Biogeochemical exploration in Sari Gunay gold deposit, Northwestern Iran

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Abstract

Biogeochemistry is a useful tool for assessing geochemical dispersion patterns. Sari Gunay epithermal gold deposit was selected in order to assess the application of biogeochemical exploration for gold in northwestern Iran. In this study, four sites were sampled in a profile perpendicular to mineralized vein with a control site two km far-off mineralized vein. A sample from each dominant plant species (*Silene conoidea, Achillea aleppica, Crepis corniculata, Centaurea virgata*) was collected in each site and after preparation, analyzed using ICP-MS method. The results show that there is an inverse relationship between distance from mineralized vein and the concentration of gold and its associated elements in *S. conoidea* and *A. aleppica* species. *S. conoidea* has higher concentration of gold (303 ppb) than other species, therefore this species is a preferable bioindicator for gold mineralization. Biological absorption coefficients for Au and its pathfinder among all three species are increased over Au mineralization vein and decrease in following order *S. conoidea> A. aleppica> C. corniculata.* There is a need for further investigation on using *S. conoidea* as an As-phytoextractor (As=163.5 ppm) in remediation for arsenic contaminated sites, which also might be helpful during mining and mineral processing in Sari Gunay and neighboring deposits.

Keywords: *Biogeochemical Exploration, Gold, Indicator Plant Species, Sari Gunay.*

Introduction

Metallic ore deposits have played an important role in the development of technology and economy of human societies. Thus, the increase in exploration activities for these ore deposits is a priority for highly industrialized society. Geochemical and biogeochemical prospecting has been widely used for mineral exploration as discovery rates of mineral deposit decline.

Different sampling mediums such as plants (Valente *et al.*, 1986: Närhi *et al.*, 2013), humus (Curtin *et al.*, 1968, 1971: Girling *et al.*, 1978, 1979: Baker, 1983), soils, stream sediments, rock samples (Banister, 1970: Boyle, 1979), groundwater (Brooks, 1982) have been used for exploration of precious metals, especially gold and its associated elements.

Biogeochemical prospecting is based on the fact that plants can uptake some elements from underlying substrate and accumulated them in their roots, foliage and etc. (Dunn, 2007). The tendency of plants to accumulate metals in their organs is dependent on plant species, metal concentrations and bioavailability in the substrate.

Plants which accumulate much higher metal concentrations from the substrate can be used as indicator plants for biogeochemical exploration (Badri and Springuel, 1994; Brooks, 1983; McInnes *et al.*, 1996) especially for detecting buried mineralization targets. A number of studies have shown that the biogeochemical prospecting is an effective and successful mineral exploration technique for disseminated Au deposits (Warren & Hajek, 1973: Girling *et al.*, 1979: Dunn, 1986: Reid, 2010, Eun Jung, 2011). In these deposits, some of the plants accumulate typical pathfinder elements such as Au, As, Hg, Sb, Ag and Tl (Warren *et al.*, 1964; Jones, 1970: Shacklette *et al.*, 1970).

The plants' response to metals in substrates can be classified to three separate behaviors (Baker, 1981; Baker & Brooks, 1989). 'Indicator' species which accumulate metals in proportion to its quantity in soil and their biogeochemical composition reflects geochemical signature of the subsurface. These plant species are used for biogeochemical exploration. 'Accumulator' species which uptake exceptionally high metal concentrations which can be useful for the phytoextraction or even phytomining of metals from metal-rich soils, ores and wastes (e.g. Anderson *et al.*, 1999). The 'excluder' species which do not take up high metal concentrations in their biomass in spite of growing on elevated metal concentrations in the subsurface.

Vast amount of mining wastes produced by mining activities and processing which can be source of contamination in abandoned mine sites. Some of the plants grown on these contaminated sites have a tendency to accumulate toxic elements like As, Hg, Cd, etc. Therefore, they can be used for remediation of contaminated sites.

In order to determine Au anomalies and rehabilitation of As contamination areas in the central- northwestern Iran, identification of Au and As indicator and accumulator plant species is helpful. The aim of current study is evaluating biogeochemical prospecting application in an epithermal gold deposit (Sari Gunay) in order to identify Au and As indicator and accumulator plant species.

Area description, methods and material

This study evaluate the potential of plant species and communities which grow on precious metals prospect (Au) to find whether they are practical in prospecting or mine rehabilitation.

The study area is an epithermal gold deposit, viz., Sari Gunay that means “yellow hill”. This deposit is located at 35°12'N 48°05'E in the Kordestan province, ~60 km northwest of the city of Hamedan, in a region of rolling hills, semiarid and marginal farmland. Sari Gunay mineralization located within a mildly alkaline latitic to trachytic volcanic complex in the central-northwestern Iran. Best mineralized veins with the highest gold grades are recognized by the presence of fine-grained arsenian pyrite and minor arsenopyrite or “sooty pyrite”. Invisible gold occurs in solid solution in the sooty pyrite which formed at vein margins and in wall rocks. Late-stage minerals in these veins include realgar, orpiment, cinnabar and extremely rare wire gold (Richards *et al.*, 2006).

The quartz-adularia-pyrite-stibnite veins striking N20E, fills middle Miocene igneous rock fractures. Mineralized vein system largely followed the zone of structural permeability first formed by the diatreme breccias and then by the quartz-tourmaline breccias. Consequently, the large zone of quartz-tourmaline brecciation on the southeastern flank of Sari Gunay hosts the main zone of gold mineralization (Fig. 1).

Intrusive and volcanic host rocks dated between 11.7 and 11.0 Ma, whereas sericitic alteration associated with an early stage of hydrothermal activity occurred between ~10.8 and ~10.3 Ma (Richards *et al.*, 2006).

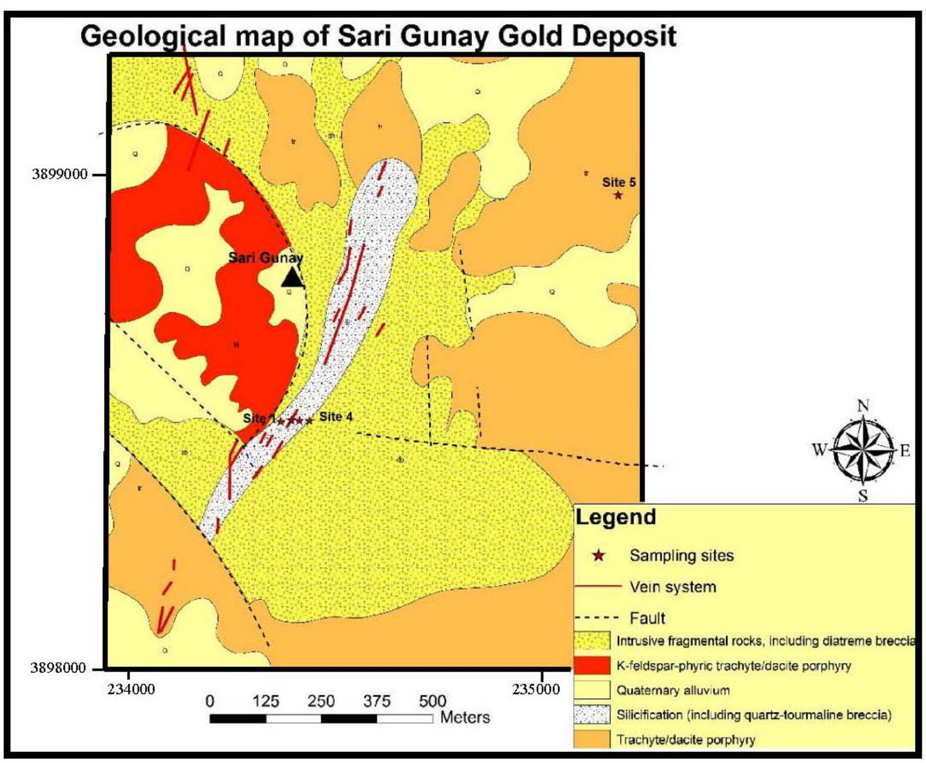


Figure 1. Geological map of the Sari Gunay gold deposit (after Richards *et al.*, 2006) and sampling sites.

Soils in the mineralized area are barely developed, and they are mainly mountain soils, especially cambisoils and lithosoils.

Four dominant plant species of *Centaurea virgata* (Fig. 2a), *Achillea aleppica* (Fig. 2b), *Silene conoidea* (Fig. 2c) and *Crepis corniculata* (Fig. 2d) were collected during orientation survey around Sari Gunay in spring season. These species are widespread, easily-recognizable and annual which also grown on top of epithermal quartz-pyrite-stibnite-realgar-orpiment vein outcrop (As site No. 2) (Fig. 3).

Plants species were identified following the local herbarium and floras (Kharazmi University herbarium). In the field, samples were cleaned with fresh-water (Tehran Herbarium, Kharazmi University), rinsed with deionized water and air-dried for several days. The air-dried plant samples were powdered homogenously, then converted to ash at 550ºC and digested for elemental analysis (Kovalevskii, 1979; Brooks, 1983; Pereira *et al.*, 2003). Analytical method included ICP-MS for Au, As, Ag, B, Be, Bi, Ba, Cd, Ce, Cs, Co, Cr, Cu, Ga, Hf, Hg, In, La, Li, Fe, Mn, Mo, Nb, Ni, Pb, Rb, Re, Sb, Sc, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, Y, Zn and Zr in LabWest Minerals Analysis Pty Ltd. of Australia. The objective of this step is to identify species which could accumulate Au and its pathfinder. It was found that the three species (*A. aleppica*, *S. conoidea*, *C. virgata*) are suitable for further studies in sites No. 1, 3, 4 and 5.

Samples were collected along a 200-m profile perpendicular to the mineralized vein. All three plant species were collected in a 5-10 m circle every 50 m. A control sampling site was chosen about 1 km away from the sampling profile. In all sites, sample from each species was taken. After preparation steps, samples were analyzed using ICP-MS method.

Results and discussion

Since the plant element concentrations are generally highest in springtime (Schiller *et al.*, 1973; Stednick *et al.*, 1987), this study was conducted in spring in two steps.

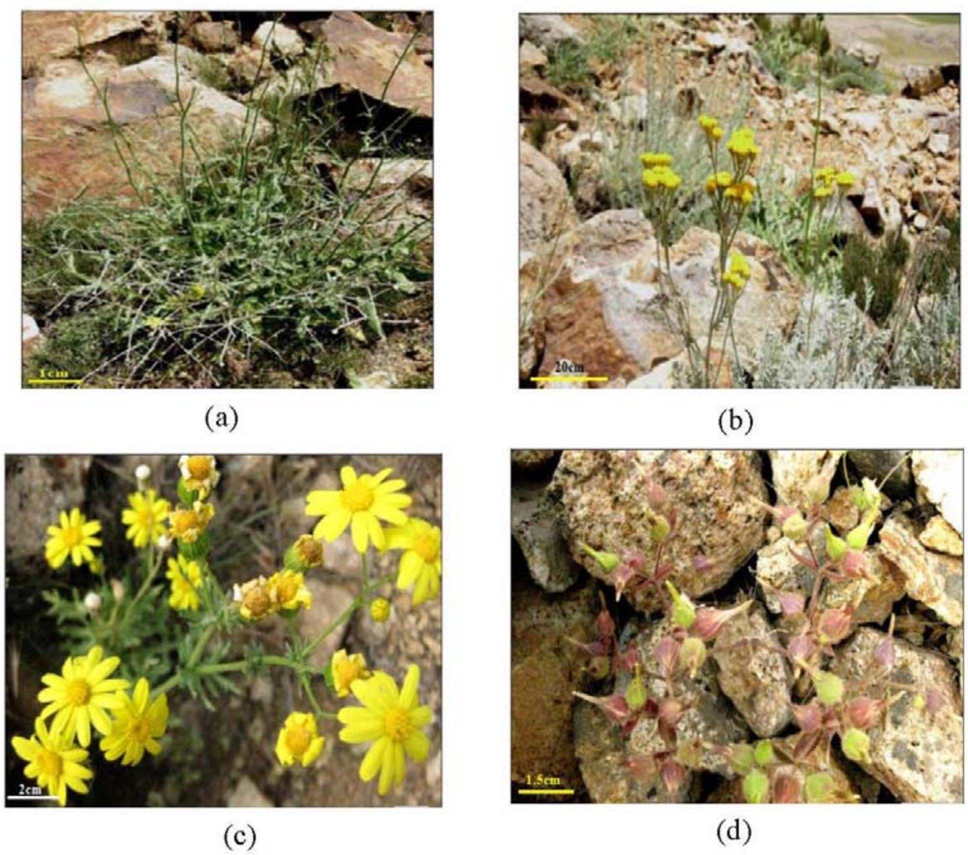


Figure 2. Plant species of (a) *Centaurea virgata*, (b) *Achille aleppica*, (c) *Silene conoidea*, (d) *Crepis corniculata*.

Figure 3. Epithermal quartz-pyrite-stibnite-realgar-orpiment vein exposure in site No. 2.

Based on chemical analysis results obtained in the orientation survey, there was relatively high concentration of Au and its pathfinder in *A. aleppica*, *S. conoidea* and *C. corniculata* species (Fig. 4). The *C. virgata* species exhibited a low concentration of target elements than another species, thus, sampling of this species suspended in the second round of sampling.

The means of element concentrations in all three plant species which collected along profile and site 5 are summarized in Table 1. The pathfinder elements associated with Au are Sb, As, Bi, Cu, Pb, Se, Ag, Te and Zn besides Au itself (Boyle & Jonasson, 1973; Boyle, 1979).

The data in Table 1 display that concentration mean of Au and its pathfinder (such as Au, As, Tl, Cs and to some extent, Sb, Cu and Pb) in plants grown on mineralization are significantly higher than those of control site (No. 5). The enrichment factor was calculated as ratio of an element concentration mean in species collected along the profile to the amount of the element in the same species in control site (Table 1). As displayed in Table 1, the enrichment factor of Au and its pathfinder in all three species decrease in the order of *S. conoidea> A. aleppica> C. corniculata.*

There is also an obvious relation between Sb and As concentration in the plant tissues and Au-As-Sb mineralized vein in all three species which reflects alteration zone (Figs. 5b-c). As noted earlier, mean concentrations of Sb and As in all three species collected in over and near Au-mineralization vein are more than those of control site in following incremental order: *C. corniculata< A. aleppica< S. conoidea*.

The absolute concentration of As usually has not particular importance but its regional pattern can help to recognize Au mineralized zone (Dunn *et al.*, 2007). The *S. conoidea* species indicates specific pattern relative to mineralized vein with having the highest concentration.

Although Sb can be readily taken up by plants in soluble forms, it is considered a non-essential element (Kabata-Pendias, 2001) and it is usually present at low-ppm levels. Over and near Au–As–Sb mineralization, there is commonly a clear but subtle relationship of Sb in plant tissues to the mineralization zone. Baroni *et al.* (1999) investigated Sb concentration of plants grown in an abandoned Sb-mining area in the southernmost part of Tuscany. The both *Achillea ageratum* and *Silene vulgaris* species were recognized as bioindicators of antimony. The behavior of these species is similar to *Cogenus* species examined in this study (Fig. 5b). Furthermore, the *Silene* genus has an ability to accumulate more antimony than *Achilla* genus. The relatively high concentrations of Sb and As in all species confirmed by presence of stibnite (as main mineral in mineralization veins) and fine-grained arsenian pyrite and minor arsenopyrite, respectively.

The background level of Au in plant tissues is sometimes quoted as 1 ppb (Markert, 1994), but it is probably about an order of magnitude lower in most environments (Kovalevsky & Kovalevskaya, 1989; Dunn, 1995a). The distribution pattern of gold concentration along the profile indicates increasing in Au content of three species over Au-mineralized vein and the highest Au concentration of 303 ppb occurs in *S. conoidea* species (Fig. 5a).
Mercury enrichment can occur over zones of concealed Au mineralization, hence, because of its volatility, Hg acts as a pathfinder element for Au and other metals (Dunn, 2007). Of the three species, only *S. conoidea* species shows specific pattern along profile with the highest content over mineralized vein (Fig. 5d).

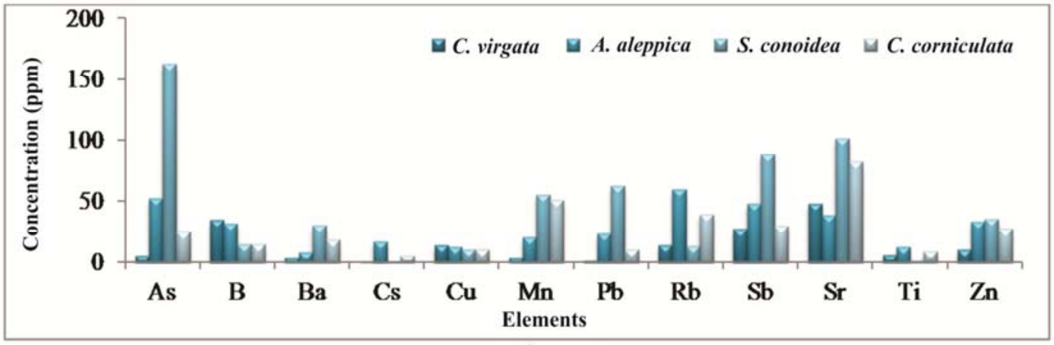
Although a Cs/Au association is not always present in vegetation, this relationship is worth scrutiny in biogeochemical studies designed to delineate Au mineralization, because of the potential of Cs to be used as a spatially associated ‘pathfinder’ element (Dunn, 2007). *A. aleppica* has the highest concentration of Cs over mineralized vein relative to the background and its distribution pattern is similar to Au (Fig. 5e).

The Cu concentration in all three species decreases by increasing distance from mineralized vein (Fig. 5f) and its mean concentration in over and nearby to mineralized vein are more than site No. 5. The high Cu concentration in several conifers were collected from over the original discovery zone at the Mt. Polley Cu-Mo-Au porphyry in central British Columbia in 1991 (Dunn, 1995a,b), and over undisturbed prospects from the surrounding area in 2005 (Dunn *et al.*, 2006 a,b) is reported.

Silene is a small plant which has reported to concentrate Pb (Dunn, 2007) and this confirms by high concentration of 62.75 ppm Pb in *S. conoidea* species in this study (Fig. 5g).

Table 1: The mean of element concentrations in all three species collected along a profile, element concentrations in No. 5 site (the control sample) and calculated enrichment factor

Elements	Species	*A. aleppica*	*C. corniculata*	*S. conoidea*	Elements	Species	*A. aleppica*	*C. corniculata*	*S. conoidea*
Au (ppb)	Mean	129.07	34	260.5	Sb (ppm)	Mean	30.45	20.27	64.77
	Control site	0.8	0.3	1.1		Control site	11.5	11.2	17.2
	Enrichment factor	161.34	113.33	236.81		Enrichment factor	2.64	1.81	3.76
As (ppm)	Mean	36.95	32.62	57.1	Hg (ppm)	Mean	0.04	0.01	0.10
	Control site	8.7	3.4	3.4		Control site	0.007	0.007	0.01
	Enrichment factor	4.24	9.59	16.79		Enrichment factor	6.07	1.57	10.5
Cs (ppm)	Mean	10.4	5.33	3.7	Cu (ppm)	Mean	9.92	5	9.7
	Control site	0.57	0.23	0.05		Control site	2.6	1.3	2.1
	Enrichment factor	18.24	23.2	74		Enrichment factor	3.81	3.84	4.61
Ag (ppm)	Mean	0.02	0.01	0.09	Pb (ppm)	Mean	16.46	6.9	50.6
	Control site	0.01	0.007	0.02		Control site	0.8	1.7	46.31
	Enrichment factor	2.68	2.16	4.5		Enrichment factor	20.57	4.05	1.09
Mo (ppm)	Mean	1.2	1.25	1.16	Tl (ppm)	Mean	1.31	2.28	2.73
	Control site	0.15	1.12	0.2		Control site	0.09	0.03	0.11
	Enrichment factor	8	1.12	5.8		Enrichment factor	14.55	61.62	24.81



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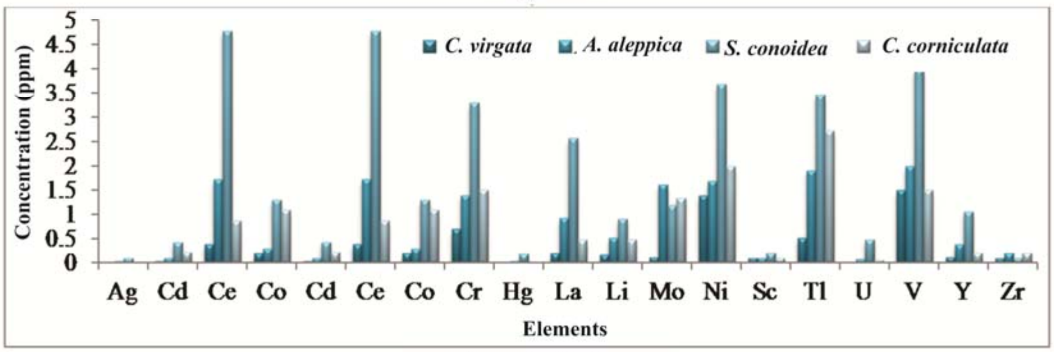

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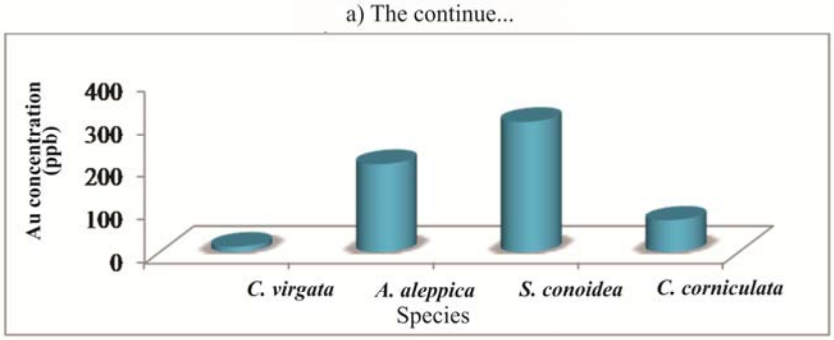

b)

Figure 4. (a) Measured element concentrations in different species over Au-mineralized vein (site No. 2), (b) the comparison of Au concentration in different species in site No. 2.

Molybdenum is a significant pathfinder for Cu–Mo, Cu–Au–Mo, W–Mo and other Mo-bearing deposits. The Mo patterns in all three species show a peak in site No. 3 (Fig. 5h) which requires further field studies.

Tl especially enriches in polymetallic deposits, including those of Au deposits associated with As, Sb and Ag. It is a highly mobile element and disperses during oxidation of sulphide ores, so it is quite readily available to plant roots (Dunn, 2007). The distribution patterns of Tl concentration along the profile do not show any obvious relation with mineralized veins (Fig. 5i).

The distribution patterns of Ag in all three species are similar to Mo and do not have any relation with Au trend along the profile (Fig. 5j). Other elements such as Ba, Cd, Cr, Co, Li, Ni, Sr, Te, U, V, Zn and Zr do not show any specific patterns relative to Au-mineralized zone.

A plant's ability to accumulate metals from soils can be quantified using biological absorption coefficient (Brooks *et al.*, 1995) as,

$$BAC=C_p/C_s$$

where Cp is an element concentration in ash and; Cs same element concentration in soil (Kovalevsky, 1995).

Plants are divided in five groups based on BAC levels: 1) very strong (BAC: 10-100), 2) strong (BAC: 1-10), 3) moderate (BAC: 0.1-1), 4) poor (BAC: 0.01-0.1), and 5) very poor (BAC: 0.001-0.01) absorption (Perelman, 1996).

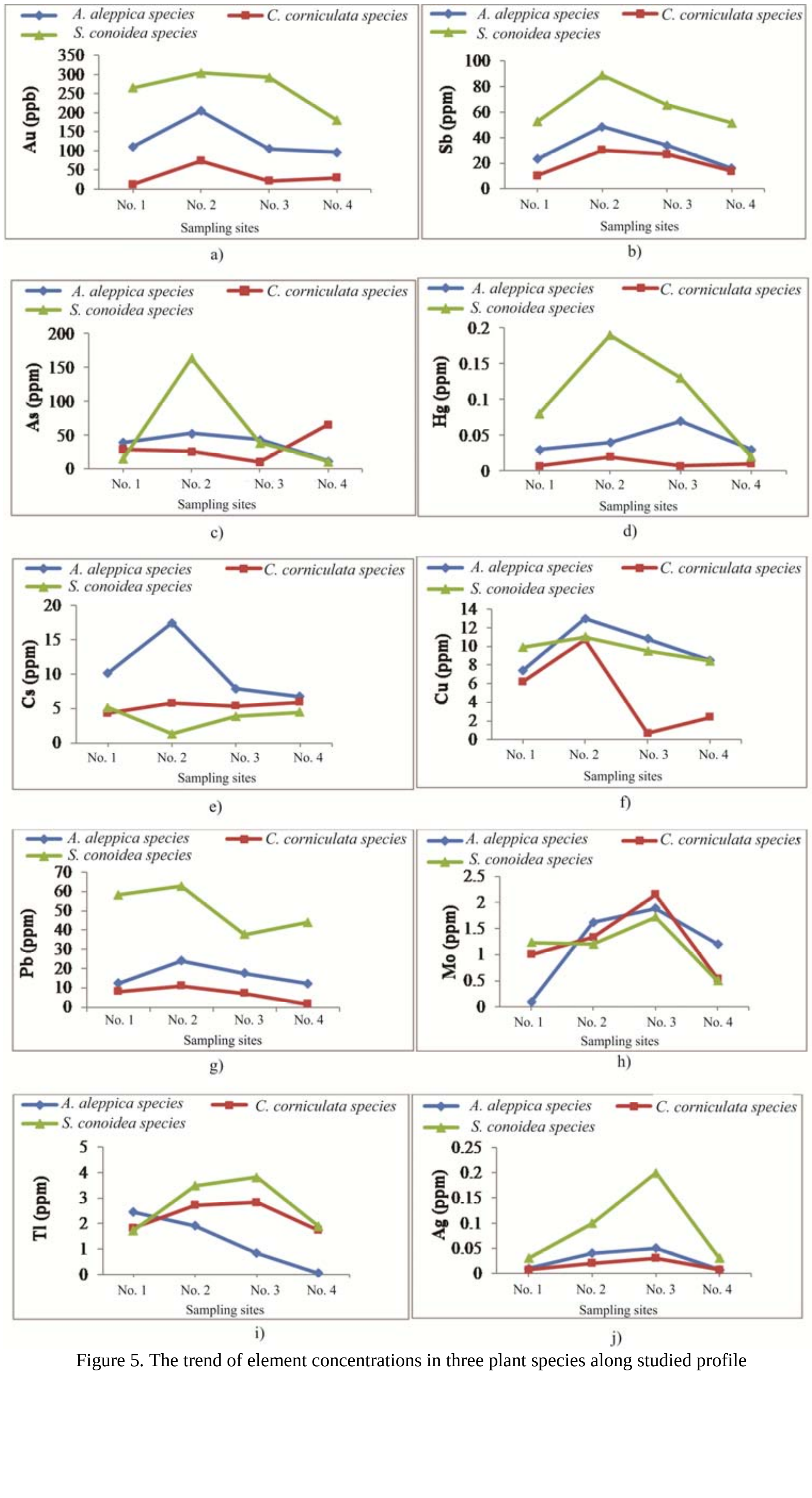

Figure 5. The trend of element concentrations in three plant species along studied profile

As area soils are barely developed and plant roots are more or less in direct contact with volcanic rocks complex, the different element concentrations in all three species were compared with lithogeochemical data which was reported by Richards *et al.* (2006). Table 2 displays the biological absorption coefficient of different elements in three species over mineralization and nearby sites. The present results suggest that BAC for Au and its pathfinder among all three species over Au mineralized vein decrease in following order *S. conoidea*> *A. aleppica*> *C. corniculata* and the BAC levels also decrease toward nearby mineralization.

Table 2. The biological absorption coefficient of elements in three species over mineralized vein (Site 2) and nearby (Sites No. 1, 3 and 4)

Elements	Sites	*S. conoidea*	*C. corniculata*	*A. aleppica*
Au	Over mineralization	Very strong absorption (49.8)	Very strong absorption (12.11)	Very strong absorption (33.6)
	Around the mineralization	-	-	-
Sb	Over mineralization	Strong absorption (5.53)	Strong absorption (1.87)	Strong absorption (3.01)
	Around the mineralization	Strong absorption (2.81)	Moderate absorption (0.84)	Strong absorption (1.21)
As	Over mineralization	Strong absorption (5.19)	Poor absorption (0.08)	Strong absorption (1.67)
	Around the mineralization	Strong absorption (1.26)	Strong absorption (2.04)	Strong absorption (1.84)
Cu	Over mineralization	Moderate absorption (0.32)	Moderate absorption (0.31)	Moderate absorption (0.38)
	Around the mineralization	Moderate absorption (0.2)	Poor absorption (0.06)	Moderate absorption (0.19)
Pb	Over mineralization	Moderate absorption (0.95)	Moderate absorption (0.16)	Moderate absorption (0.36)
	Around the mineralization	Moderate absorption (0.97)	Moderate absorption (0.11)	Moderate absorption (0.29)

Conclusions

The following conclusions can be drawn based on the results of biogeochemical sampling in a profile perpendicular to the Au-mineralized vein and control site in Sari Gunay deposit in northwestern Iran:

The mean concentration of Au, As, Tl, Cs and to some extent Sb, Cu and Pb in plant samples collected in the vicinity and over Au-vein are higher than those of control location.

Among the sampled species, *S. conoidea* and then *A. aleppica* show significant results and generate anomalies of Au and its pathfinder, so they may be considered as bioindicator for Au exploration.

The highest Au and As concentrations observed in *S. conoidea* species.

The biological absorption coefficient of Au and its pathfinders in the plant samples decrease in the order of *S. conoidea*> *A. aleppica*> *C. corniculata*.

The anomalous Au and As in samples over gold veins on Sari Gunay demonstrate that biogeochemical prospecting can be used successfully for gold exploration in the similar regions and *S. conoidea* can also be used as bio-indicator to help detect the Au mineralization and remediation of As-contaminated area.

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