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## Trace Elements Geochemistry of Niğde (Turkey) Antimony Deposits

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**Abstract** Niğde Massif is the southeast part of the CACC (Central Anatolian Crystalline Complex) which is composed of magmatic and metamorphic rocks. Within the massif is antimony mineralization of epithermal origin. According to the trace element geochemistry results of amardı (Niğde-Turkey) Sb mineralization. Hierarchical clusters are observed from the dendrograms for trace elements each other, indicating relatively high independency for each cluster. For Sb ore samples, Cd, Sn, Hf, Pb, Sr, In, I, Se, Te, Cs, Ni, Br, Te, Bi, Cu and As are very well correlated with each other and form a cluster which association with Rb, Tl, Nb, Mo, Th, Co, Zr, Zn, Hg, Ga, Ge and Y. La, Ce and W cluster joined only much later. Cd, Sn, Hf, Pb, In, I, Se, Te, Cs, Ni, Br, Te, Bi, Cu and As form the first cluster; Cd, Sn, Hf, Pb, In, I, Se, Te, Cs, Ni, Br, Te, Bi, Cu and As associated as the second cluster and La, Ce and W form the third cluster.

**Keywords** Antimony, Trace elements, Geochemistry, Niğde

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### 1. Introduction

Anatolia is known as an economically important metallogenic province in the Alpine–Himalayan Belt [1]. The Tethyan Eurasian Metallogenic Belt (TEMB; [2]) extending from Western Europe through Anatolia to Iran is one of the world's major metal producing belts hosting many volcanogenic massive sulfide, porphyry-type (copper–gold and copper–molybdenum), low- and high-sulfidation epithermal (gold and gold–silver), mesothermal (lead, zinc, copper), and skarn (iron–copper, lead–zinc)-type deposits. The TEMB formed because of the convergence and collision of the Indian, Arabian and African tectonic plates with the Eurasian tectonic plate [3]. Turkey antimony deposits are located in the Ktahya (Simav, Gediz), İzmır (demiř), Tokat (Turhal), Niğde (Camardı, Gmřler), Balıkesir (İvrindi Susurluk) Bursa (İnegl) and Bilecik (Sğt) provinces (Figure 1). The antimonite mineralizations in the Niğde Massif have an important place in Turkish mining. There are many Sb ± Hg, Sb + Hg, Sb ± Hg ± W and Hg ± Sb ore minerals that have been operated in the area in the past. The most important ones are Rasih-lhsan Sb + Hg ± W occurrences, Armutlar Tepe and Sinirsi Tepe Sb ± Hg occurrences, Ekinlik Tepe and Mehmetler Yurdu Sivrisi Tepe Hg ± Sb mineralizations [4]. The largest amount of ore production was conducted in the Rasih-lhsan occurrences [5,6], among these minerals operated by galleries and cuttings until 1980's. Antimony mineralizations associated with kapılı granitoid cutting the Gmřler, Kaleboynu and Ařıgediđi formations in the Niğde massif between Niğde and amardı are investigated. The Niğde Massif is an isolated crystalline dome near the inner-Tauride suture in Central Turkey and represents the southern most part of the Central Anatolian Crystalline Complex (CACC, [7]), which includes the Kırřehir and Akdađ Massifs in the north. It is bounded on the east by the sinistral Ecemiř Fault (Tertiary) and on the South by the Ulukıřla sedimentary basin. So far, there are many geological based researches in the region. These studies generally can be divided into three groups. The first is the studies carried out to determine the basic geological features of the region [8-9-10-11-12]. The second group especially belongs to the Sb ± Sn ± W ± Hg mineralization in the region [13-14-15]. The third group is related to environmental geochemistry [16-17].





continental crust [18-20]. Pressure conditions during emplacement were probably around 3–4 kbar [10]. The Üçkapılı Granitoid usually shows very weak ductile fabrics. It is locally associated with a dense array of dikes with variable orientations, crosscutting at a high angle the foliation of the metamorphic rocks. These features might suggest that the emplacement of the Üçkapılı Granitoid was post-tectonic. The main body, however, has been identified as a late-kinematic intrusion, recording the same shearing deformation as its host rocks [12].

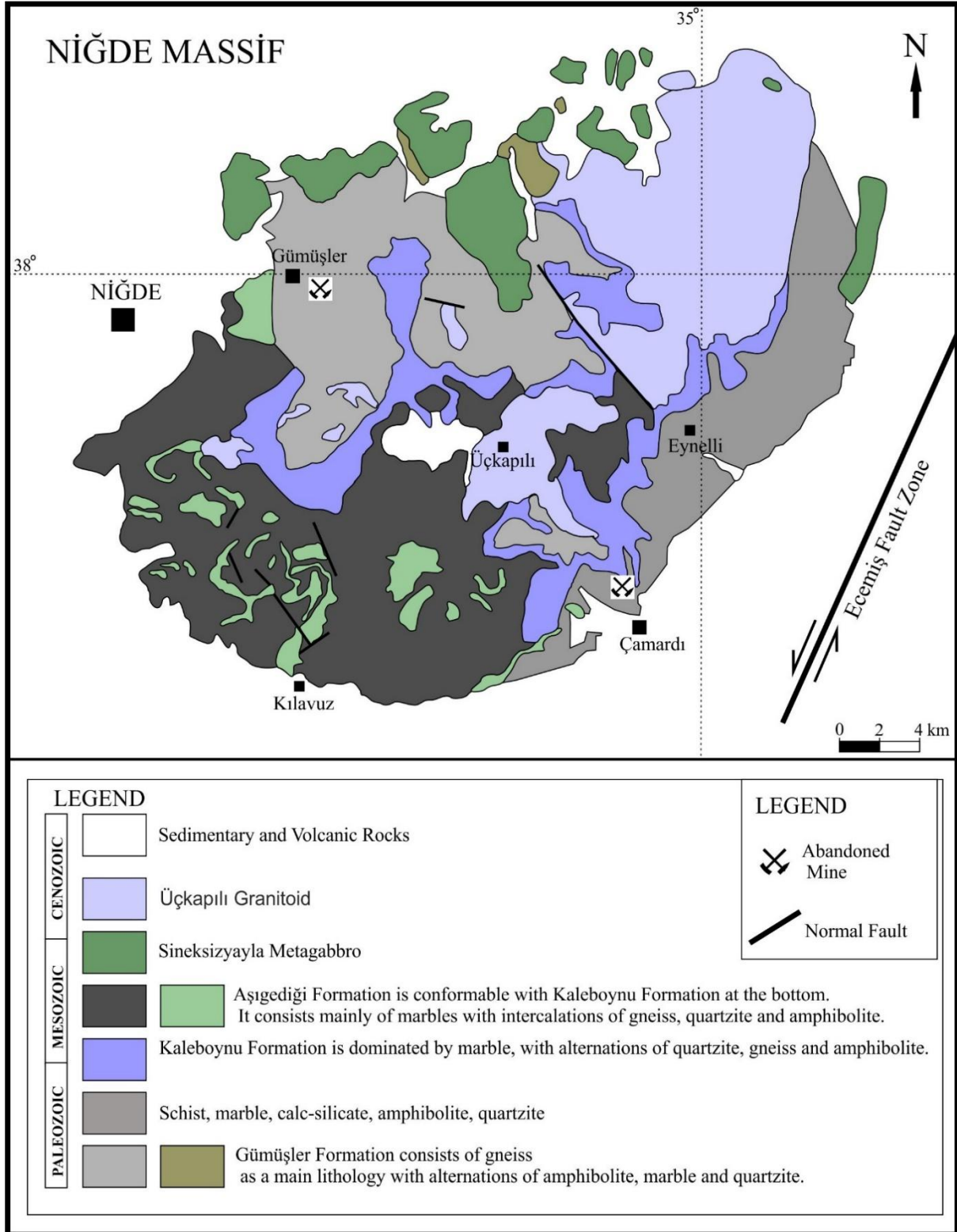


Figure 2: Generalized geological map of the Niğde Massif [18].



### 3. Madsan Sb Mineralization in Nigde Massif

The Sb mineralization in the region is located in a wide area between Gümüşler and Çamardı (Nigde). Gümüşler Sb deposits are located in Armutlar Tepe, Sinirsi Tepe, Ekinlik Tepe, Mehmetler Yurdu Sivrisi Tepe, Çamardı deposits are located in Gediz Plateau and Madsan (east of Tandırılık ridge). The deposits had been operated by open pit and underground mining operation methods until 1980. Today, there are no ore areas mined in the region. The mineralization in the study area are located in discontinuities in the Gümüşler, Kaleboynu and Aşıgediği formations. The Sb mineralization is classified as “simple antimony”-type (also known as quartz-stibnite, syntectonic stibnite and mesothermal Sb-Au). This corresponds to the granite-related vein-type (and replacement) deposits in the classification of Dill (2010) [21] and as epithermal using Lindgren's (1933) [22] definition. The mineral assemblage of the Gumusler (Nigde-Turkey) deposit includes scheelite, barite, stibnite, gold (up to 37.3 ppm) together with cinnabarite and Sb-sulphosalts. The Sb–Hg–W and Ba–Sb ore bodies are fracture bound with disseminations and veinlets of Hg–Sb in brecciated zones. The mineralization is genetically related to postmagmatic fluids associated with the Cenomanian granitic magmatism [4]. The Üçkapılı Granodiorite that intruded the Gümüşler Metamorphics crops out as small patches around the Madsan antimony deposit [13].

The Madsan Sb deposit is hosted by white marbles, calc-silicate marbles and sericitized gneisses of the Gümüşler Metamorphics of the Central Anatolian Metamorphics [23]. The Madsan mineralizations are (1) quartz-stibnite veins along the marble-gneiss contacts and at the crests of folded calc-silicate marbles, (2) quartz-pyrite-stibnite veins along the foliation planes of the gneisses, (3) quartz-pyrite veins along the foliation and fracture planes of the gneisses, and (4) quartz veins along the marble-gneiss contacts [13].

In this study, Sb ore samples taken from Madsan abandoned open pit mine (Figure 3) were studied. The samples are quartz vein bearing samples in classifications made by Kuşçu and Erler (1999) [13].



*Figure 3: Abandoned open pit mine*



The outer surfaces of the samples are of varying colors, ranging from redish to yellowish and brownish due to the alteration. Stibnite ( $Sb_2S_3$ ) and cinnabar ( $HgS$ ) were identified as ore minerals in the ore samples. (Figure 4). Stibnite mineralization was detected in the form of veins and veinlets as fracture and crack fillers. Ore vein thicknesses are generally between 0.5-10 cm (Figure 5, a-b-c) and are located in quartzite or altered quartzites. The thickness of the veinlets is reduced to 100  $\mu m$  (Figure 6, a-b). The stibnites are generally anhedral, with no evidence of deformation except pressure lamellae (Figure 6). The edges of stibnite is surrounded by a thin belt-shaped mercury from cinnabar minerals. Generally, cinnabars are 10-20  $\mu m$  thick.



Figure 4: Stibnite ( $Sb_2S_3$ ) and cinnabar ( $HgS$ ) were identified as ore minerals in the ore samples.



Figure 5: a-b-c. Ore veins seen as fracture and crack filling

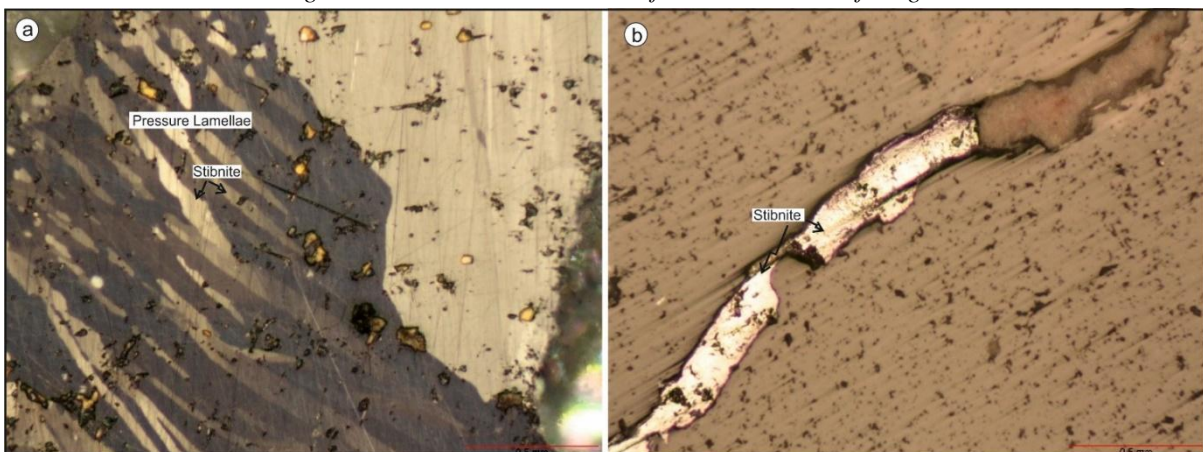


Figure 6: a- pressure lamellae b- crack filling

#### 4. Geochemistry

The main oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, MnO and SO<sub>3</sub>) were determined by XRF method and the trace elements (Co, Ni, Zn, Ga, Ge, As, Sc, Br, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Hf, Ta, W, Au, Hg, Tl, Pb, Bi and Th) were determined by ICP-MS method on four ore samples selected from the study area. The results are shown in Table 1. These results were evaluated statistically.

**Table 1:** Geochemical analysis results

	1	2	3	4
<b>Major oxides</b>				
SiO <sub>2</sub>	68.42	41.44	88.06	56.42
Fe <sub>2</sub> O <sub>3</sub>	0.98	1.65	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	0.94	0.45	1.05	0.168
MgO	0.28	0.51	0.30	0.02
CaO	1.18	0.26	3.28	41.04
SO <sub>3</sub>	15.02	31.47	5.90	0.12
Na <sub>2</sub> O	0.51	0.49	0.07	0.08
K <sub>2</sub> O	0.48	0.52	0.25	0.01
TiO <sub>2</sub>	0.04	0.14	0.01	0.02
P <sub>2</sub> O <sub>5</sub>	0.03	0.08	0.15	0.01
MnO	0.01	0.01	0.03	0.06
LOI	1.13	1.73	0.72	2.73
Total	89.02	78.75	99.83	100.68
<b>Trace Elements (ppm)</b>				
Co	62.00	30.10	47.70	17.60
Ni	19.60	20.70	7.80	2.20
Cu	37.80	41.80	1.10	1.20
Zn	95.80	14.20	8.60	0.50
Ga	8.30	2.40	4.60	3.30
Ge	8.20	2.20	2.60	1.00
As	1827.00	2249.00	163.30	31.60
Se	0.90	1.00	0.90	0.50
Br	5.70	6.40	2.00	0.70
Rb	18.30	11.30	6.60	1.00
Sr	1414.00	12.40	279.00	125.20
Y	7.40	2.30	1.00	8.80
Zr	30.00	17.00	22.20	6.90
Nb	16.00	12.00	5.00	4.20
Mo	17.00	13.00	5.00	3.50
Cd	5.10	82.00	4.10	1.70
In	5.20	39.00	6.90	1.10
Sn	33.60	705.00	1.80	1.20
Sb	3034.00	228800.00	311.80	123.20
Te	20.00	24.00	15.60	1.40
I	22.00	64.00	52.30	2.30
Cs	104.00	95.00	76.90	3.80
Ba	116400.00	144.00	25530.00	141.10
La	27.00	21.00	93.10	8.90
Ce	24.00	29.00	64.00	11.00
Hf	9.80	29.80	2.80	3.30
Ta	11.00	14.40	4.10	3.30
W	16.90	123.90	660.00	43.10
Au	<0.1	<0.1	14.60	<0.1
Hg	714.90	15.50	4.20	2.50
Tl	36.80	20.40	11.50	2.30
Pb	49.00	196.10	13.30	4.10
Bi	7.30	10.80	1.50	1.00
Th	3.50	2.20	0.90	1.10



**5. Conclusions**

**Hierarchical Cluster Analysis**

Three clusters are observed from the dendrograms (Figure 7) for trace elements each other, indicating relatively high independency for each cluster. For Sb ore samples, Cd, Sn, Hf, Pb, Sr, In, I, Se, Te, Cs, Ni, Br, Ta, Bi, Cu and As are very well correlated with each other and form a cluster which association with Rb, Tl, Nb, Mo, Th, Co, Zr, Zn, Hg, Ga, Ge and Y is shown in Figure 7. La, Ce and W cluster joined only much later. Cd, Sn, Hf, Pb, In, I, Se, Te, Cs, Ni, Br, Te, Bi, Cu and As form the first cluster; Cd, Sn, Hf, Pb, In, I, Se, Te, Cs, Ni, Br, Te, Bi, Cu and As associated as the second cluster and La, Ce and W form the third cluster.

**Interelement Relationships**

Table 2 shows the positive and negative relationships of the elements in the correlation matrix distributions of the analyzed trace elements. Correlation coefficient does not explain the causal relations between variables. According to the calculated correlation coefficient, the linear relation values are is very weak between 0.00-0.25, weak between 0.26-0.49, moderate between 0.50-0.69, strong between 0.70-0.89 and very strong between 0.90-1.00 [24].

Trace elements belonging to the Üçkapılı granitoid were published by Kurt et. al (2013). The following results were obtained when comparing the average values of the trace elements of the Üçkapılı granitoid with the values of Cu, Pb, Sr, Ba, Ta, Cs, Zn, Ga, Rb, Th, Nb, Zr and Y trace elements obtained in this study (Table 3). For the evaluated elements (Cu, Pb, Sr, Ba, Ta, Cs, Zn, Ga, Rb, Th, Nb, Zr and Y), the average of the values found in the Üçkapılı granite and ore samples was taken into account. In this sense, mean values of Cu, Pb, Sr, Ba, Ta and Cs show an increase in Sb ore samples. However, the mean values of Zn, Ga, Rb, Th, Nb, Zr and Y show an increase in the Üçkapılı granitoid. In this evaluation, all the elements which have increased in Sb ores (Cu, Pb, Sr, Ba, Ta and C) are in the first group in hierarchical cluster analysis, and elements which have increased in granitoid (Zn, Ga, Rb, Th, Nb, Zr and Y) is in the second group.

It has been found that the solutions which are separated from the Üçkapılı granitoid in the epithermal phase and caused the Sb mineralization in the region are enriched in Cu, Pb, Sr, Ba, Ta and Cs and consumed significantly in terms of Zn, Ga, Rb, Th, Nb, Zr and Y when compared to granitoid (Table 3).

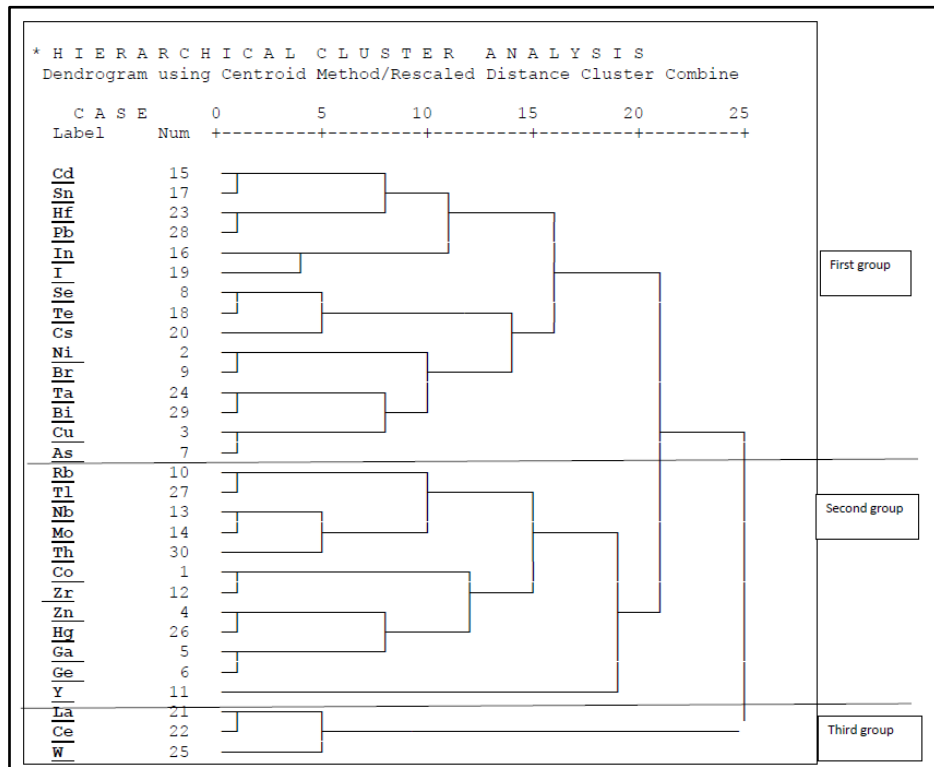


Figure 7: Dendrogram of trace elements of ores



Table 2: Coefficient correlation between the trace elements on Çamardı Sb mineralizations.

	Co	Ni	Cu	Zn	As	Sr	Rb	Y	Zr	Nb	Mo	Cd	In	Sn	Sb	Te	I	Ce	Ba	La	Ce	Hf	Ta	W	Hg	Tl	Pb	Bi	Th	U							
Co	1,00																																				
Ni	0,51	1,00																																			
Cu	0,35	0,99	1,00																																		
Zn	0,91	0,62	0,66	1,00																																	
As	0,37	0,31	0,24	0,99	1,00																																
Sr	0,18	0,61	0,55	0,99	0,96	1,00																															
Rb	0,32	0,97	1,00	0,54	0,18	0,50	1,00																														
Y	0,60	0,82	0,66	0,34	0,18	0,41	0,71	1,00																													
Zr	0,44	1,00	0,98	0,58	0,25	0,56	0,99	0,79	1,00																												
Nb	0,30	0,90	0,84	0,88	0,70	0,89	0,81	0,72	0,87	1,00																											
Mo	0,13	0,42	0,39	0,57	0,98	0,97	0,32	0,21	0,37	0,79	1,00																										
Cd	-0,16	-0,25	-0,05	0,34	0,33	0,24	-0,13	-0,72	-0,22	-0,05	0,40	1,00																									
In	0,38	0,65	0,49	0,91	0,93	0,83	0,47	0,72	0,59	0,88	0,79	-0,24	1,00																								
Sn	0,61	0,95	0,97	0,95	0,58	0,82	0,98	0,61	0,95	0,98	0,70	0,10	0,78	1,00																							
Sb	0,61	0,94	0,96	0,85	0,55	0,80	0,99	0,65	0,95	0,98	0,67	0,05	0,71	1,00																							
Te	-0,28	0,62	0,66	-0,21	-0,55	-0,24	0,71	0,56	0,67	0,21	-0,43	-0,46	-0,10	0,34	0,38	1,00																					
I	-0,20	0,65	0,65	-0,19	-0,52	-0,21	0,71	0,63	0,69	0,25	-0,41	-0,55	-0,03	0,35	0,39	0,99	1,00																				
Ce	-0,28	0,63	0,67	-0,19	-0,54	-0,23	0,71	0,54	0,68	0,22	-0,42	-0,44	-0,11	0,36	0,39	0,99	0,99	1,00																			
Ba	-0,31	0,61	0,64	-0,22	-0,57	-0,26	0,70	0,53	0,66	0,19	-0,45	-0,45	-0,13	0,33	0,36	0,99	0,99	0,99	1,00																		
La	0,57	0,52	0,56	-0,19	-0,32	-0,12	0,44	0,36	0,52	0,27	-0,32	-0,34	0,31	0,17	0,22	0,70	0,68	0,62	0,60	1,00																	
Ce	0,36	0,39	0,34	0,60	0,44	0,65	0,76	0,49	0,65	0,69	0,48	-0,51	0,97	0,78	0,81	0,40	0,47	0,40	0,38	0,38	1,00																
Ba	0,18	0,46	0,41	0,67	0,48	0,88	0,35	0,29	0,41	0,61	1,00	0,31	0,85	0,71	0,69	-0,40	-0,37	-0,39	-0,42	-0,34	-0,23	1,00															
La	-0,14	-0,17	-0,42	-0,15	0,12	-0,02	-0,37	0,39	-0,24	-0,05	-0,04	-0,72	0,40	-0,32	-0,29	-0,28	-0,17	-0,30	-0,29	0,20	0,49	0,29	0,03	1,00													
Ce	0,43	-0,03	-0,27	-0,18	0,02	-0,05	-0,22	0,54	-0,08	0,02	-0,11	-0,46	0,42	-0,24	-0,20	-0,07	0,03	-0,10	-0,09	0,36	0,66	0,41	-0,03	0,98	1,00												
Hf	-0,14	0,79	0,81	0,02	-0,36	-0,03	0,85	0,60	0,81	0,41	-0,22	-0,35	0,04	0,54	0,57	0,87	0,88	0,88	0,87	0,36	0,63	0,51	-0,19	-0,37	-0,17	1,00											
Ta	0,25	0,68	0,68	0,44	0,07	0,41	0,99	0,77	0,88	0,38	0,22	-0,20	0,41	0,85	0,97	0,78	0,79	0,79	0,77	0,84	0,51	0,78	0,25	-0,36	-0,19	0,99	1,00										
W	0,22	-0,30	-0,53	-0,40	-0,13	-0,27	-0,47	0,29	-0,53	-0,26	-0,29	-0,77	0,17	-0,51	-0,47	-0,18	-0,09	-0,21	-0,20	0,09	0,52	0,13	-0,22	0,87	0,89	-0,33	-0,43	1,00									
Hg	0,77	0,53	0,53	0,99	0,93	0,88	0,46	0,34	0,49	0,85	0,88	0,44	0,78	0,80	0,77	0,79	0,79	0,79	0,77	0,84	0,51	0,78	0,25	-0,36	-0,19	0,99	1,00										
Tl	0,90	0,87	0,82	0,95	0,74	0,91	0,78	0,66	0,87	1,00	0,82	0,05	0,87	0,80	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,88	0,88	1,00									
Pb	-0,13	0,98	0,78	-0,02	-0,39	-0,05	0,83	0,64	0,80	0,39	-0,26	-0,41	0,05	0,51	0,54	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	1,00								
Bi	0,20	0,95	0,67	0,40	0,02	0,36	0,96	0,71	0,97	0,72	0,17	-0,21	0,27	0,85	0,88	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	1,00							
Th	0,61	0,83	0,86	0,79	0,68	0,87	0,81	0,45	0,81	0,89	0,79	0,29	0,68	0,98	0,97	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	0,81	1,00						
U	0,23	0,98	0,98	0,43	0,06	0,39	0,99	0,71	0,98	0,74	0,20	-0,20	0,40	0,84	0,86	0,79	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	0,80	1,00				





**Table 3:** Comparison of Sb ore and granitoid trace elements.

Elements	Average values of Üçkapılı granitoid (Kurt et al., 2013)	Average of this work	
Cu	6.20	20.47	Increase
Pb	2.14	65.62	in ore
Sr	135.58	457.65	
Ba	538.53	35553.78	
Ta	1.03	8.20	
Cs	3.10	69.92	
Zn	44.71	29.77	Increase
Ga	17.42	4.65	in rock
Rb	106.84	9.3	
Th	11.70	1.92	
Nb	13.64	9.30	
Zr	152.34	4.87	
Y	31.86		

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