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Assessment of Sessile Oak (*Quercus petraea* L.) Leaf as Bioindicator for Exploration Geochemistry

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The element contents of sessile oak (*Quercus petraea* L.) leaves which grow on hydrothermally altered area with high element contents were studied at Gümüşhane and its near vicinity. The aim of this study is to determine threshold element contents of *Q. petraea* L. leaves growing on the area. For this purpose, oak leave samples collected were analyzed by inductively coupled plasma-mass spectrometry for concentrations of some elements which were the group of most common trace elements in exploration geochemistry studies. The assessment of the element contents of the oak leaf is based on the descriptive statistics and computations of threshold values of leaves depending on statistical parameters and average element contents of the plants growing on lands in normal background values for the elements. According to Q–Q (normal quantile–quantile) plots, the Kolmogorov–Smirnov tests etc., all the elements, do not pass normality tests. Because of that, threshold values of the elements in leaves of oak were computed by median+median absolute deviation (MAD) and median+2MAD used in raw values for the elements. The data revealed that concentration levels of the examined elements in the leaves in the study area were determined as above and/or exceeded the upper limit of the normal range than in leaf of oak (*Q. petraea* L.) which grows on lands with normal elements background. Therefore, it is concluded that leaves of *Q. petraea* L. can be used as bioindicator in exploration geochemistry, especially for base metal ore deposits.

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1. Introduction

Since known ore deposits have been depleted in time, there is a need for discovery of new, especially buried ore deposits. Various exploration methods, such as geophysical prospecting, soil geochemical prospecting, and exploration drilling, have been used to clarify anomalous zones in soils above buried mineralization but these methods are laborious and expensive. The presence of thick or transported soil layer could render geochemical prospecting methods ineffective due to the issue of sample representativeness of the underlying substrate [1]. Biogeochemical prospecting can be effective in this kind of areas. As stated by Brooks et al. [1], this method involves the sampling and chemical analysis of plant tissues to obtain information about the underlying substrate. The basis of biogeochemical prospecting is that plants uptake elements from soil or under its through their roots, and accumulate elements in their organs, such as roots, shoots, and leaves. Therefore, if certain plants contain abnormally high concentrations of certain elements, they can be used as bioindicators of the substrate's geochemical attributes (e.g., presence of mineralization). Moreover, the biogeochemical approach to mineral prospecting is cost effective compared with other prospecting techniques. The major limitation of a biogeochemical approach to mineral exploration is, however, often due to poor knowledge of element uptake and cycling by various plant species. In generally, hydrothermally altered areas and soils developing in alteration areas (pointing to buried ore deposits) can have high contents of elements especially metals such as Cu, Pb, Zn, Mo, As, even Ag, Au, etc. [2–4]. Therefore, biogeochemical prospecting has been effective at detecting buried mineralisation and has been used extensively in different countries and in many terrains and climates since particularly the beginning of the second half of the 20th century [5–9].

The sessile oak (*Q. petraea* L.), a very common species in Gümüşhane and East Black Sea region-rich in term of ore deposits, are needed to investigate bioindicator capacity of element accumulation. In this study a biogeochemical orientation survey was conducted in order to investigate the potential as an exploration method in the vicinity of hydrothermally altered area in the Canca, Gümüşhane in Turkey. The principal objectives of this study were to determine concentration ranges of sessile oak leaves, to study the geochemical characteristics, to investigate the bioindicator capacity for mineral exploration and to evaluate the applicability of biogeochemical prospecting for mineralizations, East Black Sea region, especially in Gümüşhane and its vicinity. Samples of leaves of sessile oak plant (*Q. petraea* L.) were collected from the target hydrothermally altered area and analyzed for some elements (Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Ba, and Pb) using inductively coupled plasma-mass spectrometry (ICP-MS). These elements were the group of trace elements most common in exploration studies for especially precious and base metal ore deposits.

2. Material and methods

2.1. Geographic and geological features of the study area

The studied area (Canca Gümüşhane — NE, Turkey) has a steep topography owing to its geological evolution

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and tectonic history. According to the Köppen climate classification, the area has a humid continental climate with mild/hot and dry summers and cold and snowy winters with average temperatures ranging between –5.8 and +4.9 °C for the winter and between 10.6 and 28.5 °C for the summer. The annual precipitation is also around 451.4 kg/m^2 on average (The Turkish State Meteorological Service statistics of the last 52 years).

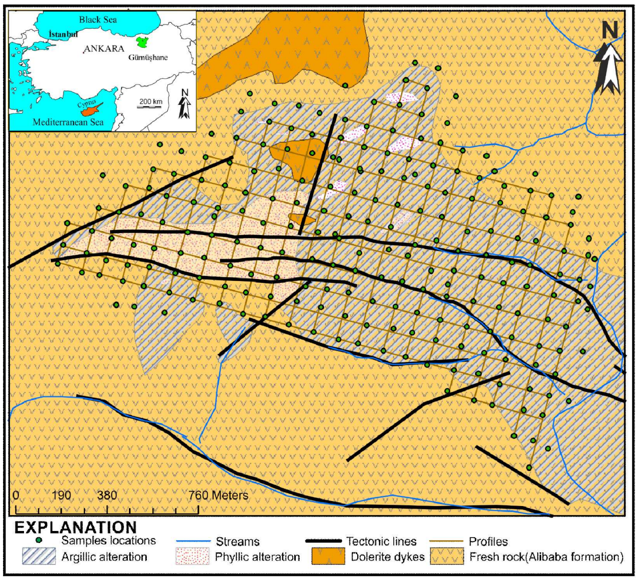

Fig. 1. Geological and location map of study area (after Vural [3]).

The area is situated at the Black Sea tectonic unit (BSTU) in east-northern Turkey (Fig. 1). The basement of the BSTU in the studied area near vicinity consists of unmetamorphosed granitic plutons [10–12]. The basement rock is unconformably overlain by an Early to Middle Jurassic volcano-clastic unit [13] which passes upward to the Late Jurassic and Early Cretaceous carbonate rocks [14]. The Late Cretaceous begins with sandy limestones at the bottom and grades upward to red pelagic limestone and then a turbiditic series consisting of sandstone, siltstone, marl and limestone, conformably overlay this carbonate platform [2]. All these units were cross cut by intrusions aged Late Cretaceous [15]. The Eocene volcanic and volcani-clastic rocks overlie the Late Cretaceous volcanic and/or sedimentary rocks with an angular unconformity [2], and are intruded by calc-alkaline granitoids of similar age [16, 17].

Considering the studied area, only the Eocene volcanic and volcani-clastic rocks [2] are exposed (Fig. 1). These rock are hydrothermally altered to argillic and phyllic alteration. The soil type of the area is grey-light brown podzolic and are composed of well-developed acidic and slightly neutral (pH= 4.06 to 7.09).

2.2. Sampling and analyzing

The area is dense with *Q. petraea* L. and two hundred-twenty leave samples of the plant were collected from the site, from mainly June to July in 2014. The sample collection and preparation procedure were explained in detail by Vural [3]. The samples were analyzed by ICP-MS following the method described by Central Research Laboratory of Gümüşhane University's procedure. Obtained values are means of three replicates per plants. For quality assurance, certified standard material was analyzed along with the leaves of *Q. petraea* L. Recovery of the certified values was at least 90%. Finally, eleven elements of Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Ba, and Pb were selected to be treated statistically. Basic statistics were used to analyze the data obtained. Minimum, maximum, arithmetic mean, median, skewness and kurtosis were used to estimate the central tendency of the data. The arithmetic mean and standard deviation were used to predict the geochemical plenty of an element, whereas the median and median absolute deviation (MAD) provided better estimators of the maximum likelihood for data with positively skewed distributions. Because these parameters are inherently stable against outliers and deviations, they give much more realistic values [4].

TABLE I

Descriptive statistic and threshold values calculated of *Q. petraea* L. leaves and data from literature.

leaves		Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Cd	Ba	Pb
Q. petraea L.[a]	range	0.21–8.4	13.6–1374.2	0.05–0.89	0.33–8.75	2.85–14.64	7.37–52.53	0.01–1.36	0.05–5.47	6.84–249.5	11.5–387.34	0.29–2.23
	mean	2.8	270.47	0.21	2.99	6.66	20.55	0.2	0.93	44.47	128.15	0.87
	median	1.86	162.8	0.15	2.77	5.97	19.15	0.14	0.71	30.21	113.35	0.83
	skewness	0.76	1.74	2.58	0.62	0.73	1.23	2.35	2.81	3.01	0.36	0.99
	kurtosis	–0.37	2.31	7.82	–0.34	0.11	1.61	7.37	11.27	10.49	–0.11	1.18
	MAD	1.23	73.025	0.05	1.33	1.05	6.01	0.09	0.42	10.93	46.17	0.24
	med+MAD	3.09	235.825	0.2	4.1	7.02	25.16	0.23	1.13	41.14	159.52	1.07
	med+2MAD	4.32	308.85	0.25	5.43	8.07	31.17	0.32	1.55	52.07	205.69	1.31
Quercus sp.[b]		0.03	0.57	0.003	0.13	0.14	0.19				0.64	0.008
Quercus sp.[c]			33–125		3–5	2–8	2–16					
Q. libani[c]			4–14		1–2	5–28	4–5					
Q. robur[d]			130–465			2.1–6.8	44–167					21.4–62.6

[a]present study; [b] [5], [c] [6]; [d] [7]; all elements in mg/kg, except Cd in μg/kg

3. Result and discussion

The central-tendency methods are applicable only when the distribution of the data fit a normal function, but this is very unusual in the geochemistry [4]. In this study, almost none of the elements studied fit a normal distribution (Table I, with a significance below 0.05 in the Kolmogorov–Smirnov and Shapiro–Wilk tests, histograms for elements, Q–Q [normal quantile–quantile] plots, and parameters such as skewness, kurtosis, etc.). Therefore, threshold values of the elements in leaves of oak were computed by median+MAD and median+2MAD used in raw values for the elements (Table I). The parameter MAD is calculated as follows:

$$\text{MAD} = median_i(|X_i - median_j(X_j)|).$$

When the data obtained were correlated with previously studies' data, the data revealed that concentration levels of the examined elements in the leaves in the study area were determined as above and/or exceeded leaf of oak which grows on lands with normal elements background in especially Mn, Zn, Cu, As, Cd, Ba, Pb.

4. Conclusion

In the context of a biogeochemical investigation of *Q. petraea* L., the elemental contents of the leave of the oak taken from Canca hydrothermally altered area were chemically analyzed and were assessed. It is concluded that the content of studied elements in the leaves of *Q. petraea* L. growing in the hydrothermally altered Canca area (element enrichments — in base metals — occurred due to hydrothermal alteration), when compared with plants grown in unaltered fields, yielded good indications for biogeochemical prospecting, especially for Mo, Cu, As, Zn and Pb and could be successfully used as bioindicator for exploration geochemistry for especially base metal deposits.

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