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The soil-plant relationship of *Salsola orientalis* S. G. Gmel. and its use in mineral prospecting from the Forumad area, Sabzevar ophiolite, Iran

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Abstract

Biogeochemical investigation on *S. orientalis*, a flora growing on the soils derived from serpentinized dunite in the Forumad area, Sabzevar ophiolite has been conducted in order to examine the plant-soil relationship in chromite prospecting. Due to engagement of Cr in the chromite crystal structure and its non-essential role in the plant's life cycle, Ni was used as pathfinder element in biogeochemical prospecting of chromite deposits. Quantitative estimation of Mn, Fe, Ca, Mg, K, Na, Cr, Ni and Co in soils and different plant organs of *S. orientalis* by using Atomic Absorption Spectroscopy (AAS) revealed that the leaf stem is the most reliable organ for ore prospecting in the Forumad area. Determination of bio-concentration factor (BCF) for Cr, Ni and Co in *S. orientalis* explicitly demonstrated that the flora adopts exclusion and accumulation mechanisms for Cr-Co and Ni, respectively. Current research signifies the excellent correlation between Cr and Ni (0.91) in host soil of the *S. orientalis* and the tendency of the plant to absorb Ni selectively enhances the chance of sampling the plant's leaf as a biogeochemical medium for the exploration of new hidden mineral deposits in the Sabzevar ophiolite belt as well as the other similar settings.

Keywords: Soil; Salsola orientalis; biogeochemical prospecting; Sabzevar ophiolite

1. Introduction

Chemical analysis of systematically sampled plant organs for metallic ore prospecting is one of the first geochemical methods to be investigated (Rose et al., 1979; Ramana Reddy, 2012). Plants root system has the ability to collect materials from great depths and wide areas; therefore biogeochemistry has a considerable advantage over soil sampling. The biogeochemical techniques provide a cost-effective means to detect the presence of ore deposits beneath the earth surface (Kovalevsky, 1987). Knowledge of soil chemistry is an essential prerequisite for the proper understanding of biogeochemical patterns and biogeochemical techniques used in mineral prospecting that are generally based on soil and plant relationships (Al-Farraj and Al-Wabel 2007; Ebong et al., 2007; Ghaderian and Baker, 2007; Ololade et al., 2007; Pratas et al., 2005; Reeves et al., 2007). Plant growing on soil is dramatically affected by the host soil composition which leads to the selection of a specific flora. Several factors, such as drainage, pH and Eh values, the nature of clay minerals, antagonistic effects of other ions and the presence of complexing agents can reduce the bioavailability of some elements in soil and consequently very little of the total contents of the elements can be utilized by plants (Kfayatullah, 2001). Plants respond to elemental composition of host soil in three ways: exclusion, indication or accumulation. Biogeochemists use soil-indicator plants to prospect ore deposits of valuable metals (Altinözlü et al., 2012; Brooks, 1998; Ghaderian and Baker, 2007; Pratas et al., 2005; Rajabzadeh et al., 2015; Reid and Hill, 2012).

Serpentine soils which are rich in iron, magnesium and associated trace elements such as Ni, Co and Cr, have for many years, been of particular interest to geochemists and botanists (Altinözlü et al., 2012, Freitas et al., 2004; Reeves et al., 2007; Sequeira and Pinto da Silva, 1991). Serpentine soils tend to be shallow and dry (Proctor and Nagy, 1992), thus plant species growing on these soils and their physiognomy are different from those of non-serpentine areas. The soils are also characterized by low concentrations of some essential nutrients such as N, P and K.

Forumad area in the Sabzevar ophiolite complex, northeastern Iran is regarded as one of the

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important mining areas for chromite ore deposits. In this area, the podiform chromites surrounded by intensely serpentinized dunite envelopes, generally formed at the basal part of the ophiolite lithological column. Despite high potential for mining activities in this area, no study has been conducted from a biogeochemical point of view. The field observations indicated that among all plant species grown at the Forumad area, *S. orientalis* had a meaningful relationship with ophiolite rocks (especially serpentinized dunite, the main host rock of the chromite ores). This species belongs to Chenopodiaceae family and its flowering season is autumn. It is extremely tolerant to water stress as it grows in summer, when there is no precipitation and the temperature can reach 40 °C. This primitive investigation helped us to achieve a comprehensive perspective about the biogeochemistry of *S. orientalis* in the Forumad area in order to examine its power as a reliable metal indicator plant. For this reason the authors decided to analyze different parts of the plant separately to find the best plant organ accumulating the highest amounts of desired metals.

2. Geological setting

The Sabzevar ophiolite is regarded as remnants of the northern branch of the Neo-Tethyan oceanic lithosphere in the Middle East that it is more likely a part of the ophiolitic ring around the Central Iran Block. The age of the ophiolite emplacement at the passive continental margin is estimated to be Late Cretaceous (Shojaat et al., 2003). The ophiolite belt in northeastern Iran appears in a region 150 km long and 10–30 km wide, trending east-west and composed of harzburgite (main rock), dunite, serpentinite, gabbro and microgabbro, diabasic dikes, pyroclastic rocks and related metamorphic rocks (Omrani et al., 2013; Rossetti et al., 2010) (Fig. 1). In some areas, the ophiolite is intensively tectonized, resulting in the formation of litho-structural unit called ophiolite mélange which includes mafic and ultramafic rocks, chert, limestone, and exotic rock blocks. In Forumad area, the harzburgites are divided into orthopyroxene-rich harzburgite and depleted harzburgite. The latter gradually converts to thick dunite bodies which may contain podiform chromites as tabular and lens shape deposits. The dispersed deposits are found in massive or nodular types (Shafaii Moghadam et al., 2009).

Forumad area is located in semi-arid to arid region with cold winters and hot summers. The average annual rainfall is 235 mm and hence physicochemical weathering progresses moderately. Topographically, the higher parts of the area are continuation of mafic-ultrmafic rocks in association with limestone, mostly found northward. Plains at the south of the study area are covered by a very thick alluvium, reaching 100 m in thickness. Due to regional dry climate and nearly high relief, soils overlaying the ultramafic rocks of the Sabzevar ophiolite in Forumad are moderately developed. Soil's color varies in the range of brown to red-brown on harzburgite zones and to gray and pale green on dunites.

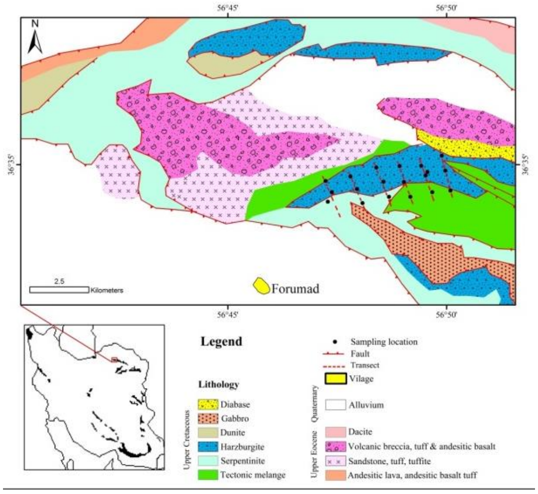

Fig. 1. Geological map of Sabzevar ophiolite in Forumad area (modified after 1/100000 map of Forumad, Geological Survey of Iran)

3. Materials and methods

3.1. Sample collection

The choice of sample spacing should be in accordance with the distribution of desired species and soils, so at the reconnaissance survey in the study area, six transects were established approximately 700 m apart in an NW-SE direction, perpendicular to the general strike of the lithology (Fig. 1). Nineteen pre-selected sample points were identified along these transects with 500 m spacing .The representative background samples of soil and plant were also collected from soils developed on non-mineralized rocks of the Sabzevar ophiolite at a distance of 2 km from the mining area. The sampling of soil (0-10 cm depth) and plant species was conducted during September 2012 from 20 locations (with 3 replications per each sample location).

3.2. Sample preparation and analytical methods

All the analysis techniques were adopted from Ghaderian and Baker (2007) in this study. All soil samples were air-dried and sieved to <2 mm. For the analysis of total elements in the soil samples, sub-samples of 4-5 g were ground to pass<190 µm sieve and then oven-dried at 70 °C. A further sub-sample of 0.5 g was transferred to a Kjeldahl digestion tube for extraction with 10 ml of a 3:1 HCl/HNO_3 mixture. Tubes were left at room temperature overnight and then were placed in a heating block. Each was covered with an air condenser and refluxed gently at 80 °C for 2 h. After cooling, the digests were filtered through a moistened 0.45 µm filter paper into a 50 ml volumetric flask. Flasks were filled up to volume with distilled water. Analyses for Ni, Cr, Co, Mn, Fe, Mg, Ca, K and Na were carried out by AAS (Shimadzu 680). To determine exchangeable elements, 20 g of air-dried <2 mm sieved soil was placed in a 100 ml screw-cap polythene bottle. Next, 50 ml of 1 M NH_4NO_3 solution was added, and finally, the suspension was shaken for 2 h at 20 °C in an end-over-end shaker. After shaking, the soil suspensions were left to stand for 5 min, and then filtered (0.45 µm filter paper). The filtrate was acidified to 0.2% HNO_3 for analysis for the above elements by AAS.

Soil pH was determined using a glass electrode after 10 g of soil had been stirred well in 30 ml distilled water in a beaker and allowed to stand for about 30 min. Total organic carbon (TOC) content was determined by dichromate digestion based on Walkley-Black method (Van Reeuwijk, 1986). The traditional pipette method was used for particle size analysis (Rowell, 1997). Inorganic C ($CaCO_3$) was quantified by the Scheibler method (Westerman, 1990).

Plant samples were separated into roots, twigs and leaves. Vegetative materials were washed well with double-distilled water and dried at 70 °C for 48 h, then placed in a food blender and pulverized to less than 2 mm size. About 1 g of dried samples was added to 25 ml beakers and turned into ash in a muffle furnace for 14 h at 520 °C. The ash was taken up in 5 ml 10% HNO_3 and the digest finally made up to 20 ml in 10% HNO_3. Plant dry matter analysis was performed for the above mentioned elements by using AAS. Quality Assurance/Quality Control procedure for vegetative samples was conducted according to protocols used for Geological Survey of Canada regional geochemical surveys (Dunn, 2007). The quality control procedures consisted of inserting analytical duplicates of some soil and plant samples at a rate of 1 in 10 samples were carried out at Chemistry Laboratory of Science and Technology Park of Iran, Fars branch.

4. Results

4.1. Soil

As depicted in Table 1, all analyzed soils contain high amounts of total elements (Cr+Ni+Co+Mn+Fe+Mg+Ca). These concentrations are in the range for typical ultramafic soils elsewhere in the world (Brooks, 1987; Alexander et al., 2007). The exchangeable fraction of Cr, Ni, Co, Mn and Fe is low, whereas the exchangeable fraction for alkali (Na and K) and alkali earth elements (Mg and Ca) is considerably high. The total concentration of Cr in soil samples varies from 130 to 1150 µg g^{-1}, whereas the exchangeable concentration of the same samples is very low, ranging between 0.1 and 2.5 µg g^{-1}. The total and exchangeable concentrations of Ni vary in the range of 108-719 and 1.2-7.6 µg g^{-1}, respectively.

Table 1. Maximum elemental concentrations of total and exchangeable phases (µg g^{-1} dry wt) in dunite and harzburgite type soils. Dunite soils (1-8), harzburgite soils (9-19) and background soil sample (20)

Site		Mn	Fe	Ca	Mg	K	Na	Cr	Ni	Co
1	Total	308	38605	10755	11608	712	276	600	347	76
	Exchangeable	4	0.8	563	57	86	24	0.5	7	0.5
2	Total	302	40372	9385	11530	1059	360	538	225	73
	Exchangeable	1	0.2	531	56	92	16	0.1	2	0.5
3	Total	265	42290	9880	11578	562	319	1150	605	181
	Exchangeable	11	1	510	57	101	20	0.3	6	1
4	Total	307	40079	10515	11658	769	235	770	370	61
	Exchangeable	3	0.1	555	57	89	16	0.6	7	0.6
5	Total	288	40609	10845	11448	492	342	535	275	56
	Exchangeable	1	0.3	554	55	91	20	0.4	4.4	0.3

6	Total	306	40880	9370	11519	831	435	617	216	61
	Exchangeable	5	1	560	56	91	26	0.5	5.5	0.5
7	Total	300	39635	10485	11448	1219	157	520	221	55
	Exchangeable	3	1.3	491	56	104	25	0.3	5.2	0.5
8	Total	261	42169	10035	11587	794	293	539	343	89
	Exchangeable	4	0.4	453	57	94	23	0.2	1.2	0.5
9	Total	307	44819	6910	11590	923	270	130	278	98
	Exchangeable	2	0.7	550	54	108	23	0.15	4	0.4
10	Total	303	40568	10545	11538	1460	453	460	231	67
	Exchangeable	3	0.4	572	55	94	25	0.8	4	0.5
11	Total	304	40459	10610	11578	515	307	492	246	68
	Exchangeable	2	0.3	571	56	88	22	2	7.6	0.3
12	Total	301	40388	10750	11600	811	474	412	207	61
	Exchangeable	3	1	571	56	85	26	0.4	4	0.2
13	Total	279	41170	7950	11440	766	235	450	223	48
	Exchangeable	15	5.5	580	57	90	55	2.5	2	0.5
14	Total	307	43245	10950	11783	834	332	303	572	148
	Exchangeable	1	3	572	56	91	14	1.8	3.5	0.5
15	Total	307	44770	10215	11498	187	275	438	277	60
	Exchangeable	3	2	571	57	76	23	0.3	7.4	0.6
16	Total	156	41544	4625	11438	1515	471	430	222	62
	Exchangeable	11	5	566	56	105	24	2.5	6.3	2
17	Total	285	42728	8956	11724	851	300	440	248	54
	Exchangeable	2	0.4	520	48	80	20	0.7	5.4	0.6
18	Total	307	40539	10335	11330	1321	350	169	210	59
	Exchangeable	7	4	564	56	98	20	1	6	0.5
19	Total	617	42048	20790	23149	1200	235	145	719	160
	Exchangeable	3	10	563	55	105	21	0.13	6.4	0.4
20	Total	307	39428	1999	11330	730	149	220	108	38
	Exchangeable	35	10.8	565	56	91	22	0.3	5.9	1

Physicochemical properties for the studied soils from the Forumad area are summarized in Table 2. The soil samples are alkaline (pH from 7.9 to 8.7) and change in texture from sandy loam to loamy sand. Total Organic Carbon (TOC) content ranges between 0.1% (site 11) and 1.4% (site 19). The average of $CaCO_3$ (wt%) in the studied soils is 24.6% ranging from 13% to 35%.

4.2. Plant

Chemical data of different plant organs of *S. orientalis* are indicated in Table 3. As it is obvious, the maximum elemental concentrations vary in different parts of the plant (root, twig and shoot). The mean value of Mn reveals that leaf stems of the plant contain the maximum levels of this element and the roots stands in the second step. The mean Fe content varies in the range of 1234 to 1730 µg g^{-1} from root to leaf. The concentration of Ca in all stems of the plant and in all sites is more than 4000 µg g^{-1}. The mean Mg concentration trend shows leaf> twig> root. Chromium concentration in leaf and twig stems of all *S. orientalis* samples is less than 10 µg g^{-1}. The concentration of Ni in the leaf stem of *S. orientalis* grows up to 500 µg g^{-1}. The results signify that there is a remarkable difference among different organs of *S. orientalis* in terms of Co accumulation, especially between leaf and root stems with a mean of 14 and 0.7 µg g^{-1} per dry weight basis.

Table 2. Selected physicochemical properties of the soils developed from ultrabasic rocks of the study area

Site	pH	TOC (%)	$CaCO_3$ (wt%)	Soil Texture
1	8.7	0.9	31	sandy loam
2	8.0	0.4	32	sandy loam
3	75	0.7	25	sandy loam
4	8.5	0.5	27	sandy loam
5	8.0	0.5	32	sandy loam
6	8.0	0.4	22	sandy loam
7	8.3	0.5	21	loamy sand
8	8.3	0.4	29	sandy loam
9	8.0	0.3	13	loamy sand
10	8.0	0.6	27	loamy sand
11	8.0	0.1	29	sandy loam
12	8.0	0.4	33	loamy sand
13	8.2	0.3	15	loamy sand
14	8.0	0.5	28	loamy sand
15	8.3	0.2	27	sandy loam
16	7.9	0.9	17	sandy loam
17	8.0	0.8	20	loamy sand
18	8.1	.8	24	sandy loam
19	8.1	1.4	15	sandy loam
20	8.1	0.5	35	sandy loam

According to Kovalevsky (1995), the bio-concentration factor (BCF) was defined as: BCF = C_P/C_S where C_P is the concentration of an element in plant and C_S is the concentration of the same element in the soil. The calculated BCF of *S. orientalis* (for Cr, Ni and Co), shown in Table 3, is based on the elements ratio in plant's leaf to the soil, indicating maximum content of 0. 1 for Cr, 1.22 for Ni and 0.38 for Co.

Table 3. Descriptive statistics of elemental concentration in different plant organs (μg g^{-1} dry wt) and determined BCF for Cr, Ni and Co of *S. orientalis* from the 20 sample sites

Element	Organ	Mean	Std. Deviation	Minimum	Maximum
Mn	leaf	112	5.4	100	120
	twig	54	2.7	50	61
	root	76	3.5	70	82
Fe	leaf	1730	27	1645	1754
	twig	1350	26	1313	1390
	root	1234	41	1143	1286
Ca	leaf	4508	87	4331	4638
	twig	4725	20	4701	4762
	root	4645	38	4600	4741
Mg	leaf	470	50	273	498
	twig	464	2.2	461	470
	root	456	38	303	474
K	leaf	792	89	628	935
	twig	730	48	632	789
	root	821	51	759	954
Na	leaf	235	64	188	453
	twig	179	5	171	189
	root	239	26	203	301
Cr	leaf	4	1.7	2	9
	twig	2	0.9	1	4
	root	17	5.1	11	31
Ni	leaf	259	85	149	500
	twig	30	8.6	19	54
	root	31	14	14	76
Co	leaf	17	8.1	9	44
	twig	2	0.5	1	4
	root	0.7	0.1	0.5	1
BCF Cr	leaf/soil	0.007	0.001	0.004	0.100
BCF Ni	leaf/soil	0.83	0.19	0.47	1.22
BCF Co	leaf/soil	0. 21	0.06	0.13	0.38

5. Discussion

Soils from the study area are classified into two distinct groups of harzburgite and dunite types. Given the fact that, serpentinized dunite envelopes chromite deposits and the soils formed on these rocks contain more Ni than other ultrabasic soil types, Ni has been used as pathfinder for chromite exploration in this study. Table 4 pertains to the Pearson correlation matrix of total concentration of elements in dunite soils. As it is clearly understandable the total chromium content of dunite soils displays very good positive correlations with Ni_{total} and Co_{total}. Thus the explorer could rely on the concentration of Ni as pathfinder for Cr prospecting in soils derived from dunite with igneous origin (Rajabzadeh et al., 2015).

Several controlling factors (e.g. pH, TOC and texture of host soil) affect the uptake mechanism of elements by plants (Duke and Williams, 2008; Naseem et al., 2009; Shallari et al., 2001). The consequence of high pH of soils in Forumad is much less uptake of Cr in comparison to Ni. Although TOC content of the studied soils was generally poor, in alkaline conditions, organic materials are capable of holding metal ions, e.g. Cr, via adsorption and keeping them out of reach of plants. Sandy loam to loamy sand nature of the soils and high relief of the sampling locations cause soils to be drained rapidly, thus Mg may easily leach out from the soils due to its high mobility and as a consequence Ca could retain in the soils. Contamination of serpentine derived soils with limy materials originated from neighboring limestone, however, it should not be ignored. Calcium has antagonistic effects on some other ions and can reduce the bioavailability of some elements in soil (Chaney et al., 2008; Kfayatullah, 2001).

Generally, due to high concentrations of potentially toxic elements (e.g. Cr, Ni, Co and Mn) and low concentrations of some essential nutrients (e.g. N, P and K), the surface of soils originated from ophiolites contain poor vegetation (Proctor and Nagy, 1992; Reeves et al., 2007). Regarding this fact, mineralized zones are generally bare in the study area. Field observations, however, demonstrated that there was a meaningful relationship between *S. orientalis* abundance and dunite soils.

Table 4. The Pearson correlation matrix of total concentration of elements in dunite soils

	Mn	Fe	Ca	Mg	K	Na	Cr	Ni	Co
Mn	1								
Fe	-.851**	1							
Ca	.094	-.479	1						
Mg	-.036	.040	-.027	1					
K	.385	-.326	-.302	-.244	1				
Na	-.043	.369	-.622	-.065	-.380	1			
Cr	-.392	.460	-.139	.421	-.463	.049	1		
Ni	-.595	.473	.084	.519	-.588	-.082	.910**	1	
Co	-.680	.619	-.250	.301	-.408	.112	.871**	.902**	1

**Correlation is significant at the 0.01 level

Chromium concentration in all plant organs of *S. orientalis* is significantly low. This finding could be attributed to insignificant transfer of this element from soil to roots and then to leaves at all sites. The higher values for Cr concentration in root of the plant can be elucidated by reduction of heavy metals phytotoxicity via compartmentalization and storage in some areas of the plant like vacuoles of epidermal and sub epidermal cells of roots (Vazquez et al., 1994). This element serves as non-essential constituent in plant metabolism and consequently is not a relevant criterion in biogeochemical prospecting for chromite deposits in ophiolite zones. In contrast, the higher content of Ni than Cr in this plant species could refer to the higher bioavailability of this metal than Cr. It is also noticeable that the concentration of Ni in leaf stem of *S. orientalis* is to a great extent more than those of its twigs and roots. Given that the study area is located in an arid to semi-arid part of Iran, twigs of plants growing in these kinds of climate are lignified to a large extent, and only play the role of conduit for mineral and water transferring to more metabolically active parts of the plant, i.e. leaves that have critical role in photosynthesis process. Additionally, some resources have proved the preferential accumulation of Ni in the leaf epidermal cells of some Ni hyperaccumulators (Boyd, 1998). Unlike Cr that is not a component of plant enzymes, Ni is a constituent of urease, and small quantities of Ni (0.01 to 5 µg g^{-1} dry wt) are essential for some plant species (Seregin and Kozhevnikova, 2006; Shanker et al., 2005).

Determination of BCF is a convenient way to quantify the relative difference in bio-availability of metals in plants and is one of the biogeochemical parameters used in mineral exploration (Ebong et al., 2007; Naseem et al., 2009). The range of BCF values in plants varies widely from 0.0001 to 10 (Brooks et al., 1995). The determined BCF for *S. orientalis* shows that the values of Cr and Co on a dry-weight basis are much lower than unit whereas for Ni it goes to1.22 with an average of 0.83. The average BCF trend shows Ni>Co>Cr, which implies that *S. orientalis* has the potential to accumulate more Ni than other determined elements. Comparison of BFCs calculated in this study with other results (Kabata-Pendias, 2001) indicated that Cr and Co have shown natural values in this plant, whereas the average value of Ni is more than 10 times greater than those reported for natural plants. It is worth noting that although the concentration of Ni in *S. orientalis* is not as much as hyper accumulators of ultramafics (Reeves, 1992), Ni content of all analyzed leaf samples shows higher content than background (108 µg g^{-1}), suggesting that *S. orientalis* absorbs this metal selectively and poses the eligibility for inclusion in biogeochemical exploration programs.

As shown in Fig. 2, a good positive correlation between Ni concentration in soils and those of *S. orientalis* leaf stem, along with the strong correlation between Ni and Cr in dunite type soils of the study area signifies the significant potential of *S. orientalis* for accumulation of Ni and elucidates the reasons for selection of Ni as pathfinder element in chromite exploration in the studied area as well as the other similar settings.

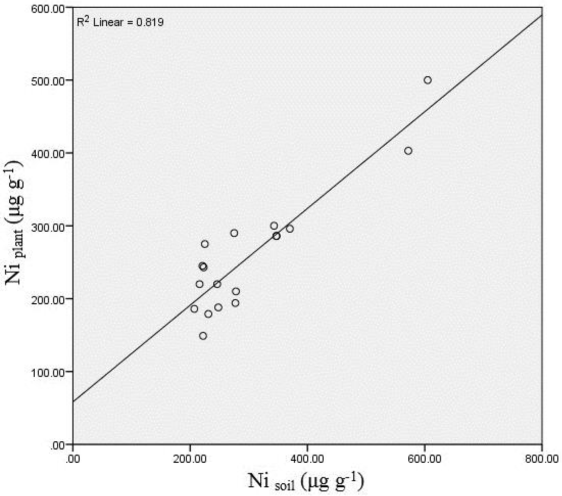

Fig. 2. Positive correlation of Ni content in soil versus those of leaf stem for *S. orientalis*

6. Conclusion

S. orientalis is a common and widespread species which has a meaningful correlation with soils formed on chromite hosting serpentinized rocks at the Forumad area. Nickel is more bioavailable than Cr and is an essential constituent of plant enzymes. *S. orientalis* accumulates this element with the maximum concentration in its leaf stem. The BCF for Ni in *S. orientalis* reveals that this plant can be considered as faithful geobotanical indicator in biogeochemical prospecting for chromite deposits in the Sabzevar ophiolite belt.

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