. *lutea* (Figure 11). There were 6 elements (U, Zr, Si, V, Cr, and As) enriched in this group. Among them, enrichments of U, Zr, and Si were the highest, in the order of U > Zr > Si, while V, Cr, and As were enriched at the same level and had a coefficient of 1. U enrichments were 14.52-fold in *Reseda lutea* var. *lutea* and 6.23-fold in *Echinops pungens* var. *pungens*.

Some elements, such as Si, V, Rb, Y, Cr, Zr, Mo, Sb, Bi, and U, were enriched in both groups. Among these 10 elements, Si, Cr, Zr, and U were enriched in all of the plant types. U, Rb, Mo, Rb, and Zr accumulated in the first group and Si was more enriched in the second group. The depleted elements for *Reichardia glauca* and *Centaurea virgata* were Ni, Cu, Zn, Se, Sr, Ba, and Pb. In all of the other plants studied, the depleted elements were Mg, P, S, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Se, Sr, Ba, and Pb.

With respect to WOSAs, all of the major elements of the ÇOS and some of the trace elements (Co, Ni, Cu, As, Rb, Sr, Zr, Mo, Cd, Ba, Pb, and U) were found to be enriched to varying extents (Table 2). Ca (15-fold), S (13-fold), Mg (10-fold), and K and Cr (2-fold) were the most enriched elements followed by Mn, V, Si, P, and Fe with enrichments of 1.0-fold to 1.4-fold. Enrichments of 26-fold for Mo, 3.4-fold for Ni, 3.7-fold for As, 3.2-fold for Sr, 2.9-fold for Cd, and 2-fold for U were observed. Furthermore, Co, Cu, Zr, and Pb showed 1.5-fold enrichment. Rb and Ba were represented by a 1-fold enrichment (Figure 12).

Discussion

The increase in concentrations of Ca and Mg indicates a carbonate source since Ca and Mg are the main alteration products of pure carbonates. In addition, the alteration of ferromagnesian minerals also yields Ca, Mg, and Fe. During the alteration of feldspars, the mobility of cations such as K^+, Na^+, and Mg^+ is increased (Köksoy, 1991).

Among the trace elements, Mo showed the highest increase (26-fold). At strong oxidation conditions in the sedimentary cycle, Mo is easily mobilised as molybdate ion. Under reducing conditions, molybdenum is precipitated as MoS_2 due to the significant amount of H_2S released and may be significantly accumulated in reduced sediments. The Mo content of carbonaceous clays and shales is high (more than 24 ppm) (Goldschmidt, 1954). Likewise, U, Co, Ni, Pb, Zn, Cu, Cd, and Sb enrichments in black shales and other sediments rich in organic material are associated with H_2S (Köksoy, 1991).

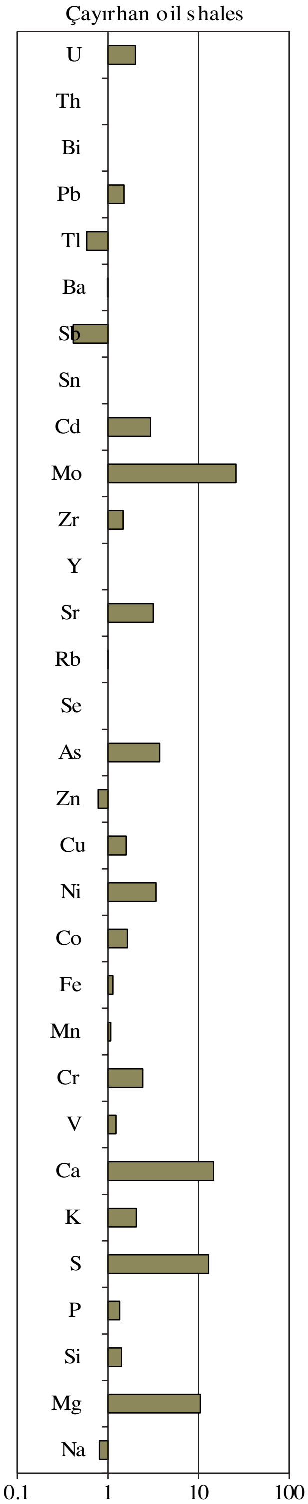

Figure 12. Element enrichment graphics of ÇOS.

Ba and Rb easily enter into the structure of K-bearing minerals, as does Sr to Ca-bearing minerals (e.g., carbonate and plagioclase). The ionic radius of Tl is very close to that of Rb. Feldspar and micas isomorphically substitute K and Rb. Tl has a chalcophile character. At the hydrothermal stage, Tl may precipitate together with Pb, Zn, and As. It is accumulated in H_2S-rich environments and may be absorbed by organic materials and clays (Şahinci, 1991).

Zr may be enriched during the crystallisation of magmatic solutions. In addition, it can replace Ca, Fe^{+2}, and Ti in carbonates, pyroxene, and apatite minerals.

Most of the elements in the periodic table may be accumulated in plants by uptake from the soil (Takada et al., 1997). Some plants uptake certain elements (Wenzel et al., 1993; Kumar et al., 1995; Adriano et al., 1997). Plant analysis is also used in geochemical surveys for the exploration of mineral deposits (Brooks, 1972; Kovalevsky, 1979; Brooks et al., 1995). The major factors affecting plant chemistry are their habitat or substrate, the rocks and soils on which they grow, weathering, and microclimate. Anthropogenic impacts may also be included. Different anatomical, morphological, and physiological properties of the roots, leaves, and bodies of plants make element accumulation in plants a complex process.

We are aware that in this study only a small part of this complex process could be considered and only limited information was achieved regarding the selected plant types, the rocks on which they grow, and their element accumulation. *Eryngium campestre* var. *virens*, *Echinophora tournefortii*, *Sideritis gulendamiae*, *Euphorbia macroclada*, *Reichardia glauca*, and *Centaurea virgata*, which constitute the first group, were enriched in Na, Si, V, Cr, Rb, Y, Zr, Mo, Cd, Sn, Sb, Tl, Bi, Th, and U, while the second group, *Echinops pungens* var. *pungens* and *Reseda lutea* var. *lutea*, were enriched in Si, V, Cr, As, Zr, U, Rb, Y, Mo, Sb, and Bi. Furthermore, Sb, Sr, Y, Sn, Th, and U were enriched in both groups and Mg, P, S, K, Ca, Mn, Fe, Ni, Cu, Zn, Se, Sr, Ba, and Pb were determined to be depleted in all the plants. In addition, Co (except for in *Reichardia glauca* and *Centaurea virgata*) and As (except for in *Reichardia glauca*, *Echinops pungens*, and *Reseda lutea)* were also found to be depleted. It was noted that concentrations of U, a radioactive element, were extremely enriched in some of the plants, by 20.0-fold in *Eryngium campestre* var. *virens*, 192.25-fold in *Echinophora tournefortii*, 111.36-fold in *Sideritis gulendamiae*, 126.15-fold in *Euphorbia macroclada*, 49.87-fold in *Reichardia glauca*, 78.10-fold in *Centaurea virgata*, 14.52-fold in *Reseda lutea* var. *lutea*, and 6.23-fold in *Echinops pungens* var. *pungens*.

Only 6 of the elements (Si, V, Cr, Zr, U, and Mo) enriched in the ÇOS are also enriched in all of the plant species under interest. Although some of the major elements (P, S, K, Ca, Fe, and Mn) and some of the trace elements (Ni, Cu, Zn, Sr, Ba, and Pb) were enriched in the ÇOS deposits, they were depleted in all of the plants. Furthermore, Tl, Sb, Rb, and Na, which are not enriched in WOSAs, were found to be accumulated in the first group of plants. These results may indicate that rock chemistry and, even more predominantly, some biologic factors might affect element accumulations in plants. It is known that plants have a strong affinity to some elements (Wenzel et al., 1993; Kumar et al., 1995; Adriano et al., 1997). For example, there are some plants (e.g., *Alyssum bertolonii* Desv.) that grow on serpentinites that have Ni content of up to 1% (Brooks, 1983). Some plants do not uptake toxic elements at levels other than tolerance limits while some can accumulate high concentrations (Baker, 1981). Under the circumstances, the 8 plant species under investigation should be evaluated in this sense. The root lengths and deep penetration capabilities of plants must also be taken into account. For example, vascular plants can uptake elements only with their roots. Unlike vascular plants, however, algae generally accumulate elements by atmospheric effects. Almost all plants give rise to soil with an acidic character and may change the oxidation state of some elements (e.g., Fe) (Reimann & Caritat, 1998).

We attempted to evaluate the major and trace element contents examined in this study from an environmental geology point of view. It should be kept in mind that elements enriched both in the ÇOS and in nearby plants may be harmful to other living things via the food chain. Therefore, water sources in the region need to be investigated in this sense and more detailed surveys should be carried out on the plants.

Conclusion

All major elements and some trace elements such as Co, Ni, Cu, As, Rb, Sr, Zr, Mo, Cd, Ba, Pb, and U were found to be enriched in the ÇOS deposits. However, Si, V, Cr, Zr, U, and Mo were enriched in the studied plant species. These data on element enrichments indicate that enrichment in plants is not directly proportional to enrichment in rocks. This result may suggest that plant element content may be affected by biological factors in addition to rock chemistry.

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